ASM HANDBOOK®

VOLUME 4

Heat Treating

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Foreword

Heat-treating technology has long been an area of deep interest and concern to ASM members. In fact, the origin of the Society can be traced back to 1913 when the Steel Treaters Club was launched in Detroit. This group joined with the American Steel Treaters Society to form the American Society for Steel Treating in 1920. It was the latter organization that issued the first bound Handbook in 1928, a volume that would serve as the prototype for future generations of the *ASM Handbook.*

During the ensuing six decades, many changes have taken place--both in terms of the positioning of the Society and the technology base it serves. In 1933 a name change to the American Society for Metals completed the transition from an organization concerned primarily with heat treating to one that served the interests of the entire metals industry. Finally in 1987, the technical scope of the Society was further broadened to include the processing, properties, and applications of all engineering/structural materials, and thus ASM International was born.

Despite these momentous changes, one fact has remained unchanged--ASM's recognition of heat treating as one of the foundations of the metals sciences and its unflagging commitment to this ever-changing technology. The publication of Volume 4 of the *ASM Handbook* is the most recent and significant example of the sustained leadership of the Society in addressing the needs of the heat treat community.

The present volume reflects the continuing research and effort that have led to a deeper understanding of the response of ferrous and nonferrous alloys to thermal treatments. For in the 10 years since publication of its 9th Edition predecessor, significant developments have taken place in quenching and hardenability studies, computer modelling of heat-treating operations, plasma-assisted case hardening methods, and improved quality control through advanced instrumentation and/or the application of statistical process control. These are but a few of the important topics that will undoubtedly contribute toward making the Heat Treating Handbook a timeless contribution to the literature.

Successful completion of such a formidable project, however, is dependent on the collective effort of a vast pool of knowledgeable and dedicated professionals. For their significant roles in this project, we are truly indebted to the ASM Heat Treating Technical Division and its subcommittees, to the Handbook Committee, to the hundreds of individual authors and reviewers, and the Handbook Editorial Staff. For their valuable contributions, we extend our thanks and gratitude.

- Stephen M. Copley
President
ASM International
- Edward L. Langer
Managing Director
ASM International

Preface

In compiling this new volume on heat treating, the challenge was to produce a book that contained subject matter strongly oriented toward industrial practice but that did not omit discussions of the underlying metallurgical fundamentals. With previously published ASM Handbooks devoted to heat treating, the omission of material on fundamentals was justified by either space limitations and/or the availability of other ASM books that described the physical metallurgy associated with thermal treatments. For example, when the 8th Edition was published in 1964, only 306 pages were related to heat treating (this Volume was divided between heat-treating technology and surface cleaning and finishing). As such, readers were referred to the classic book *Principles of Heat Treatment* by M.A. Grossmann and E.C. Bain, which was also published in 1964 by ASM. A similar situation arose in 1981 when the expanded 9th Edition Heat Treating Handbook was published. In the year prior to this publication, a completely revised version of the Grossmann/Bain book was prepared by G. Krauss and subsequently published by ASM.

The 1980s proved to be a dynamic period for heat-treating technology--a decade that witnessed the introduction of new alloys and processes as well as new "tools" for understanding the response of heat-treated materials. For example, new alloys under active development or brought to market during the 1980s that were not described in previous heat-treating Handbooks included duplex stainless steels, microalloyed (HSLA) steels, low-cobalt maraging steels, austempered ductile iron, directionally solidified and single-crystal superalloys, and aluminum-lithium alloys.

Changes in processing include improvements in continuous annealing, induction heating, and surface hardening operations using lasers or electron beams, the commercial viability of plasma-assisted case-hardening processes, and advances in thermomechanical processing.

But by far the most dramatic changes in heat-treat technology that have marked the past decade have been those involving newly developed tools for improving process characterization and process control. These include improved instrumentation for controlling furnace temperature, furnace atmosphere, and surface carbon content, the practical

application of statistical process control (SPC), and the use of computer modelling for both the prediction of hardness profiles after quenching and the quantitative modelling of properties after tempering or case hardening. It is this latter category of computer modelling that necessitates the inclusion of material on the basic principles or fundamentals of heat treating. For example, there are several articles in this Volume that deal with computer-assisted prediction of steel hardening and hardenability as a function of heat treatment parameters. In this regard, the primary measures of steel hardening are the end-quench hardenability curves (Jominy curves), isothermal transformation (IT) curves, and continuous cooling transformation (CCT) curves. In order to understand how computer programs can be used to calculate such diagrams, some brief background information is provided in several key articles to emphasize how these diagrams make possible the selection of steel and the design of proper heat treatments.

Principal Sections

Volume 4 has been organized into eight major sections:

- Heat Treating of Steel
- Surface Hardening of Steel
- Heat-Treating Equipment
- Process and Quality Control Considerations
- Heat Treating of Cast Irons
- Heat Treating of Tool Steels
- Heat Treating of Stainless Steels and Heat-Resistant Alloys
- Heat Treating of Nonferrous Alloys

A total of 71 articles are contained in these sections. Of these, 16 are new, 17 were completely rewritten, with the remaining articles revised and/or expanded. In addition, several important appendices supplement the Volume. These include a glossary of terms, a temper color chart for steels, and tabulated austenitizing temperatures for steels. A review of the content of the major sections is given below; highlighted are differences between the present volume and its 9th Edition predecessor. Table 1 summarizes the content of the principal sections.

Table 1 Summary of contents of Volume 4, Heat Treating, of the ASM Handbook

Section title	Number of articles	Pages	Figures[(a)]	Tables[(b)]	References
Heat Treating of Steel	16	253	355	123	430
Surface Hardening of Steel	18	203	305	69	324
Heat-Treating Equipment	6	62	83	17	43
Process and Quality Control Considerations	9	135	130	43	190
Heat Treating of Cast Irons	5	42	67	19	27
Heat Treating of Tool Steels	4	56	48	34	20
Heat Treating of Stainless Steels and Heat-Resistant Alloys	3	51	41	53	23
Heat Treating of Nonferrous Alloys	10	124	147	77	72

Total	**71**	**926**	**1176**	**435**	**1129**

(a) Total number of figure captions; most figures include more than one illustration.

(b) Does not include in-text tables or tables that are part of figures

Heat Treating of Steel. This section begins with two entirely new articles that introduce the reader to the physical metallurgy of heat-treated steels and newly developed methodologies for quantitatively predicting transformation hardening in steels. These companion papers set the stage for a series of articles that describe specific types of heat treatments. Of particular note is the definitive treatise on "Quenching of Steel" by Bates, Totten, and Brennan. Featuring some 95 figures and 23 tables, this 55 page article has been substantially revised and expanded from previous Editions. Other highlights include new articles on continuous annealing, cryogenic treatment of steel, and thermomechanical processing of microalloyed steel. The section concludes with completely rewritten articles on heat-treat procedures for ultrahigh strength steels, maraging steels, and powder metallurgy ferrous alloys.

Surface Hardening of Steel. As explained in the introductory article to this section, emphasis has been placed on *thermally driven, diffusion processes* that induce solid-state transformation hardening. These processes include flame hardening, high-energy processes that utilize laser beams or electron beams, and conventional surface treatments such as carburizing, nitriding, and carbonitriding.

It is important to note the significant processing characteristics between the aforementioned processes and surface modification techniques 'such as ion implantation, PVD/CVD coatings, and surface melting/surface alloying processes that will be described in future volumes of this Handbook series. For example ion nitriding, which is described in this section, and nitrogen ion implantation are two distinctly different techniques for producing a case hardened surface layer. The implementation of each process, the characteristics of the case layers produced, the metallurgical strengthening mechanisms generated, and the economics and end use of each, are quite different.

Ion nitriding is a thermally driven, equilibrium, diffusion process that produces a relatively deep (100 to 400 μm), hardened, case layer. Nitrogen ion implantation is a non-thermal, non-equilibrium, physically driven, ballistic alloying process, which produces a relatively shallow (1 μm), extremely hard case layer. Ion nitriding is implemented at high temperatures in a glow discharge atmosphere, while nitrogen ion implantation is carried out at room temperature, at high vacuum, in a dedicated atomic particle accelerator. Case layer strengthening in ion nitrided surfaces is due primarily to formation of transition metal nitride precipitates, while strengthening in nitrogen ion implanted surfaces is due primarily to dislocation pinning. A summary of processing comparisons is given in Table 2.

Table 2 Process characteristics comparison

Process	Type	Process time, h	Process temperature		Process pressure, torr	Case depth[a], μm	Hardness[a], HRC
			°C	°F			
Ion nitriding	Thermal diffusion	10-30	500-1100	900-2000	0.2-5.0	400	62-67
Nitrogen ion	Physical	1-6	<150	<300	10^{-6}	1	80-90

(a) Value for steel

Key additions to this section include articles that describe increasingly used processes such as plasma-assisted case hardening methods, boriding, and the Toyota diffusion process. Of critical importance to this section is the article "Microstructures and Properties of Carburized Steels" by G. Krauss which examines the correlation between processing, structure, and resulting fatigue, fracture, and wear properties of case-hardened steels.

Heat-Treating Equipment. Types of heat-treating furnaces, the materials used to construct furnaces, and the advantages and limitations associated with each are described next. More emphasis has been placed on furnace energy efficiency and proper design than in previous Editions.

Process and quality control considerations are more important than ever to heat treaters. Reliable sensors, computerized control equipment, and process control of heating and cooling and furnace atmospheres are described in detail in this section. Supplementing this material are new articles on the recognition and prevention of defects in heat-treated parts and the use of computer programs for designing heat-treat operations and predicting the properties of heat-treated steels.

Because the heat-treating industry is being challenged to introduce statistical concepts in order to minimize variability and ensure consistent quality of heat-treated parts, an important article on "Statistical Process Control of Heat-Treating Operations" is also included. Emphasis is on the practical application of SPC concepts in order to demonstrate to heat treaters how to identify critical process parameters that influence product quality and how to establish methods to monitor and evaluate such parameters.

Heat treating of cast irons is described in five articles. The "Introduction to Heat Treating of Cast Irons" was completely rewritten for this Volume. The remaining four articles contain new information on austempering of ductile iron and procedures for heat treating highly alloyed abrasion-resistant, corrosion-resistant, and heat-resistant cast irons.

Heat Treating of Tool Steels. Because tool steels must be processed to develop specific combinations of wear resistance, resistance to deformation or fracture under high loads, and resistance to softening under elevated temperatures, proper heat treating is critical. This section describes the procedures and equipment necessary to meet these criteria.

Heat Treating of Stainless Steels and Heat-Resistant Alloys. Procedures and process control for heat treating the principal types of stainless steels and superalloys are discussed in this section. The article on "Heat Treating of Superalloys" was completely rewritten for this Volume and includes information on both wrought and cast alloys, many of which are used in the aerospace industry. The article on refractory metals and alloys is completely new to the Handbook series.

Heat Treating of Nonferrous Alloys. The principles which govern heat treatment of nonferrous alloys are first described in this final section of the Handbook. Differences between ferrous and nonferrous processing are highlighted. Nine articles follow on heat treating of specific classes of nonferrous alloys.

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Principles of Heat Treating of Steels

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Introduction

A STEEL is usually defined as an alloy of iron and carbon with the carbon content between a few hundreds of a percent up to about 2 wt%. Other alloying elements can amount in total to about 5 wt% in low-alloy steels and higher in more highly alloyed steels such as tool steels and stainless steels. Steels can exhibit a wide variety of properties depending on composition as well as the phases and microconstituents present, which in turn depend on the heat treatment. In subsequent articles in this Section, various types of heat treatment are described in detail. In this article, an outline of the physical metallurgy associated with heat treating of steels will be given and some important "tools" will be introduced. Deliberately no microstructures are shown as a well-illustrated article exists in "Microstructures, Processing, and Properties of Steels," by G. Krauss in *Properties and Selection: Irons, Steels, and High-Performance Alloys,* Volume 1 of *ASM Handbook.* A companion article that emphasizes information systems for predicting microstructures and hardnesses of quenched steels follows (see the article"Quantitative Prediction of Transformation Hardening in Steels" in this Volume).

The Fe-C Phase Diagram

The basis for the understanding of the heat treatment of steels is the Fe-C phase diagram (Fig. 1). Because it is well explained in earlier volumes of *ASM Handbook*, formerly *Metals Handbook* (Ref 1, 2, 3), and in many elementary textbooks, it will be treated very briefly here. Figure 1 actually shows two diagrams; the stable iron-graphite diagram (dashed lines) and the metastable Fe-Fe_3C diagram. The stable condition usually takes a very long time to develop, especially in the low-temperature and low-carbon range, and therefore the metastable diagram is of more interest. The Fe-C diagram shows which phases are to be expected at equilibrium (or metastable equilibrium) for different combinations of carbon concentration and temperature. Table 1 provides a summary of important metallurgical phases and microconstituents. We distinguish at the low-carbon end ferrite (α-iron), which can at most dissolve 0.028 wt% C at 727 °C (1341 °F) and austenite (γ-iron), which can dissolve 2.11 wt% C at 1148 °C (2098 °F). At the carbon-rich side we find cementite (Fe_3C). Of less interest, except for highly alloyed steels, is the δ-ferrite existing at the highest temperatures. Between the single-phase fields are found regions with mixtures of two phases, such as ferrite + cementite, austenite + cementite, and ferrite + austenite. At the highest temperatures, the liquid phase field can be found and below this are the two phase fields liquid + austenite, liquid + cementite, and liquid + δ-ferrite. In heat treating of steels, the liquid phase is

always avoided. Some important boundaries at single-phase fields have been given special names that facilitate the discussion. These include:

- A_1, the so-called eutectoid temperature, which is the minimum temperature for austenite
- A_3, the lower-temperature boundary of the austenite region at low carbon contents, that is, the $\gamma/\gamma + \alpha$ boundary
- A_{cm}, the counterpart boundary for high carbon contents, that is, the $\gamma/\gamma + Fe_3C$ boundary

Sometimes the letters c, e, or r are included. Relevant definitions of terms associated with phase transformations of steels can be found in Table 2 as well as the Glossary of Terms in this Volume and Ref 3. The carbon content at which the minimum austenite temperature is attained is called the eutectoid carbon content (0.77 wt% C). The ferrite-cementite phase mixture of this composition formed during cooling has a characteristic appearance and is called pearlite and can be treated as a microstructural entity or microconstituent. It is an aggregate of alternating ferrite and cementite lamellae that degenerates ("spheroidizes" or "coarsens") into cementite particles dispersed with a ferrite matrix after extended holding close to A_1.

Table 1 Important metallurgical phases and microconstituents

Phase (microconstituent)	**Crystal structure of phases**	**Characteristics**
Ferrite (α-iron)	bcc	Relatively soft low-temperature phase; stable equilibrium phase
δ-ferrite (δ-iron)	bcc	Isomorphous with α-iron; high-temperature phase; stable equilibrium phase
Austenite (γ-iron)	fcc	Relatively soft medium-temperature phase; stable equilibrium phase
Cementite (Fe_3C)	Complex orthorhombic	Hard metastable phase
Graphite	Hexagonal	Stable equilibrium phase
Pearlite		Metastable microconstituent; lamellar mixture of ferrite and cementite
Martensite	bct (supersaturated solution of carbon in ferrite)	Hard metastable phase; lath morphology when <0.6 wt% C; plate morphology when >1.0 wt% C and mixture of those in between
Bainite	. . .	Hard metastable microconstituent; nonlamellar mixture of ferrite and cementite on an extremely fine scale; upper bainite formed at higher temperatures has a feathery appearance; lower bainite formed at lower temperatures has an acicular appearance. The hardness of bainite increases with decreasing temperature of formation.

Table 2 Definitions of transformation temperatures in iron and steels

See the Glossary of Terms in this Volume for additional terminology.

Transformation temperature. The temperature at which a change in phase occurs. The term is sometimes used to denote the limiting temperature of a transformation range. The following symbols are used for iron and steels.

Ac_{cm}. In hypereutectoid steel, the temperature at which the solution of cementite in austenite is completed during heating.
Ac_1. The temperature at which austenite begins to form during heating, with the c being derived from the French *chauffant.*
Ac_3. The temperature at which transformation of ferrite to austenite is completed during heating.
Ae_{cm}, Ae_1, Ae_3. The temperatures of phase changes at equilibrium.
Ar_{cm}. In hypereutectoid steel, the temperature at which precipitation of cementite starts during cooling, with the r being derived from the French *refroidissant.*
Ar_1. The temperature at which transformation of austenite to ferrite or to ferrite plus cementite is completed during cooling.
Ar_3. The temperature at which austenite begins to transform to ferrite during cooling.
Ar_4. The temperature at which delta ferrite transforms to austenite during cooling.
M_s (or Ar''). The temperature at which transformation of austenite to martensite starts during cooling.
M_f. The temperature at which martensite formation finishes during cooling.

Note: All of these changes, except the formation of martensite, occur at lower temperatures during cooling than during heating and depend on the rate of change of temperature.

Source: Ref 2

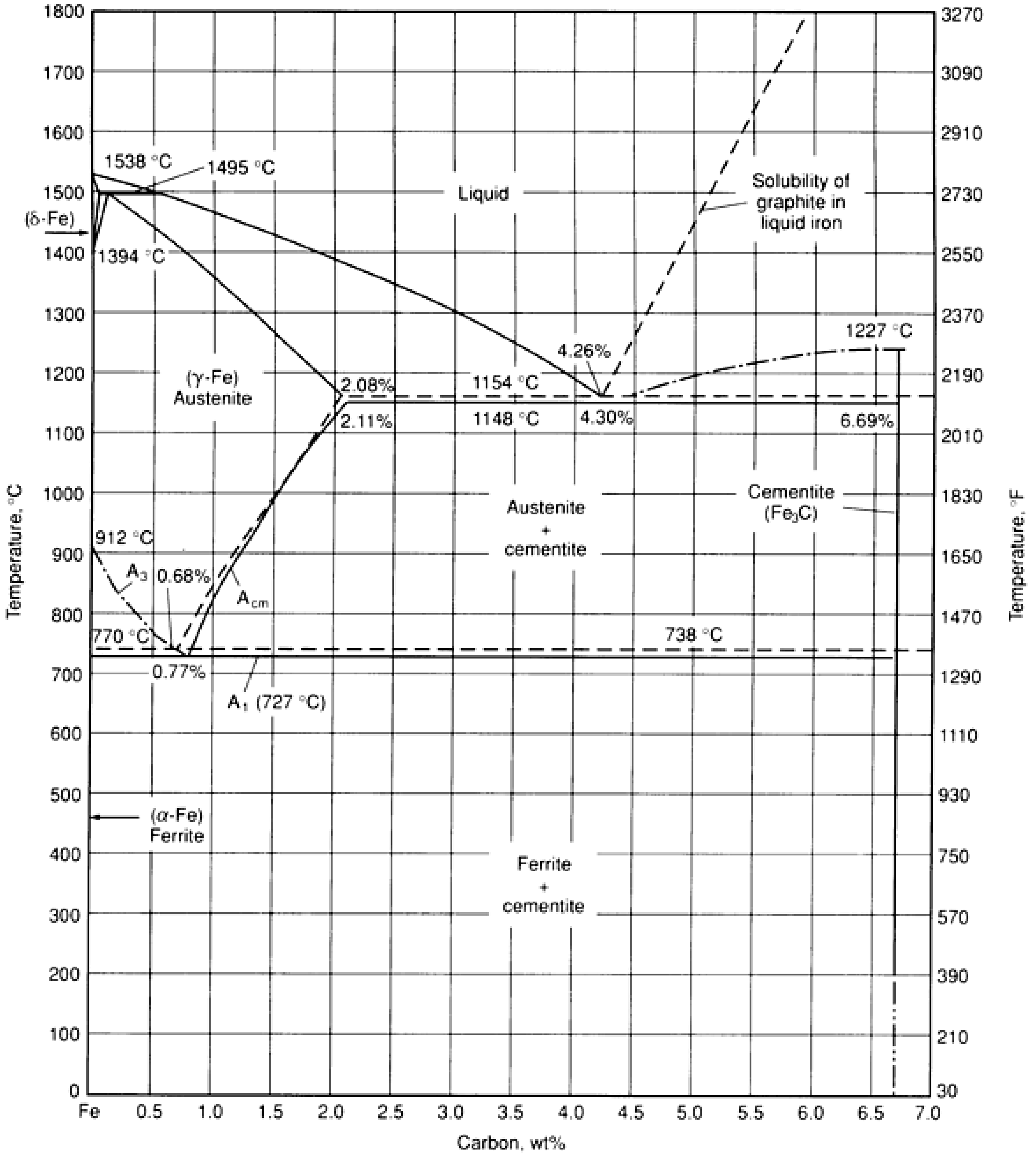

Fig. 1 The Fe-C equilibrium diagram up to 6.67 wt% C. Solid lines indicate $Fe-Fe_3C$ diagram; dashed lines indicate iron-graphite diagram. Source: Ref 1

The Fe-C diagram in Fig. 1 is of experimental origin. The knowledge of the thermodynamic principles and modern thermodynamic data now permits very accurate calculations of this diagram (Ref 4). This is particularly useful when phase boundaries must be extrapolated and at low temperatures where the experimental equilibria are extremely slow to develop.

If alloying elements are added to the iron-carbon alloy (steel), the position of the A_1, A_3, and A_{cm} boundaries and the eutectoid composition are changed. Classical diagrams introduced by Bain (Ref 5) show the variation of A_1 and the eutectoid carbon content with increasing amount of a selected number of alloying elements (Fig. 2). It suffices here to mention that (1) all important alloying elements decrease the eutectoid carbon content, (2) the austenite-stabilizing elements manganese and nickel decrease A_1, and (3) the ferrite-stabilizing elements chromium, silicon, molybdenum, and tungsten increase A_1. These classifications relate directly to the synergisms in quench hardening as described in the articles "Quantitative Prediction of Transformation Hardening in Steels" and "Quenching of Steel"in this Volume.

Modern thermodynamic calculations allow accurate determinations of these shifts that affect the driving force for phase transformation (see below). These methods also permit calculation of complete ternary and higher-order phase diagrams including alloy carbides (Ref 6). Reference should be made to the Calphad computer system (Ref 7).

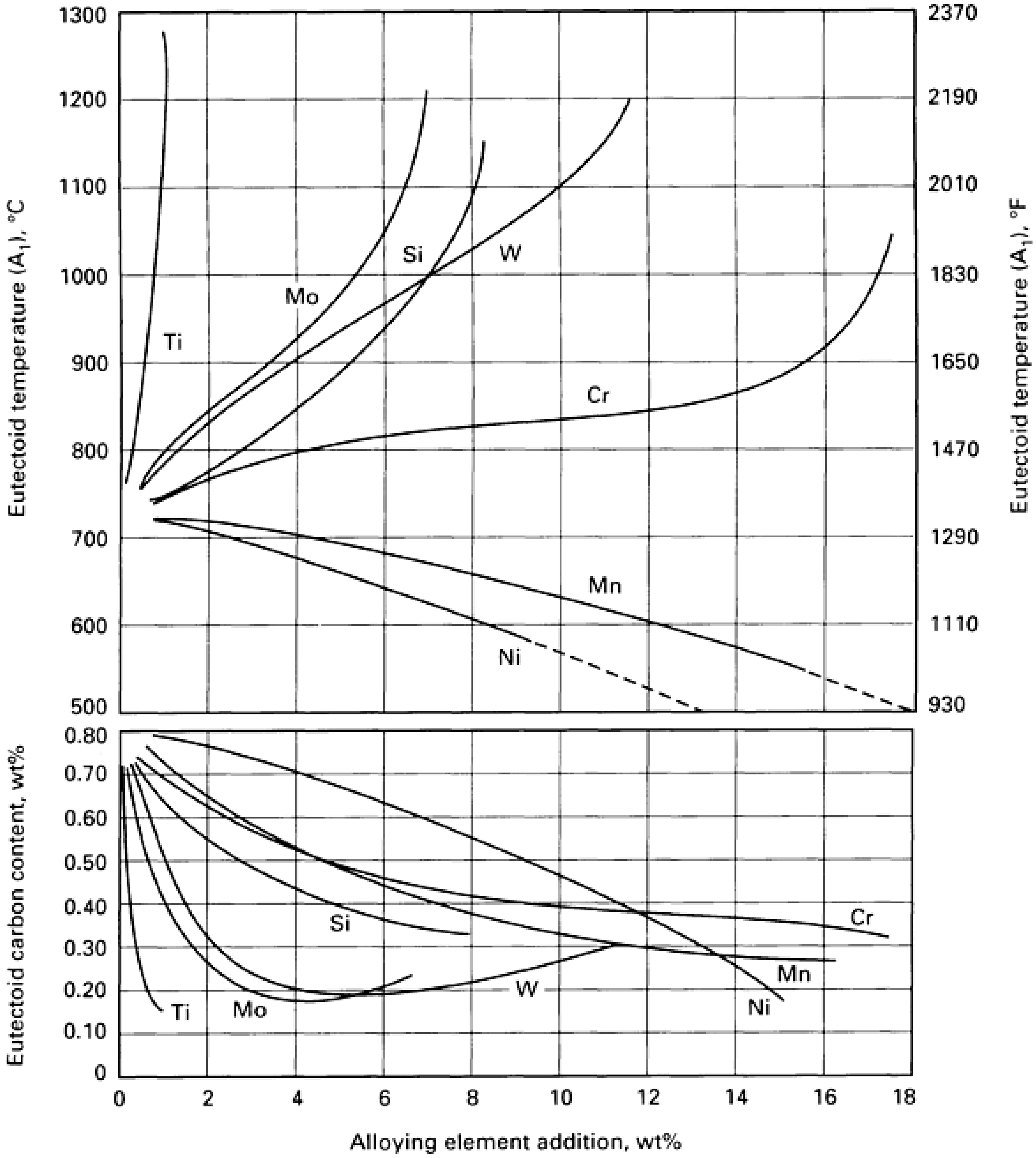

Fig. 2 Influence of alloying element additions on eutectoid temperature and eutectoid carbon content. Source: Ref 5

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Transformation Diagrams

The kinetic aspects of phase transformations are as important as the equilibrium diagrams for the heat treatment of steels. The metastable phase martensite and the morphologically metastable microconstituent bainite, which are of extreme importance to the properties of steels, can generally form with comparatively rapid cooling to ambient temperature, that is, when the diffusion of carbon and alloying elements is suppressed or limited to a very short range. Bainite is a eutectoid decomposition that is a mixture of ferrite and cementite. Martensite, the hardest constituent, forms during severe quenches from supersaturated austenite by a shear transformation. Its hardness increases monotonically with carbon content up to about 0.7 wt%. If these unstable metastable products are subsequently heated to a moderately elevated temperature, they decompose to more stable distributions of ferrite and carbide. The reheating process is sometimes known as tempering or annealing.

The transformation of an ambient temperature structure like ferrite-pearlite or tempered martensite to the elevated-temperature structure of austenite or austenite + carbide is also of importance in the heat treatment of steel.

One can conveniently describe what is happening during transformation with transformation diagrams. Four different types of such diagrams can be distinguished. These include:

- Isothermal transformation diagrams describing the *formation* of austenite, which will be referred to as ITh diagrams
- Isothermal transformation (IT) diagrams, also referred to as time-temperature-transformation (TTT) diagrams, describing the *decomposition* of austenite
- Continuous heating transformation (CHT) diagrams
- Continuous cooling transformation (CCT) diagrams

Isothermal Transformation Diagrams

This type of diagram shows what happens when a steel is held at a constant temperature for a prolonged period. The development of the microstructure with time can be followed by holding small specimens in a lead or salt bath and quenching them one at a time after increasing holding times and measuring the amount of phases formed in the microstructure with the aid of a microscope. An alternative method involves using a single specimen and a dilatometer which records the elongation of the specimen as a function of time. The basis for the dilatometer method is that the microconstituents undergo different volumetric changes (Table 3). A thorough description of the dilatometric method can be found in Ref 8.

Table 3 Volume changes due to different transformations

Transformation	**Volume change, %[(a)]**
Spheroidized pearlite-austenite	4.64-2.21 × (%C)
Austenite-martensite	4.64-0.53 × (%C)
Austenite-lower bainite	4.64-1.43 × (%C)
Austenite-upper bainite	4.64-2.21 × (%C)

Source: Ref 19

(a) Linear changes are approximately one-third the volume changes.

ITh Diagrams (Formation of Austenite). During the formation of austenite from an original microstructure of ferrite and pearlite or tempered martensite, the volume (and hence the length) decreases with the formation of the dense austenite phase (see Fig. 3). From the elongation curves, the start and finish times for austenite formation, usually defined as 1% and 99% transformation, respectively, can be derived. These times are then conveniently plotted on a temperature-log time diagram (Fig. 4). Also plotted in this diagram are the Ac_1 and Ac_3 temperatures. Below Ac_1 no austenite can form, and between Ac_1 and Ac_3 the end product is a mixture of ferrite and austenite. Notice that a considerable overheating is required to complete the transformation in a short time. The original microstructure also plays a great role. A finely distributed structure like tempered martensite is more rapidly transformed to austenite than, for instance, a ferritic-pearlitic structure. This is particularly true for alloyed steels with carbide-forming alloying elements such as chromium and molybdenum. It is important that the heating rate to the hold temperature be very high if a true isothermal diagram is to be obtained.

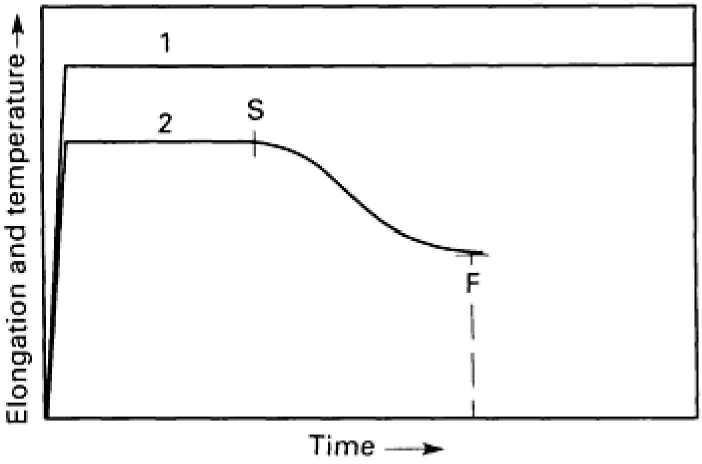

Fig. 3 The procedure for determining isothermal heating (ITh) diagrams. Line 1: Temperature versus time. Line 2: Elongation versus time. S represents the start and F the finish of the transformation of the original microstructure to austenite transformation, respectively.

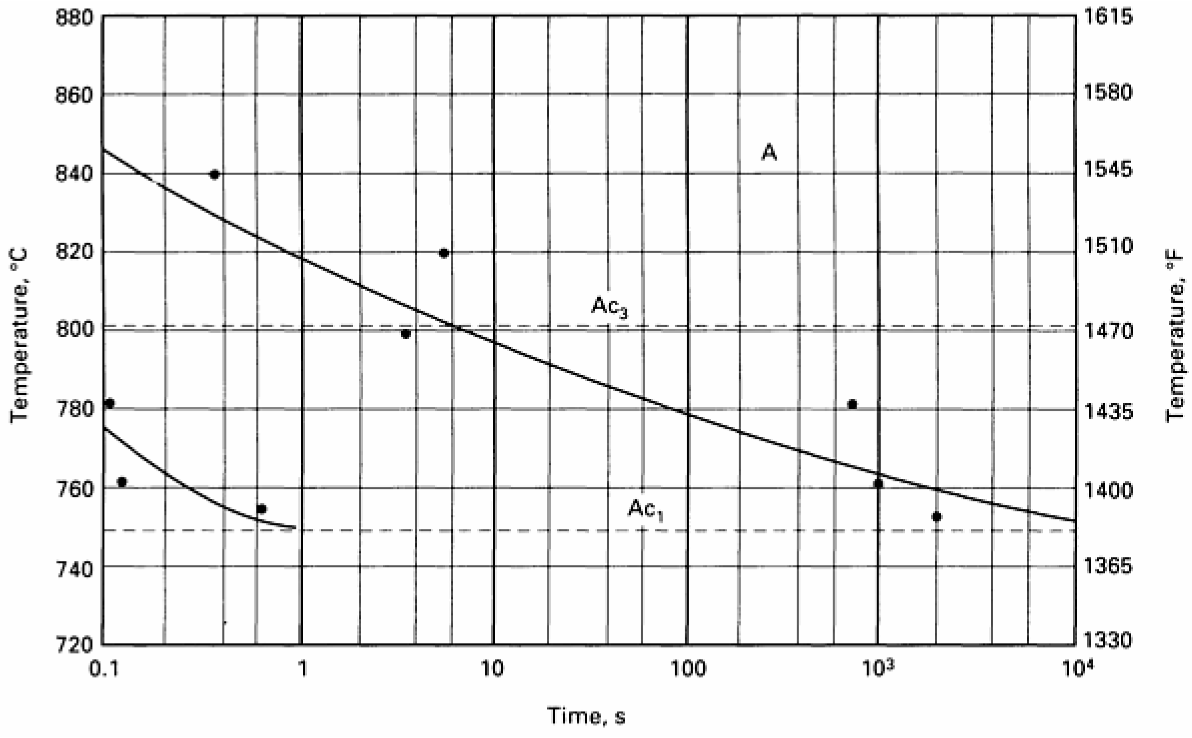

Fig. 4 Isothermal heating diagram for AISI 4140 steel. Heating rate to reach holding temperature is 1020 °C/s (1835 °F/s). Between Ac_3 and Ac_1, the final structure is a mixture of austenite and ferrite. A, austenite. Source: Ref 9

The ITh diagram is not as common as the isothermal cooling diagrams described next. Heating diagrams are useful in short time heat treatments like induction and laser hardening. An extensive collection of ITh diagrams can be found in Ref 10.

IT Diagrams (Decomposition of Austenite). The procedure starts at a high temperature, normally in the austenitic range after holding there long enough to obtain homogeneous austenite without undissolved carbides, followed by rapid cooling to the desired hold temperature (Fig. 5). An example of an IT diagram is given in Fig. 6. The cooling was started from 850 °C (1560 °F). The A_1 and A_3 temperatures are indicated as well as the hardness. Above A_3 no transformation can occur. Between A_1 and A_3 only ferrite can form from austenite. In Fig. 6, a series of isovolume fraction curves are shown; normally only the 1% and 99% curves are reproduced. Notice that the curves are C-shaped. This is typical for transformation curves. A higher-temperature set of C-shaped curves shows the transformation to pearlite and a lower-temperature set indicates the transformation to bainite. In between is found a so-called austenite bay, common for certain low-alloy steels containing appreciable amounts of carbide-forming alloying elements such as chromium or molybdenum.

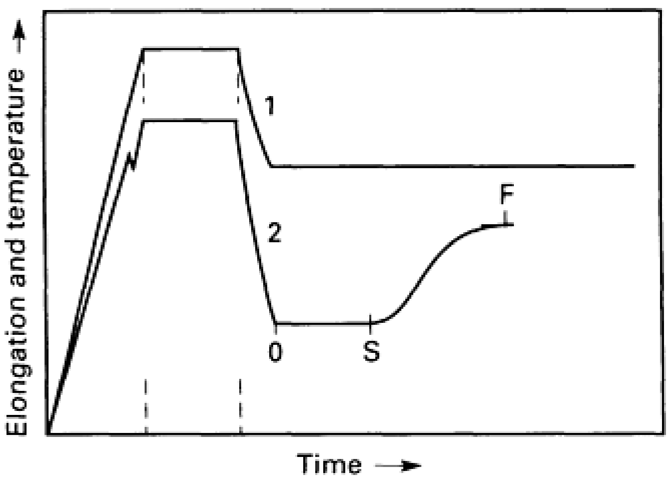

Fig. 5 The procedure for determining isothermal cooling (IT) diagrams. Line 1: Temperature versus time. Line 2: Elongation versus time. S represents the start and F the finish of austenite decomposition, respectively.

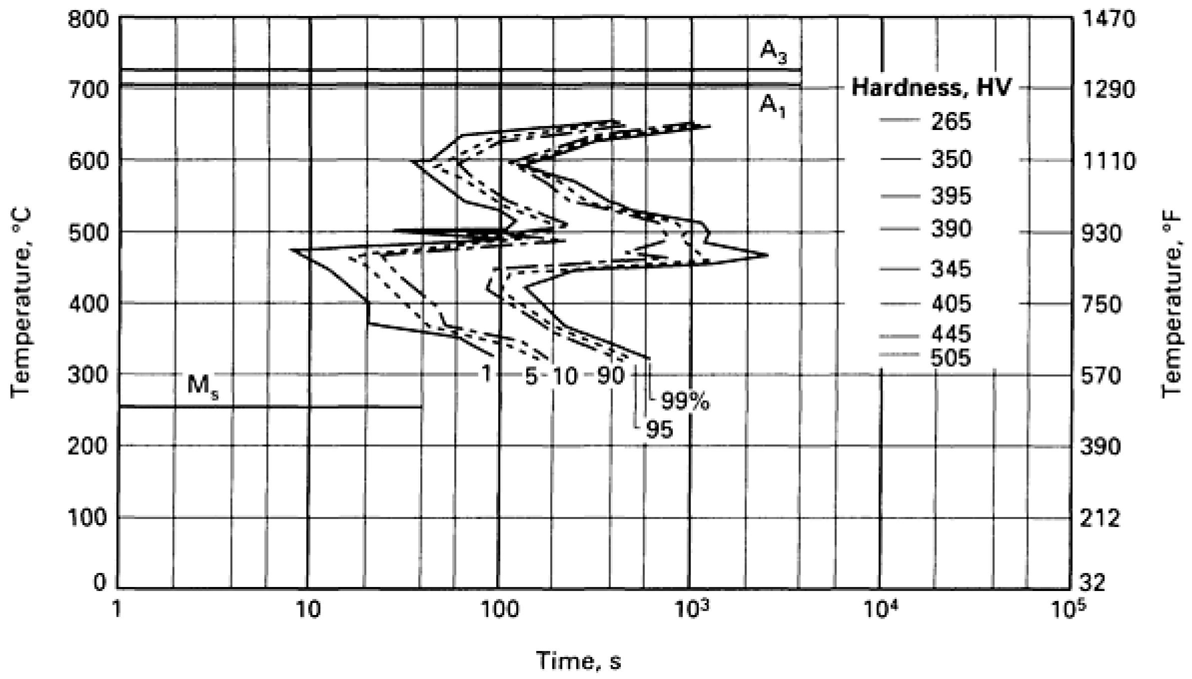

Fig. 6 Isothermal transformation diagram for a steel with 0.39% C, 0.86% Mn, 0.72% Cr, and 0.97% Ni. The upper C-shaped curves describe transformation to pearlite; the lower C-shaped curves to bainite. Ferrite is not visible. The column on the right side of the figure indicates the hardness after completed transformation measured at room temperature. Source: Ref 11

The transformation start curve shows as an upper-limiting estimate of the time (in seconds) for nucleation, τ. The isovolume fraction curves τ_x can semiempirically be described by a relation of the type (Ref 12):

$$t_x = \frac{\exp(Q/RT)}{2^{N/8}.\Delta T^3} f.I(X) \qquad \textbf{(Eq 1)}$$

where x is the volume fraction of the transformed phase, Q is an activation energy related to the boundary diffusion activation energies for the alloying elements, N is the ASTM grain size number for austenite, T is the temperature (in degrees Kelvin), ΔT is the undercooling (A_3 - T) for ferrite, (A_1 - T) for pearlite and an empirical value for bainite, f is a

linear function of the volume fractions of carbon and alloying elements and *I* is the volume fraction integral giving the dependence of the transformed phase on the volume fraction.

The combined effect of the $I/\Delta T^3$ factor, which increases with decreasing undercooling (that is, increasing temperature) and the exp (Q/RT) factor, which increases with decreasing temperature, results in long nucleation times, τ_x, for high and low temperatures and short nucleation times for intermediate temperatures. The C-shape can thus be obtained and understood. The factor $2^{N/8}$ is included to take into consideration the fact that the transformation rate is larger for smaller austenite grain sizes.

Figure 6 also indicates the martensite start temperature, M_s, which is time independent. A number of numerical expressions for the composition dependence of M_s have been suggested (Ref 13). One commonly used expression is (Ref 14):

$$M_s(°C) = 512-453C-16.9Ni + 15Cr-9.5Mo + 217(C)^2-71.5(C)(Mn)-67.6(C)(Cr) \quad \textbf{(Eq 2)}$$

where the alloying elements are represented by their weight percents. If the hold time in the austenitic range is too short the C-shaped cooling curves may be shifted to shorter times. This is the case in Fig. 7 where an IT diagram obtained after 6 s at 950 °C (1740 °F) is compared with an IT diagram after 10 min at 860 °C (1580 °F). The shift may be due to incomplete carbide dissolution or a smaller grain size after short austenitizing time.

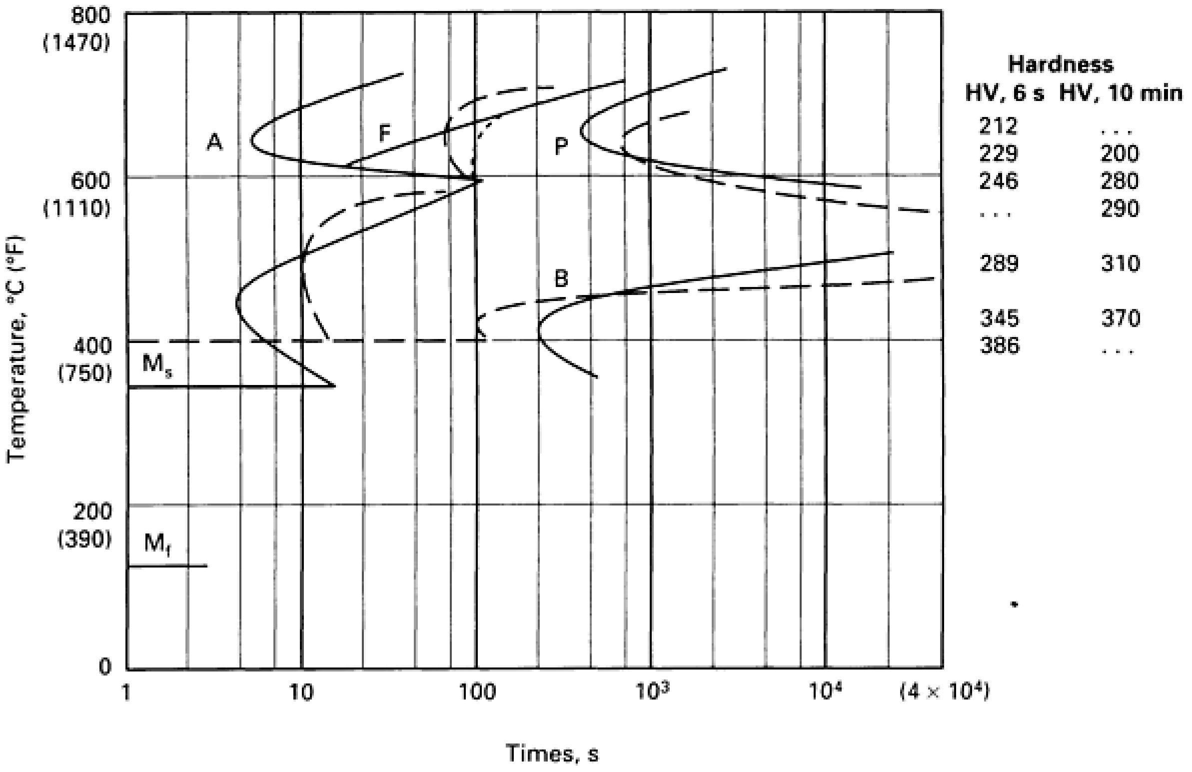

Fig. 7 Comparison of IT cooling diagrams for AISI 4140 steel after 6 s austenitizing time at 950 °C (1740 °F) (solid lines) and after 10 min austenitizing time at 860 °C (1580 °F) (dashed lines). Hardness values are also given for both heat-treated conditions. Source: Ref 9

Isothermal transformation curves can be found in standard graphs obtainable from the International Organization for Standardization (ISO), the Metallurgical Society of AIME, and ASM International (Ref 15). There is also a well-known German collection (Ref 10).

CHT Diagrams

In practical heat treatment situations, a constant temperature is not required, but rather a continuous changing temperature during either cooling or heating. Therefore, more directly applicable information is obtained if the diagram is constructed from dilatometric data using a continuously increasing or decreasing temperature. Figure 8 shows an example for continuous heating of the same steel as in Fig. 4. Indicated again are Ac_1 and Ac_3 and the same remarks as before are valid. The diagram was derived with constant heating rates and curves for 130 °C/s (265 °F/s), 10 °C/s (50 °F/s), and 0.2 °C/s (32 °F/s) are shown. Notice that the start and finish of the transformations are delayed relative to the isothermal diagram. This is generally true when one compares an isothermal and a continuous diagram, regardless of whether they are for heating or cooling.

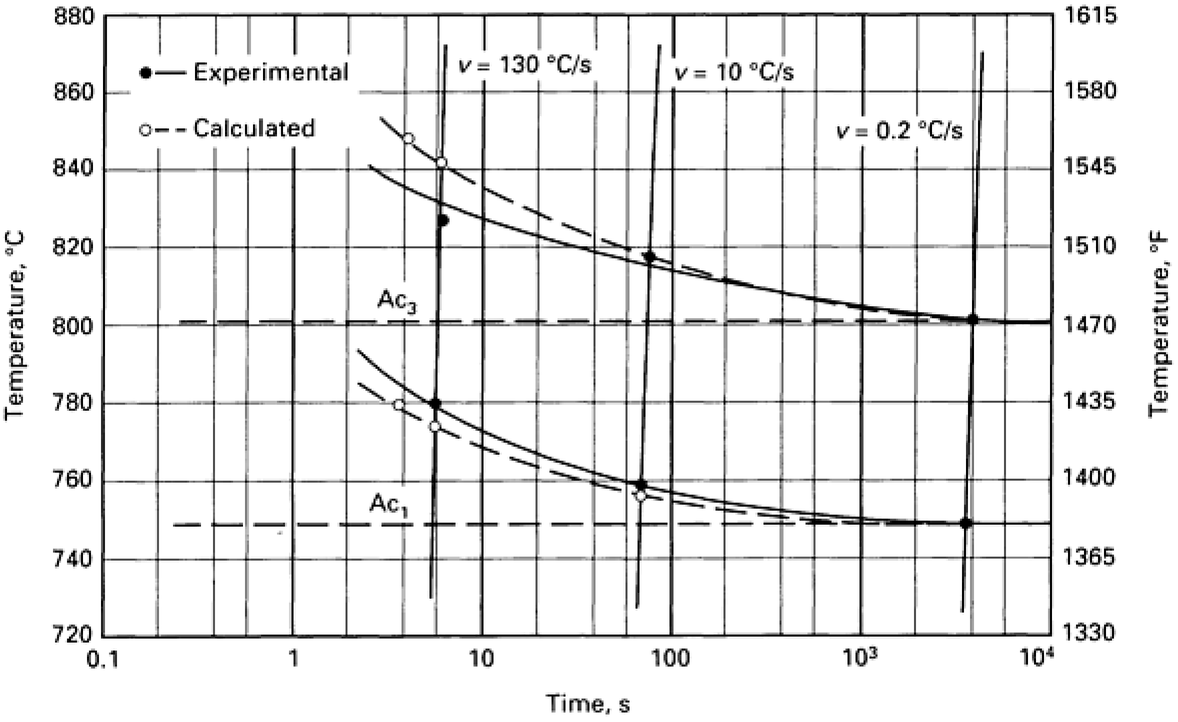

Fig. 8 Continuous heating transformation diagram for AISI 4140 steel. The phase being formed is austenite. Source: Ref 9

Like the ITh diagrams, the CHT diagrams are useful in predicting the effect of short-time austenitization that occurs in induction and laser hardening. One typical question is how high the maximum surface temperature should be in order to achieve complete austenitization for a given heating rate. Too high a temperature may cause unwanted austenite grain growth, which produces a more brittle martensitic microstructure. Reference 10 provides information on austenite grain growth as well as CHT diagrams.

CCT Diagrams

As for heating diagrams, it is important to clearly state what type of cooling curve the transformation diagram was derived from. Use of a constant cooling rate is very common in experimental practice. However, this regime rarely occurs in a practical situation. One can also find curves for so-called natural cooling rates according to Newton's law of cooling. These curves simulate the behavior in the interior of a large part such as the cooling rate of a Jominy bar at some distance from the quenched end. Close to the surface the characteristics of the cooling rate can be very complex as will be described below. In the lower part of Fig. 9 is shown a CCT diagram (fully drawn lines) for 4130 steel. Ferrite, pearlite, and bainite regions are indicated as well as the M_s temperature. Note that the M_s temperature is not constant when martensite formation is preceded by bainite formation, but typically decreases with longer times.

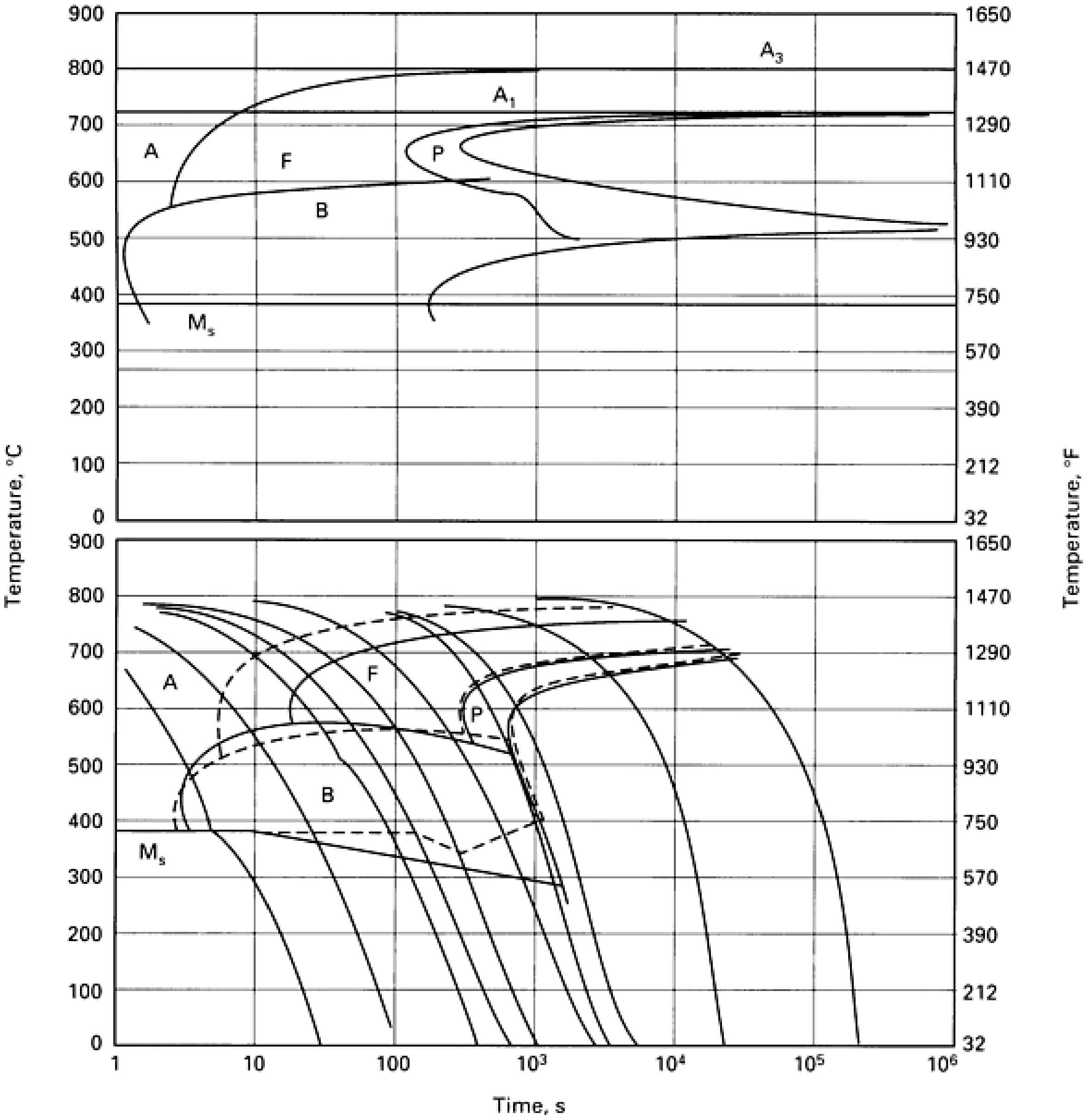

Fig. 9 Isothermal transformation (upper) and CCT (lower) diagrams for AISI 4130 steel containing 0.30% C, 0.64% Mn, 1.0% Cr, and 0.24% Mo. The IT diagram illustrates the input data representation for calculations described in the text. The CCT diagrams are computed (dashed lines) and experimentally determined (solid lines). Source: Ref 10, 11

The effect of different cooling curves is shown in Fig. 10. Each CCT diagram contains a family of curves representing the cooling rates at different depths of a cylinder with a 300 mm (12 in.) diameter. The slowest cooling rate represents the center of the cylinder. As shown in Fig. 10, the rate of cooling and the position of the CCT curves depend on the cooling medium (water produced the highest cooling rate followed by oil and air, respectively). The more severe the cooling medium, the longer the times to which the C-shaped curves are shifted. The M_s temperature is unaffected.

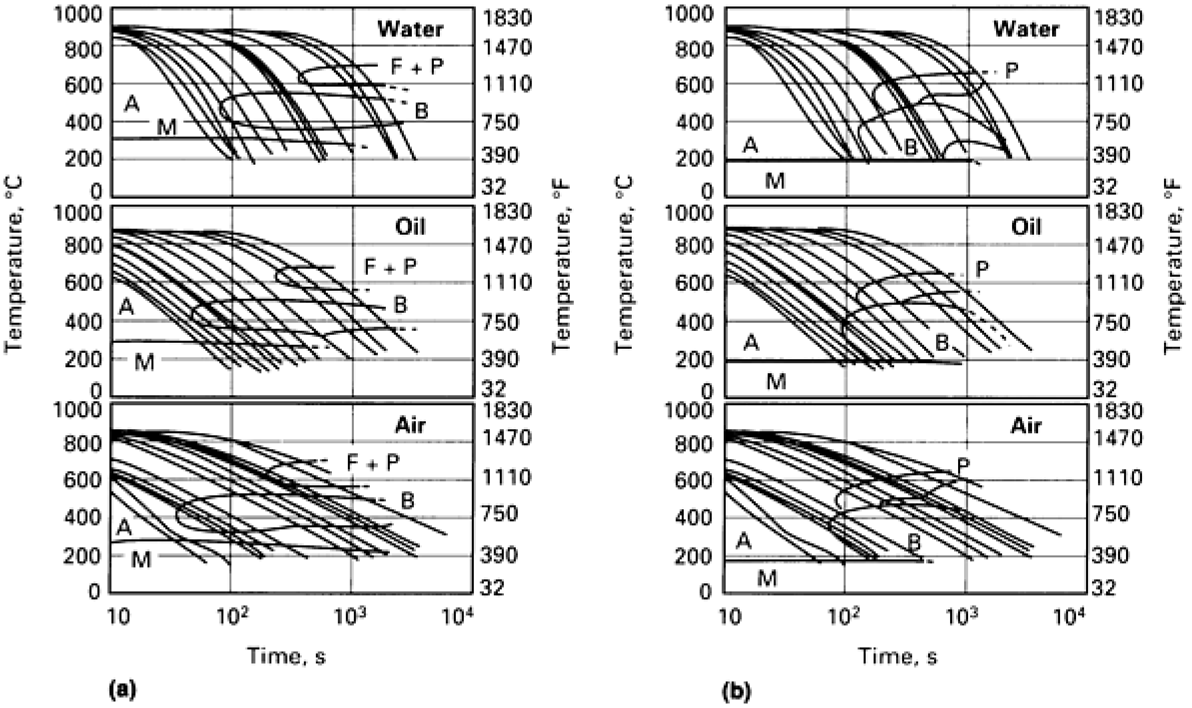

Fig. 10 Examples of CCT diagrams for low-alloy steels. (a) CCT diagrams of a chromium-molybdenum steel using simulated cooling curves for water, oil, and air. Source: Ref 16. (b) Computer-calculated CCT diagrams of a nickel-chromium steel containing 0.77 wt% C based on the cooling curves for water, oil, and air given in (a). Source: Ref 17

It should be noted, however, that transformation diagrams cannot be used to predict the response to thermal histories that are very much different from the ones used to construct the diagrams. For instance, first cooling rapidly to slightly above M_s and then reheating to a higher temperature will give more rapid transformation than shown in the IT diagram because nucleation is greatly accelerated during the introductory quench. It should also be remembered that the transformation diagrams are sensitive to the exact alloying content within the allowable composition range.

Various attempts have been made to facilitate the use of CCT diagrams by including the effect of the dimension of the workpiece and cooling medium on the microstructure and hardness obtained. Two such approaches have been described by Atkins (Ref 18) and Thelning (Ref 19). Experimental cooling curves were derived by Atkins for round bars of various diameters at fractional radii (*R*) 0.5 and 0.8 from the center during cooling in water, oil, and air. The cooling curves were used in dilatometer measurements to get the transformation temperatures and the resulting microstructures and hardnesses were also noted. A diagram of this type is shown in Fig. 11. From the diagram, one can correlate that a specimen, 2 mm (0.08 in.) in diameter being cooled in air, corresponds to a bar somewhat less than 40 mm (1.6 in.) in diameter cooled in oil, or to a bar 50 mm (2 in.) in diameter quenched in water. Shown in the upper part of the figure are the amount and type of microstructure; the lower part gives hardnesses after hardening and tempering at various temperatures.

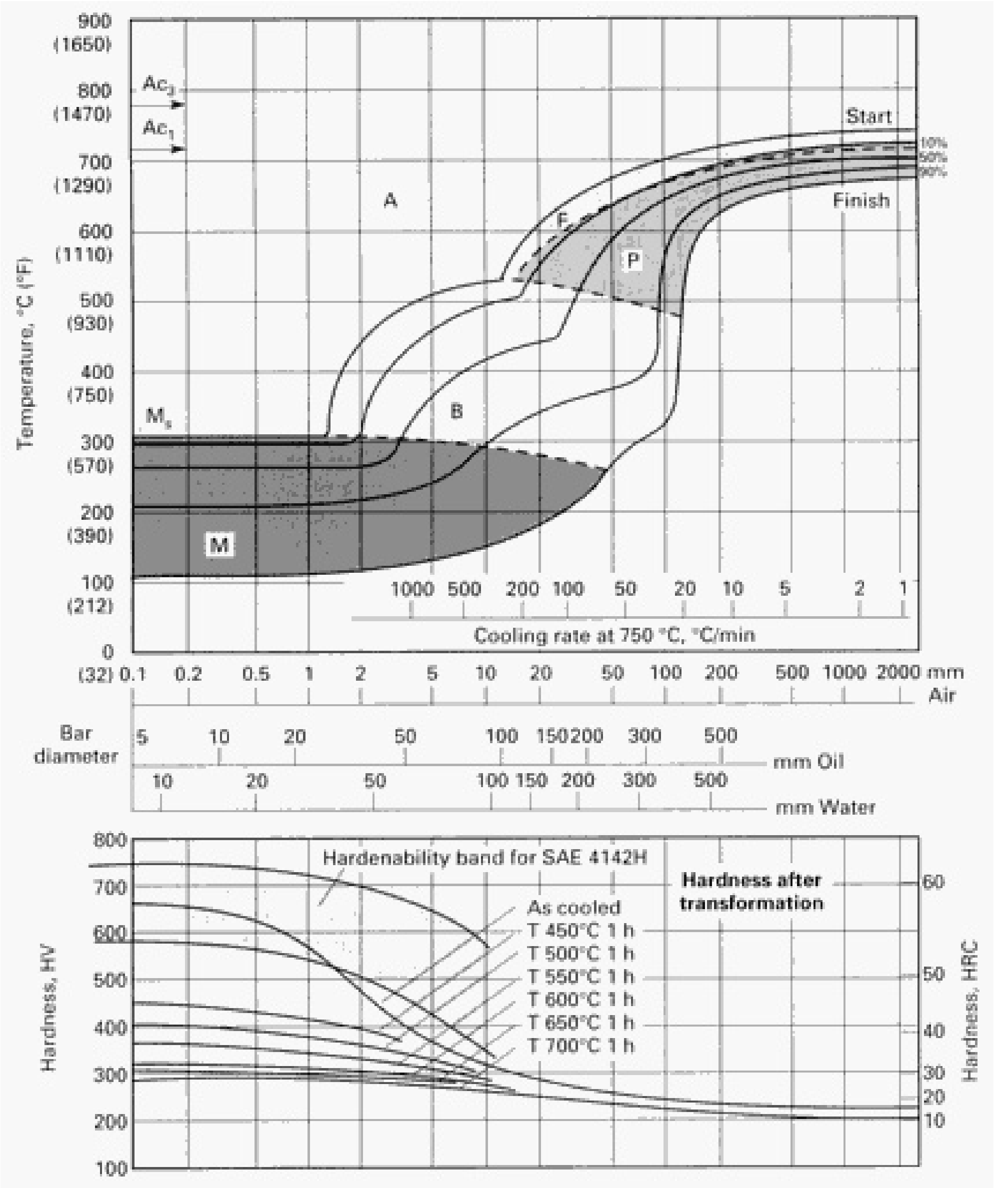

Fig. 11 A CCT diagram for 1.25Cr-0.20 Mo steel (SAE/AISI 4140-4142) that was austenitized at 860 °C (1580 °F). The vertical lines in the upper diagram give the cooling rate for the center of bars with different diameters when quenching in different media. The lower part of the figure shows the hardness after hardening and tempering (T) at various temperatures. Source: Ref 18

Thelning used the cooling curves just mentioned to derive dilatometer curves and presented the results in diagrams of the type shown in Fig. 12. From this diagram the structural constituents and hardness values that exist at 0.8 *R* and at the center of bars of various dimensions after cooling in water or oil can be determined.

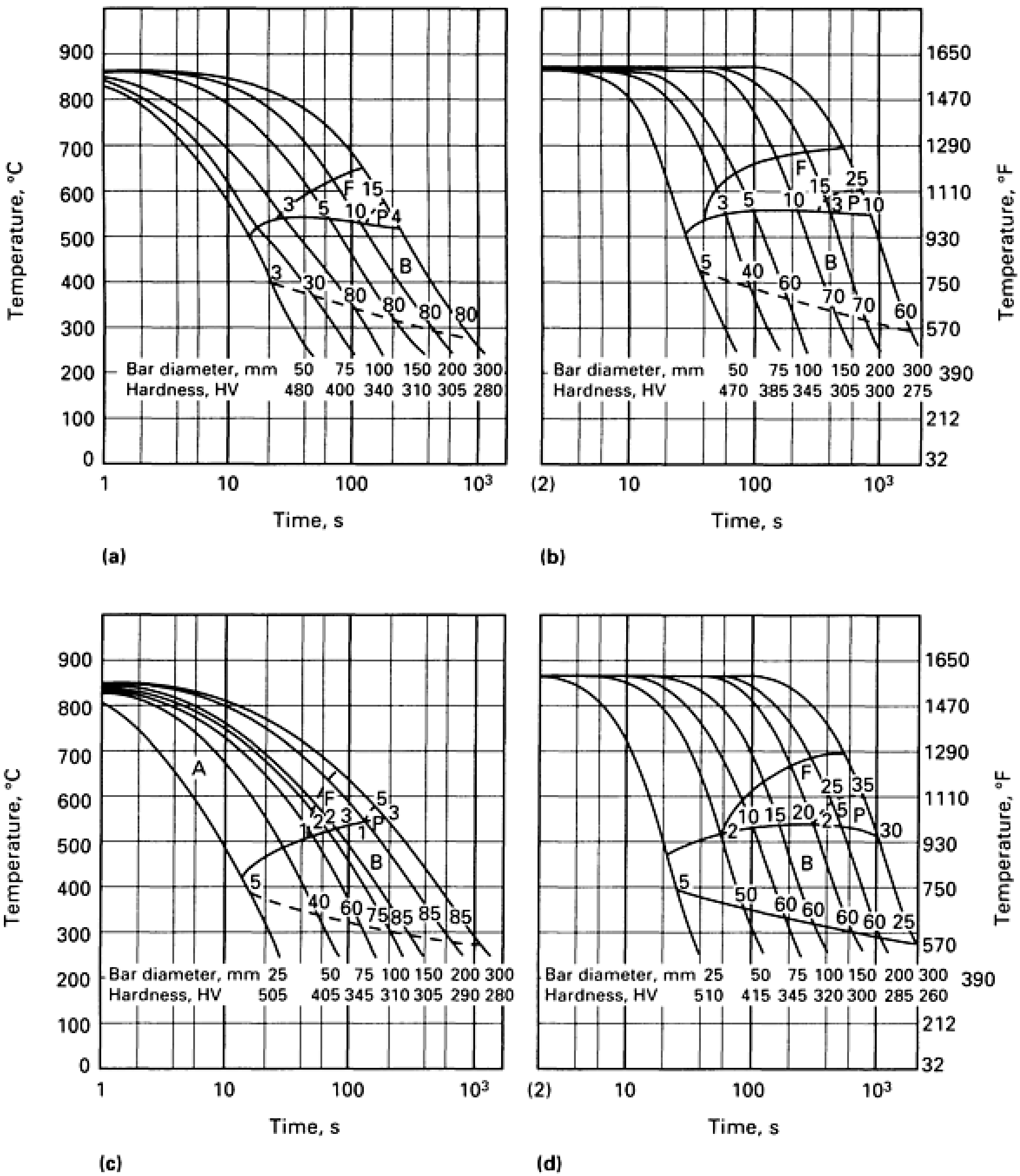

Fig. 12 CCT diagrams for AISI 4130 steel. (a) Water quench, 0.8 *R* specimen. (b) Water quench, center of specimen. (c) Oil quench, 0.8 *R* specimen. (d) Oil quench, center of specimen. Source: Ref 19

Computer Simulation of Transformation Diagrams

Because the experimental determination of transformation diagrams is costly and tedious, there is great interest in calculating these diagrams (Ref 20, 21). An effective computer model would allow the exact shape of the cooling curves discussed above to be determined.

The problems associated with developing such programs are twofold and involve the calculation of the TTT diagram and the calculation of the CCT diagram from the isothermal one. Because solving the first problem from first principles for a given steel composition is a formidable task, empirical correlations or semiempirical procedures are in current use (Ref 12). The second problem is much easier to handle, and several successful approaches have been tried. One of these will be presented below while alternative approaches are described in the following article in this Section (see"Quantitative Prediction of Transformation Hardening in Steels").

As a basis for the calculation, the Johnson-Mehl-Avrami expression that describes the diffusional transformation of austenite to either ferrite, pearlite, or bainite can be used:

$$v = 1 - \exp(-b \cdot t^{n}) \qquad \textbf{(Eq 3)}$$

where v is the transformed volume fraction, t is the time, and b and n are temperature-dependent constants; b and n are evaluated from the given TTT diagram except for ferrite for which it is assumed that n = 1. More generally, it can be stated that:

$$n = \frac{\log[\ln(1-v_s)/\ln(1-v_s)]}{\log[t_s(T)/t_f(T)]} \qquad \textbf{(Eq 4)}$$

$$b = \frac{-\ln(1-v_s)}{t_s(T)} \qquad \textbf{(Eq 5)}$$

where the subscripts s and f indicate start and finish, respectively. In a TTT diagram, v_s is usually chosen to be 1% and v_f 99%, but other percentages may also be chosen. The experimental C-shaped curves in the TTT diagrams are approximated by spline functions when stored in the computer. The cooling curve is approximated by a staircase, the step length being equal to the time step. The phase transformation is then calculated isothermally during each time step. This is equivalent to using the Scheil-Avrami additivity rule, which is described in the article "Quenching of Steel" in this Volume (see the discussion on quench factor analysis).

Note that in the general case several transformation products coexist and compete. For each phase being formed, a separate set of equations is written. For ferrite, the maximum volume fraction possible above A_1 is less than unity and is given by application of the lever rule to the multi-component phase diagram.

The martensitic transformation relation is based on the following expression (Ref 22):

$$v_M = (1 - v_F - v_P - v_B - v_C)\,(1 - \exp(-0.011 \cdot (M_s - T))) \qquad \textbf{(Eq 6)}$$

where F, P, B, and C represent ferrite, pearlite, bainite, and cementite, respectively.

A comparison between measured and calculated CCT diagrams derived by linear cooling is shown in Fig. 9. The agreement is quite satisfactory. Figure 10 shows that the effect of different cooling rates on the CCT diagram is well reproduced by the calculations.

The model described above has been refined by incorporating a nucleation stage before the diffusional-growth stage (Ref 21). Scheil's principle of additivity of incubation fractions has been used, that is, for each time step, denoted as Δt_i, the fraction $\Delta t_i/\tau_{iIT}$ is calculated where τ_{iIT} is the time to the start of the transformation of the temperature prevailing during the time step. The fractions are then summed:

$$\sum \frac{\Delta t_i}{t_{iIT}}$$

When this sum attains unity, the incubation period is over. The nonadditivity of pearlitic and bainitic nucleation is accounted for by a correction factor of the Scheil sum at the transition from pearlite to bainite.

The calculation of the CHT diagram from the ITh diagram on heating is quite analogous. Good agreement between calculated and measured CHT curves where linear heating was applied is shown in Fig. 8.

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Hardenability Concepts

The goal of heat treatment of steel is very often to attain a satisfactory hardness. The important microstructural phase is then normally martensite, which is the hardest constituent in low-alloy steels. The hardness of martensite is primarily dependent on its carbon content as is shown in Fig. 13. If the microstructure is not fully martensitic, its hardness is lower. In practical heat treatment, it is important to achieve full hardness to a certain minimum depth after cooling, that is, to obtain a fully martensitic microstructure to a certain minimum depth, which also represents a critical cooling rate. If a given steel does not permit a martensitic structure to be formed to this depth, one has to choose another steel with a higher hardenability (the possibility of increasing the cooling rate at the minimum depth will be discussed later). There are various ways to characterize the hardenability of a steel. Certain aspects of this will be discussed in the following article in the Section and has also been described in detail in previous *ASM Handbooks*, formerly *Metals Handbooks* (Ref 23). The CCT diagram can serve this purpose if one knows the cooling rate at the minimum depth. The CCT diagrams constructed according to Atkins or Thelning presented above are particularly suitable.

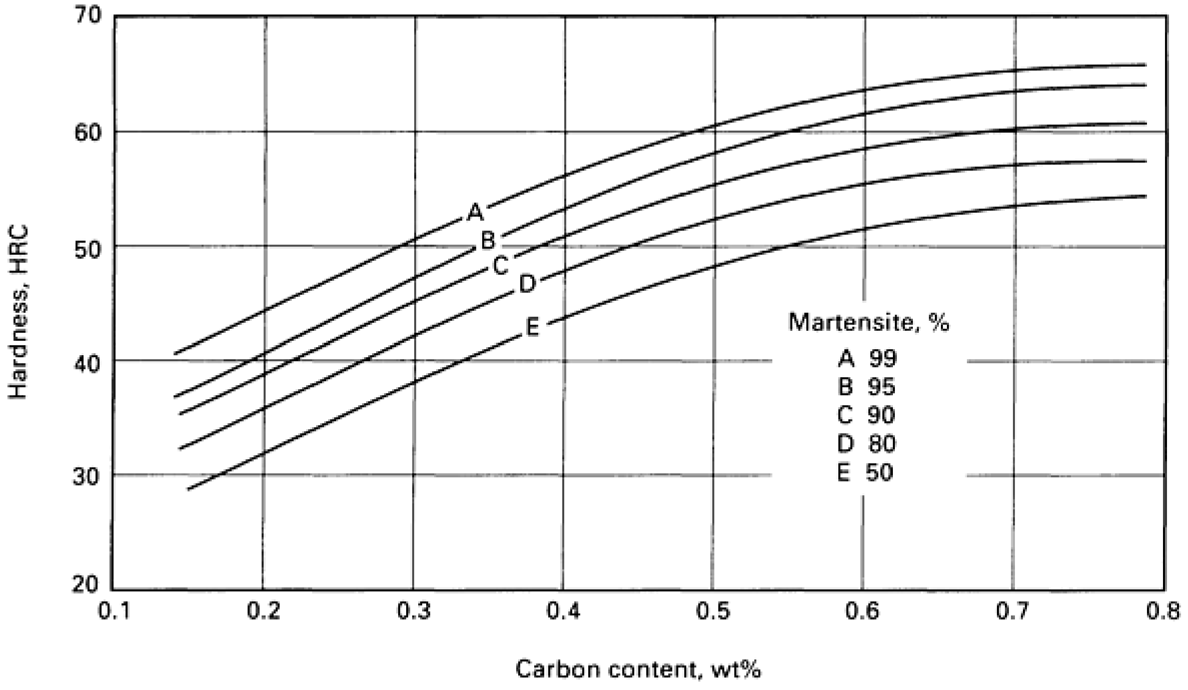

Fig. 13 Relationship between hardness, carbon content, and amount of martensite

Grossmann Hardenability Test. Another method using cylindrical test bars is the classical one of Grossmann (Ref 24). A number of cylindrical steel bars of different diameters are hardened in a given cooling medium. By means of metallographic examination, the bar that has 50% martensite at its center is singled out and the diameter of this bar is designated as the critical diameter (D_0). This D_0 value is valid for the particular cooling medium used as well as its cooling intensity. An ideal cooling situation is when the surface of the test bar is immediately cooled to ambient temperature, that is, an infinite cooling rate at the surface. Although such cooling cannot be carried out in practice, one can mathematically extrapolate this situation and derive the ideal Grossmann diameter, D_I, defined as the bar diameter that, when the surface is cooled at an infinite rate, will yield a structure containing 50% martensite at the center of the specimen. The value of D_I obtained is a measure of the hardenability of the steel and is independent of the cooling medium. Using this method, D_I values have been determined for low- and medium-carbon steels with different carbon contents and grain sizes. The additional effect of alloying elements has been determined for a number of alloying elements and is expressed as hardenability factors, f, which are multiplying factors corresponding to the percentage of alloying element present. The ideal diameter, D_I, for a certain steel can then be expressed as:

$$D_I = D_0 \cdot f_1 \cdot f_2 \cdot f_3 \ldots$$

where f_1, f_2, f_3 are the factors for alloying elements 1, 2, 3. . ., respectively, and D_0 applies to Fe-C alloys.

Diagrams have been developed that convert D_I to D_0 for the cooling medium of interest. The ISO has also developed diagrams to convert from rectangular to round sections.

The Grossmann method is frequently used but gives a very approximate measure of hardenability. However, it can be reliably employed to compare steels of different compositions. More detailed information on the Grossmann method and the calculation of D_I values from the chemical composition can be found in Ref 19 and in the article "Quenching of Steel" in this Volume.

Jominy End-Quench Test. The most commonly used experimental method for hardenability is the well-known Jominy test (Ref 23). For this test a round bar specimen that is 100 mm (4 in.) in length and 25 mm (1 in.) in diameter is used. The specimen is heated to the austenitizing temperature of the steel with a holding time of 20 min. One endface of the specimen is quenched by spraying it with a jet of water. This causes the rate of cooling to decrease progressively from the quenched end along the length of the bar. When it is cool, two diametrically opposite flats that are 0.4 mm (0.015 in.)

deep and parallel to the axis of the bar, are ground and the hardness is measured along the flats. The hardness values are plotted on a diagram at specified intervals from the quenched end. To get good reproducibility, the time and temperature of austenitizing, the grinding of the flats to avoid burning, and the placement of the specimen in the hardness tester should be carefully controlled. It is also important to protect the specimen against decarburization. Less critical are the water temperature, the diameter of the spraying nozzle, the height of the water jet, and the time to move the specimen from the furnace to the fixture. For steels with very high or very low hardenability, neither the Grossmann nor the Jominy methods are well suited and other methods are used. These methods are well covered in Volume 1 of *ASM Handbook*, formerly 10th Edition of *Metals Handbook* (Ref 23) and in Ref 24.

The rate of cooling at different distances from the quenched end is approximately independent of the steel used because the thermal conductivity and heat capacity of hardenable steels do not vary very much and the heat transfer at the cooled end is steel independent. Therefore, the Jominy bar presents a range of cooling curves that can be used to estimate a CCT diagram. The cooling rates are not linear but rather of the natural type according to Newton's law of cooling. The volume fractions of the various constituents of the microstructure are evaluated quantitatively at different Jominy distances as well as hardness measurements. Conversely, the Jominy curve can be calculated from the TTT diagram using the computer methods described above and expressions that give the hardness for the different phases (Ref 18). The total hardness is then the weighted average. Figure 14 shows the agreement between calculated and experimental Jominy curves that can be achieved.

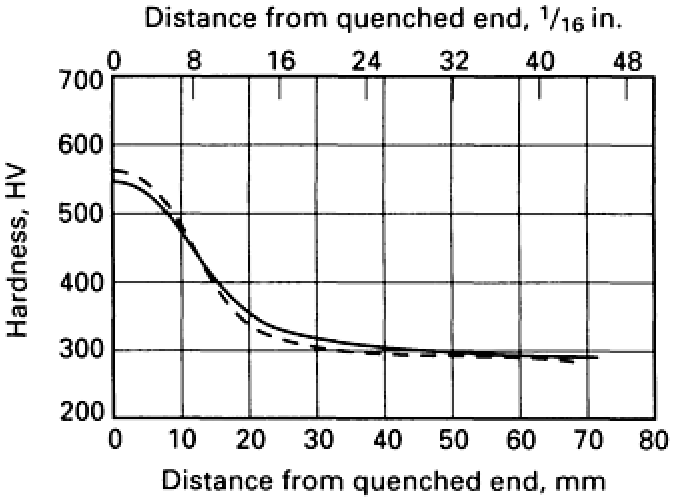

Fig. 14 Calculated hardness (dashed line) and reported hardness (solid line) from a Jominy test of AISI 4130 steel. Source: Ref 10, 11

There is an economic trend to reduce the amount of experimental Jominy testing and replace it by the calculation of Jominy curves from the chemical composition and the grain size. Several regression formulas have been developed for different grades of steel which are quite accurate for a limited composition range. A more general approach will be described in the article "Quantitative Prediction of Transformation Hardening in Steels" that immediately follows.

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Principles of Tempering of Steels

As pointed out earlier in this article, martensite is a very hard phase in steel. It owes its high hardness to a strong supersaturation of carbon in the iron lattice and to a high density of crystal defects, especially dislocations, and high- and low-angle boundaries. However, except at low carbon contents, martensitic steels have insufficient toughness for many applications. Tempering of martensitic steels, by heating for a certain time at temperatures below the A_1, is therefore introduced to exchange some of the strength for greater ductility through reduction of the carbon supersaturation initially present and replacing it with more stable structures. Additionally, the retained austenite associated with martensite in steels containing more than about 0.7 wt% C can be decomposed during the tempering process. In carbon steels containing small percentages of the common alloying elements, one distinguishes the following stages during tempering (Ref 3):

- *Stage 1* (20 to 100 °C, or 70 to 212 °F). Short-range diffusion of carbon atoms to dislocations and martensite plate boundaries; formation of carbon clusters
- *Stage 2* (100 to 200 °C, or 212 to 390 °F). Precipitation of transition carbides, especially ϵcarbide ($Fe_{2.4}C$)
- *Stage 3* (200 to 350 °C, or 390 to 660 °F). Transformation of retained austenite to ferrite and cementite
- *Stage 4* (250 to 700 °C, or 480 to 1290 °F). Formation of ferrite and cementite. Spheroidized carbides in a matrix of equiaxed ferrite grains comprises well-tempered steels, that is, tempered for long times at temperatures approaching 700 °C (1290 °F)

In steels alloyed with chromium, molybdenum, vanadium, or tungsten, formation of alloy carbides occurs in the temperature range 500 to 700 °C (930 to 1290 °F).

During stage 1, the hardness increases slightly while during stage 2, 3, and 4 the hardness decreases. Figure 15 shows the hardness of some steels after tempering for 2 h at different temperatures.

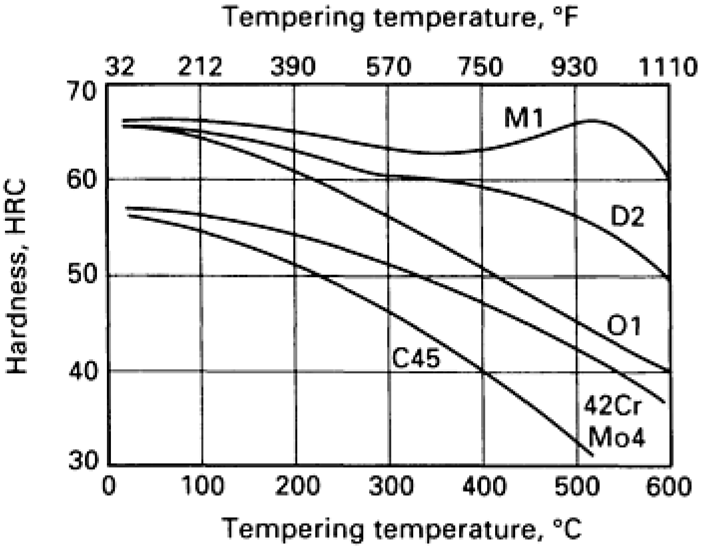

Fig. 15 Tempering curves for some current steels. The steel 42CrMo4 is equivalent to AISI 4142 and C45 to AISI 1045. Source: Ref 19

Hollomon and Jaffe (Ref 25) showed that the relation between hardness and time and temperature of tempering can be expressed graphically by plotting hardness as a function of a tempering parameter *P,* where:

$$P = T(k + \log t)$$

In this expression, T is the temperature (in degrees Kelvin), k is a constant with a value of about 20, and t is the time in hours. The physical background to this empirical expression is the fact that the various tempering reactions are thermally activated diffusional processes.

The toughness of a steel increases with decreasing hardness. However, when certain impurities such as arsenic, phosphorus, antimony, and tin are present, a toughness minimum termed "temper embrittlement" may occur in the temperature range 350 to 600 °C (660 to 1100 °F) due to segregation of impurities to grain boundaries. Temper embrittlement is a problem when parts are exposed to temperatures in the critical range for rather long times and is a concern for parts exposed to these temperatures while in service or when heat treating very massive parts which require long times to heat and cool. It is not a concern, even for susceptible alloys, if small parts are exposed to these temperatures for an hour or so during heat treatment, then used at ambient temperatures. Nuts and bolts, for example, made of various types of steels, are tempered in this temperature range with no problems as long as they are used at lower temperatures. The time for embrittlement to occur at differing tempering temperatures shows a C-shaped curve behavior in a temperature-log time diagram similar to what is found in transformation diagrams (Fig. 16). The long times in the upper temperature range are due to low thermodynamic driving force and in the lower temperature range to slow diffusion. Temper embrittlement can be removed by reheating the steel above 600 °C (1110 °F) followed by rapid cooling, for example, water quenching.

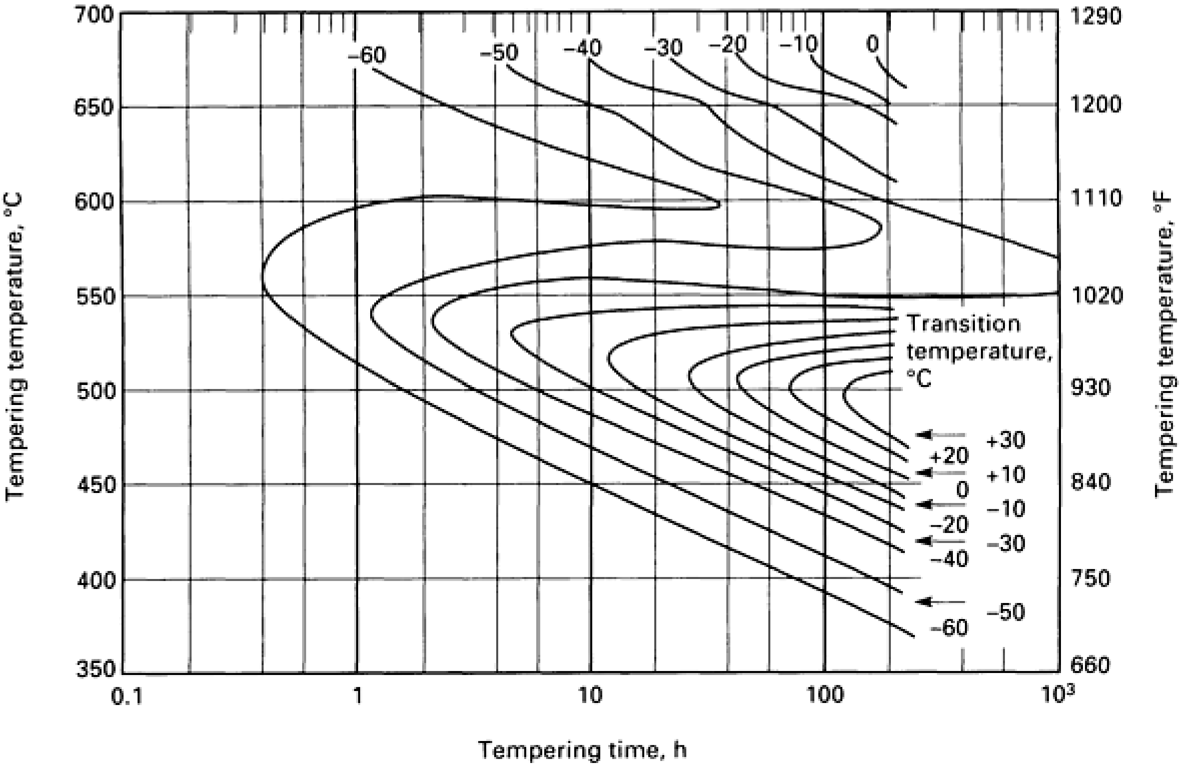

Fig. 16 Dependence of transition temperature on tempering temperature and time for SAE 3140 steel containing 0.40% C, 0.80% Mn, 0.60% Cr, and 1.25% Ni. Water quenched from 900 °C (1650 °F). Source: Ref 26

Another type of embrittlement that affects high-strength alloy steels is tempered martensite embrittlement (also known as 350 °C, or 500 °F, embrittlement), which occurs upon tempering in the range of 205 to 370 °C (400 to 700 °F). It differs from temper embrittlement in the strength of the material and the temperature exposure range. In temper embrittlement, the steel is usually tempered at a relatively high temperature, producing lower strength and hardness, and embrittlement occurs upon slow cooling after tempering and during service at temperatures within the embrittlement range. In tempered martensite embrittlement, the steel is tempered within the embrittlement range, and service exposure is usually at room temperature. Therefore, temper embrittlement is often called two-step temper embrittlement, while tempered martensite embrittlement is often called one-step temper embrittlement. Detailed information on both temper embrittlement and

tempered martensite embrittlement, including time-temperature diagrams for embrittled steels, can be found in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook* (see Ref 27).

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Cooling Media and Quench Intensity

The depth of hardness at a given work-piece dimension is determined by the chemical composition of the steel, the austenite grain size as established during the austenitizing treatment, and the cooling rate. The steel is normally chosen on the basis of hardenability. The choice of cooling medium, on the other hand, is less exact and crude rules are normally applied (unalloyed steel is quenched in water, alloy steels in oil, and high-alloy steels in air). Molten salt is often used for bainitic hardening of medium-carbon steels and martempering of carburized parts (salt temperature above M_s for the case). Judicious selection of cooling medium is critical for obtaining optimum mechanical properties, avoiding quench cracks, minimizing distortion (to be discussed below), and improving reproducibility in hardening. Of most interest are the liquid quenching media, and they also show the most complicated cooling process. More detailed information on cooling (quench) media can be found in the article "Quenching of Steel" in this Volume.

Three Stages of Quenching. The most commonly used liquid quenching media are water and its solutions (brine and caustic solutions), oils, and polymer solutions. During the quenching of steel in liquid media, the process may be split up into the following three stages:

- The vapor blanket stage
- The boiling stage
- The convection stage

Figure 17 shows a typical cooling curve for an oil and at the same time shows what happens at the surface of a steel that is being quenched.

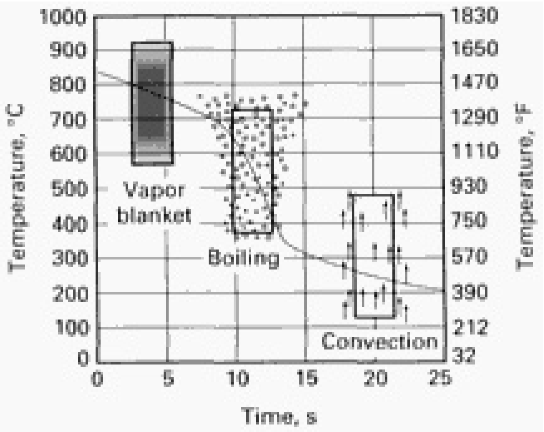

Fig. 17 The three stages of quenching. Source: Ref 19

In the vapor blanket stage the surface temperature is so high that the cooling medium is vaporized and a thin vapor is formed around the part. Heat transfer occurs by radiation through the vapor blanket, which thus acts as an insulating layer. The cooling rate is therefore low. The time duration of the vapor blanket stage can vary considerably among different cooling liquids and is also affected by the surface condition (for example, the presence of oxide scale) and how densely the work-pieces are loaded on the furnace tray.

The boiling stage starts when the surface temperature has decreased to the point where the heat of radiation does not sustain a stable vapor blanket. The liquid that is brought into contact with the hot surface boils immediately and vapor bubbles leave the metal surface and provide efficient heat transfer. This gives a high rate of heat extraction.

The convection stage starts when the surface temperature has decreased to the boiling point of the cooling medium. The heat transfer occurs by direct contact between surface and liquid. The cooling rate is low and is affected primarily by quench viscosity and convection rate.

Evaluating Quenching Media. There are a great number of different methods for evaluating quenching media. Frequently, a 12.5 mm diameter by 60 mm long (0.5 × 2.5 in.) cylinder (probe) made of a nickel-base alloy or stainless steel is used. A thermocouple is located at the center of the testing body and is connected to a recording instrument. Examples of such cooling curves are shown in Fig. 18. Of more interest in many situations is the cooling rate, also shown in Fig. 18, obtained by differentiation of the cooling curves. These types of curves are useful for comparison between quenching media and judging the condition of a certain medium. Earlier a silver ball, 20 mm (0.08 in.) in diameter, was employed as the probe. The cooling curves from such measurements are even more difficult to apply to hardness predictions because silver has very different thermal properties and the physical properties at the surface are not representative of steel.

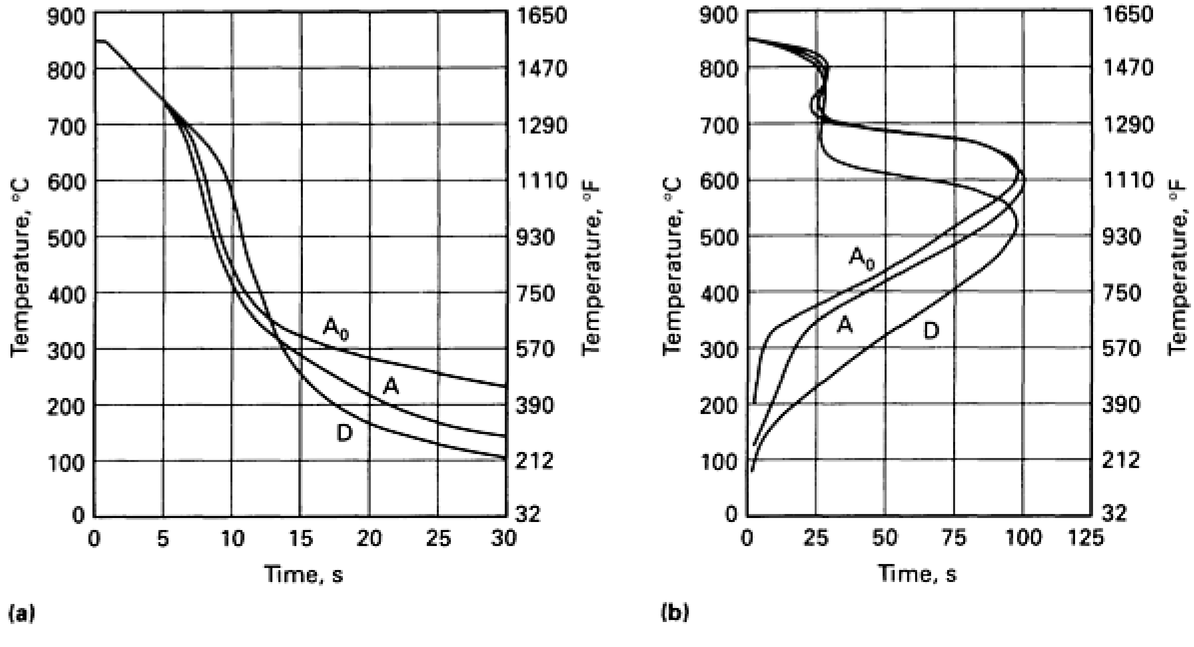

Fig. 18 Temperature-time curves (a) and temperature-cooling rate curves (b) obtained using an Alloy 600 probe. A and D are two oils with slight agitation, and A_0 is the oil A with no agitation. Source: Ref 28

Visual observations have shown that the breakdown of the vapor blanket starts at edges where the radius of curvature is small. The length of the test specimen can therefore affect the duration of the vapor blanket stage.

Figure 19 shows the temperature at different depths below the surface of an Inconel probe quenched in oil. This figure illustrates that the different quench stages are more pronounced closer to the specimen surface and that the resulting

temperature curves differ more from either linear or natural cooling curves. The conventional CCT curves must then be used with caution for hardening response predictions.

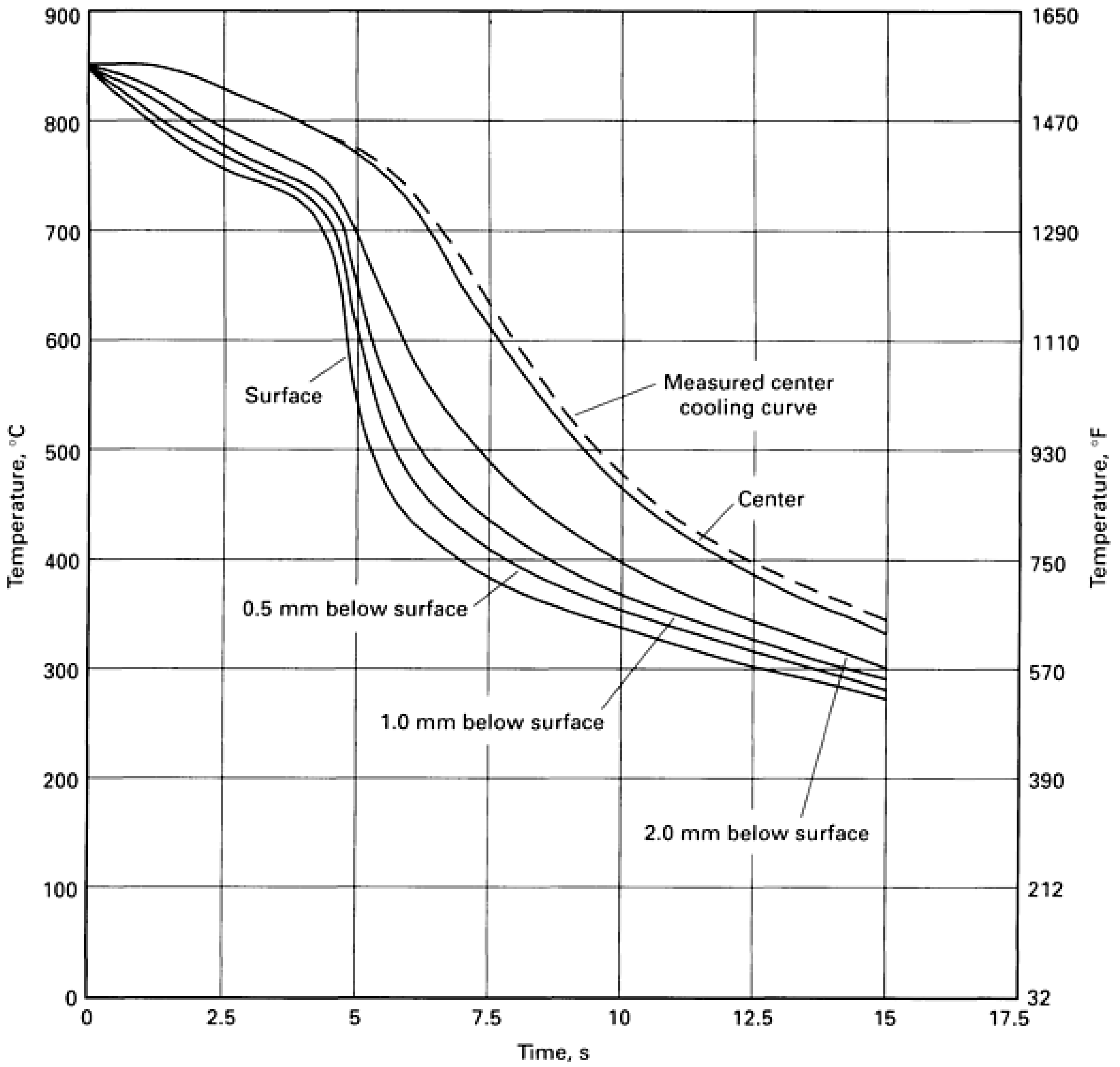

Fig. 19 Calculated cooling curves obtained using an Alloy 600 probe based on the heat flow curve in Fig. 20. Source: Ref 29

The curves in Fig. 19 are calculated using the temperature measured 2 mm (0.08 in.) below the surface. The calculation is based on the solution of the heat-flow equation. The experimental curve is assumed to be the boundary condition when determining the temperature-time history of the probe. The calculated temperature gradient through the surface is then employed to solve the heat transfer through the outer surface, which can then be expressed as a function of the surface temperature (Fig. 20). The heat-transfer function thus derived can be used to solve the heat-flow equation for the part of interest and to derive the temperature distribution in the part as a function of time, provided that the same state of quenching medium agitation prevails. A more accurate heat-transfer function is obtained if the experimental curve is measured closer to the surface. However, this is experimentally more difficult.

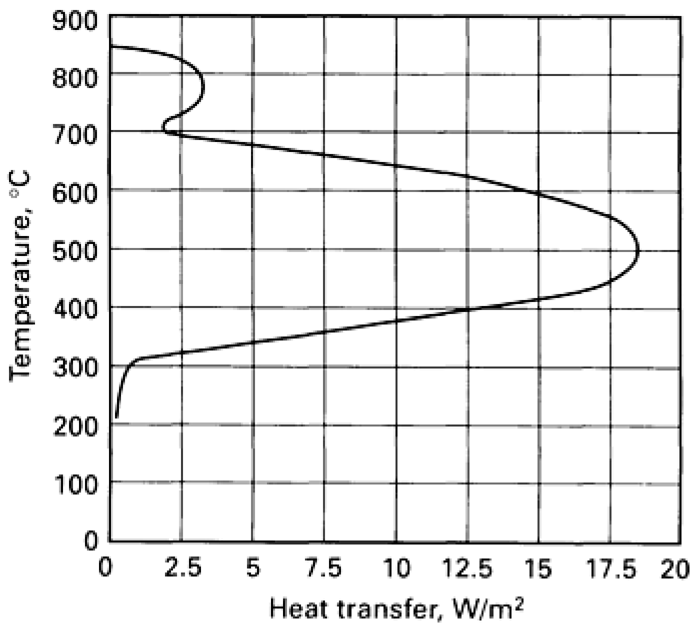

Fig. 20 Heat transfer as a function of surface temperature of the test probe used in Fig. 19. The curve is calculated from temperature measurements 2.0 mm (0.08 in.) below the probe surface. Source: Ref 29

In the classical literature, the quench severity concept, or the Grossmann number, is used. This is a single temperature independent value for each state of agitation of oil, water, and brines, respectively. It is a much cruder measure of the quench intensity than the heat-transfer function. The Grossmann number (*H*-value) is defined by $H = h/2k$, where h is the coefficient of heat transfer at the metal-quenchant interface and k is the thermal conductivity. See the article "Quenching of Steel" in this Volume for a more detailed discussion of the Grossmann number.

Very often it is stated that a short-lived vapor blanket stage will enhance the hardening result. This is not always correct as has been pointed out by Thelning (Ref 19). The most important consideration is the rate of cooling through the temperature ranges in which the diffusion-dependent transformations take place. Therefore, the characteristics of the steel must be considered at the same time as the quenching medium. It should also be noted that by adding certain organic substances to an oil or water quenchant, the cooling characteristics can be modified by extending the vapor blanket stage or delaying the transition from the boiling stage to the convection stage.

A more recently developed method is computer-controlled spray cooling (Ref 30). Using this technique, it is possible to program fast cooling past the pearlite nose on the CCT diagram, have a very slow cooling just above M_s, followed by a moderate cooling during the martensite transformation.

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Thermal Stresses during and Residual Stresses after Heat Treatment

Heat treatment of steel, especially martensitic hardening, is usually accompanied by the evolution of large residual stresses, that is, stresses that exist without any external load on the part considered. Causes for such stresses include:

- Thermal expansion or contraction of a homogeneous material in a temperature gradient field
- Different thermal expansion coefficients of the various phases in a multiphase material
- Density changes due to phase transformations in the metal
- Growth stresses of reaction products formed on the surface or as precipitates, for example, external and internal oxidation

Residual stresses can be divided into three categories. A macroresidual stress is the average of the residual stress in many adjacent grains of the material. If a work-piece is cut or material is removed, the presence of macroresidual stress will cause a distortion. The introduction of macroresidual stresses into a workpiece by heat treatment or plastic deformation may also cause a distortion of the part. The pseudo-macroresidual stress is the average of the residual stress in many grains of one phase in a multiphase material minus the macroresidual stress. The microresidual stress in a part is the total residual stress minus the macroresidual and the pseudo-macroresidual stress. The residual stresses considered in this section are of the macrotype. Stresses that exist during the entire heat-treatment process will also be discussed in the following paragraphs.

The subject of residual stresses after heat treatment of steel has been studied extensively in the recent literature (Ref 31, 32, 33) and is also discussed in the article "Defects and Distortion in Heat-Treated Parts" in this Volume. The principle for the creation of thermal stresses on cooling is shown in Fig. 21 for a 100 mm (4 in.) diameter bar that was water quenched from the austenitizing temperature of 850 °C (1560 °F). The surface temperature (S) decreases more rapidly than the core temperature (C), and at time *w*, the temperature difference between the surface and core is at a maximum of about 550 °C (1020 °F). This means that the specific volume is greater in the core than in the surface. The volume contraction in the surface is prevented by the higher specific volume in the core. The thermal stress is approximately proportional to the temperature difference and is tensile in the surface and compressive in the core. Large thermal stresses are favored by low thermal conductivity, high heat capacity, and high thermal expansion coefficient. Other factors increasing the temperature difference and thermal stresses are large thickness dimensions and high-cooling intensity of the cooling medium. A large yield stress at elevated temperatures will decrease the degree of plastic flow and thus the residual stress, while the yield stress at the ambient temperature puts an upper limit on the residual stress.

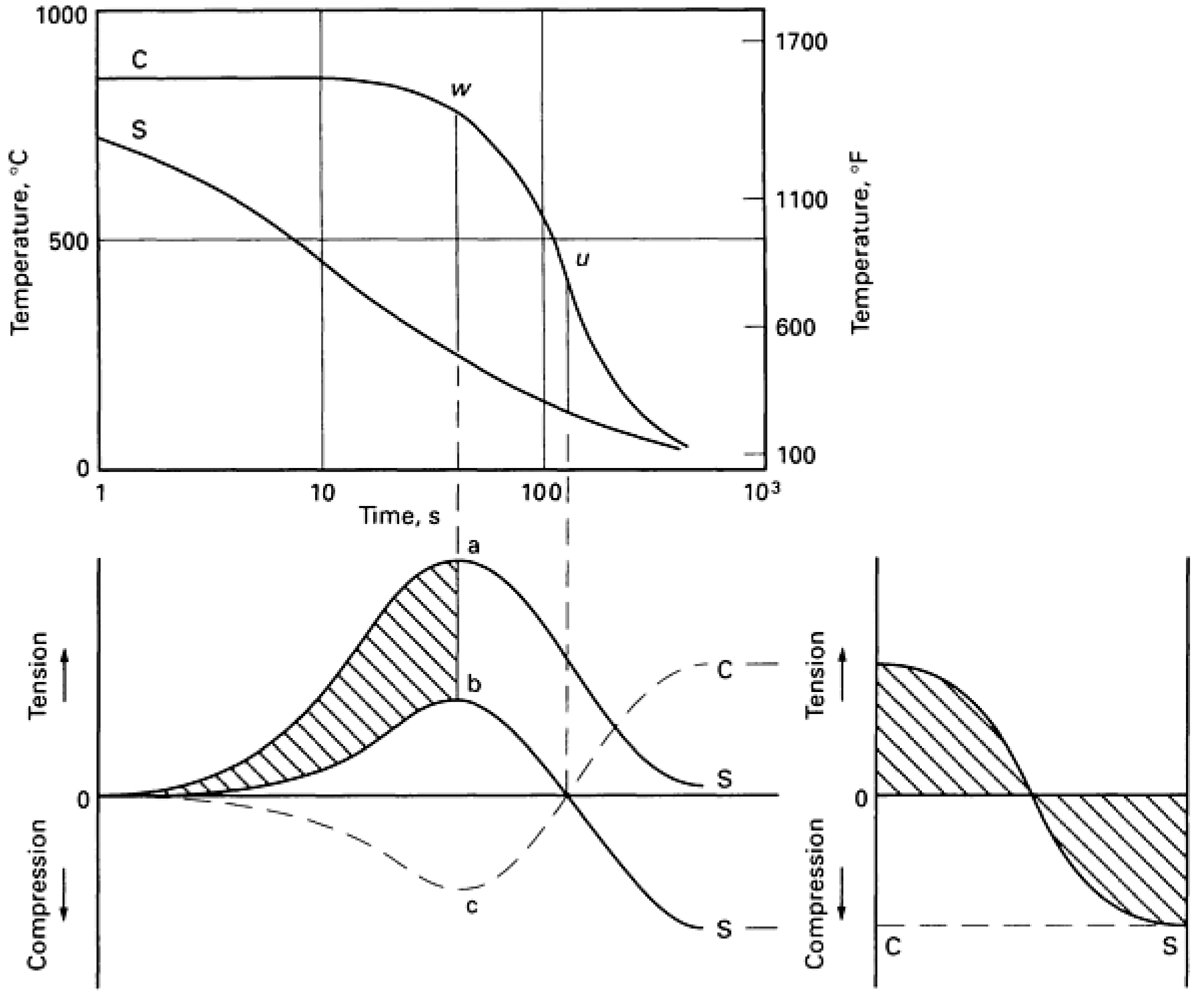

Fig. 21 Formation of thermal stresses on cooling in a 100 mm (4 in.) steel specimen. C designates the core, S the surface, *u* the stress reversal time instant, and *w* the time instant of maximum temperature difference. The top graph shows the temperature variation with time at the surface and in the core; the graph below shows the hypothetical thermal stress, a, which is proportional to the temperature difference between the surface and the core, the actual stress at the surface, b, which can never exceed the yield stress, and the actual stress in the core, c. To the right is shown the residual stress distribution after completed cooling as a function of the specimen radius. Source. Ref 33

The added effect of transformation of austenite to martensite in steel is demonstrated in Fig. 22. At time t_1, the surface temperature falls below the M_s temperature and the surface starts to transform. The surface expands and the thermal tensile stresses are counteracted. The stress reversal takes place earlier than when transformation stresses are not taken into consideration. At time t_2, the core transforms, causing another stress reversal. After cooling, transformation-induced tensile stresses at the surface dominate over the thermally induced compressive stresses.

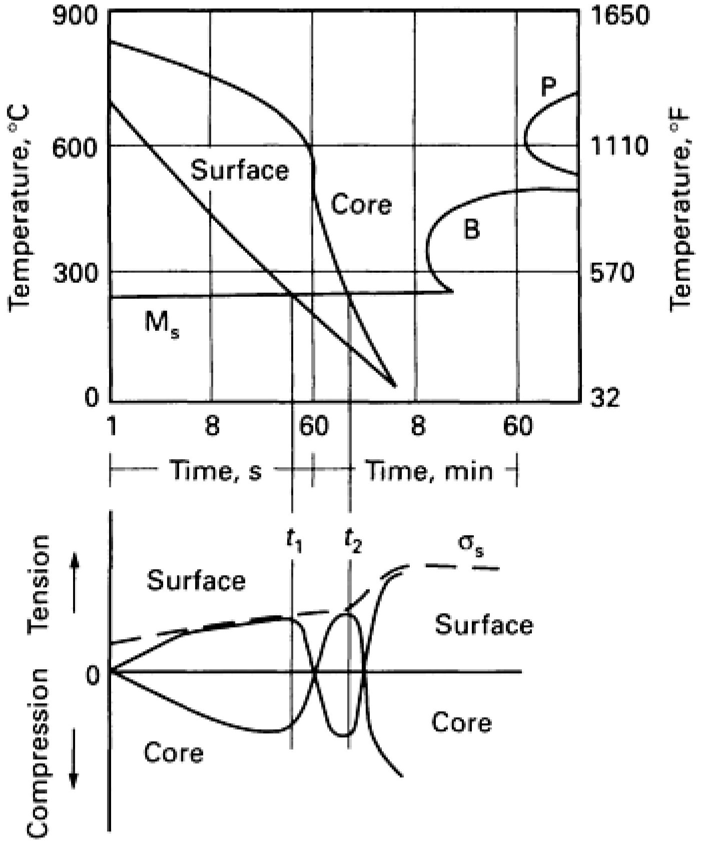

Fig. 22 Formation of residual stress on cooling considering thermal expansion and the austenite to martensite transformation. The dashed line is the yield stress, σ_s, at the surface. See text for details. Source: Ref 34

In order to predict hardening stresses quantitatively, it is necessary to consider interactions among various factors. As shown in Fig. 23, these include: (1) phase transformations, (2) latent heat, (3) thermal stress, (4) transformation stress and plasticity, (5) heat generation due to deformation, and (6) mechanically induced transformation. The most important of these are interactions 1, 3, and 5. Interaction 6, however, is also a very important factor. When discussing mechanically induced transformation, at least three different effects should be mentioned (Ref 36). The first is that the M_s temperature is decreased by hydrostatic pressure and raised by tensile stress (see Fig. 24, which shows an increase of ~15 °C (~27 °F) for a high-carbon steel). The second effect is the transformation plasticity, which is a permanent strain that occurs during an ongoing phase transformation under applied stress lower than the yield stress. It is displayed in Fig. 24 as an increase in the elongation from about 1% under an applied stress of 18 MPa (2.6 ksi) to 3% under 285 MPa (41 ksi) applied stress. The third effect is the incubation time of the nonmartensitic transformations, which is prolonged by hydrostatic pressure (Ref 37) and shortened by tensile stress (Ref 38). This is particularly important for large dimensions. It has also been shown that a separate steel sample that is inserted into a cylinder of the same hardenable steel (Carney-type test) has a higher hardness value than the material in the same position in a homogeneous steel cylinder. The inserted steel specimen has the same temperature history, but is not exposed to hardening stresses.

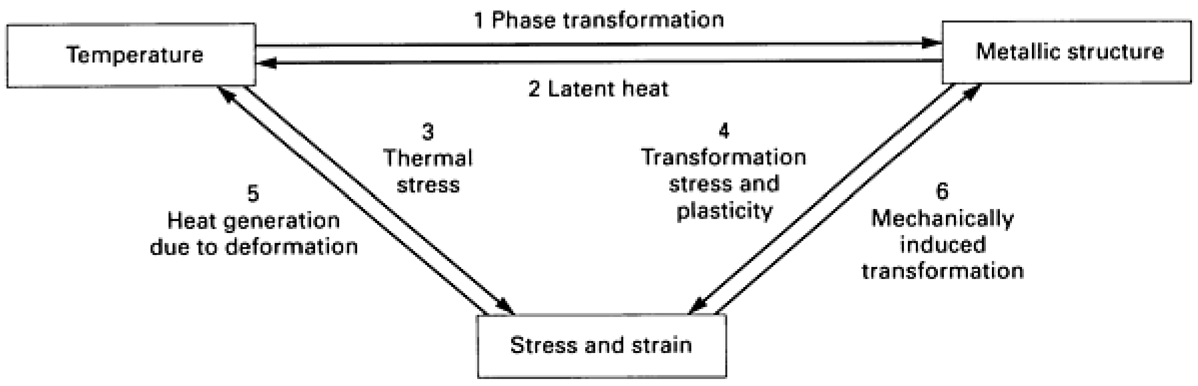

Fig. 23 The interactions between various factors of importance for residual stress generation. Source: Ref 35

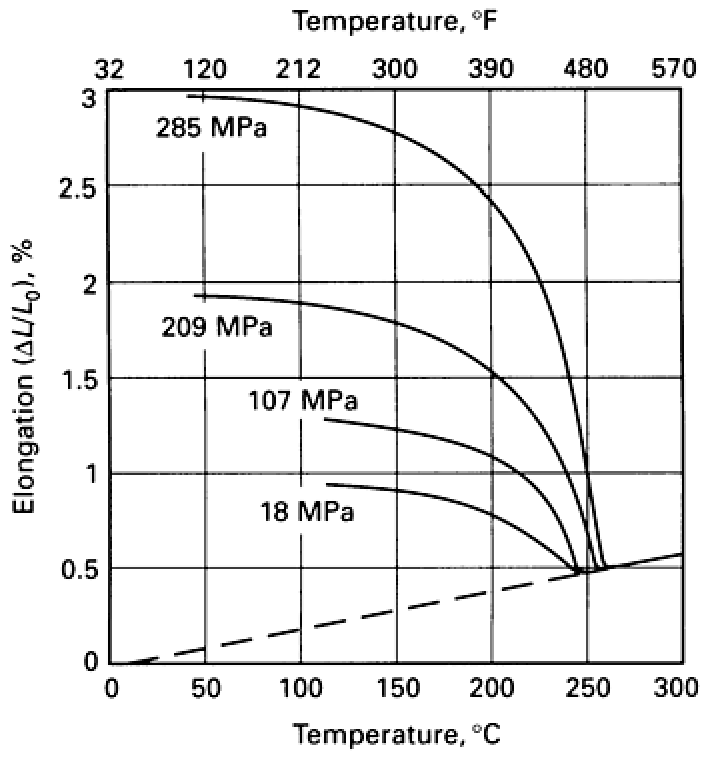

Fig. 24 Dilatometer curves for a steel with 0.6 wt% C for different applied tensile stresses. Source: Ref 36

Through Hardening. A series of computer calculations for a 50 mm (2 in.) diameter 0.6 wt% low-alloy steel cylinder illustrating the stress variation with time and the effect of the cooling medium (that is, the heat-transfer function) are shown in Fig. 25. In Fig. 25, which shows quenching in 20 °C (70 °F) oil, the transformation takes place well after the stress reversal in both surface and core. Some slight plastic deformation occurs in the surface in connection with the surface transformation, but otherwise the behavior is elastic. The effect of the transformation on the residual stress distribution is very slight. Quenching in 20 °C (70 °F) water is shown in Fig. 26. The transformation of the surface occurs before the stress reversal and transformation of the core occurs well after the stress reversal. The surface transformation helps to push the surface stress rapidly into compression, and compression yielding occurs. Before the core transformation, the core deforms plastically. With the onset of the core transformation, the tensile stress in the core is decreased, and the resulting deformation is elastic.

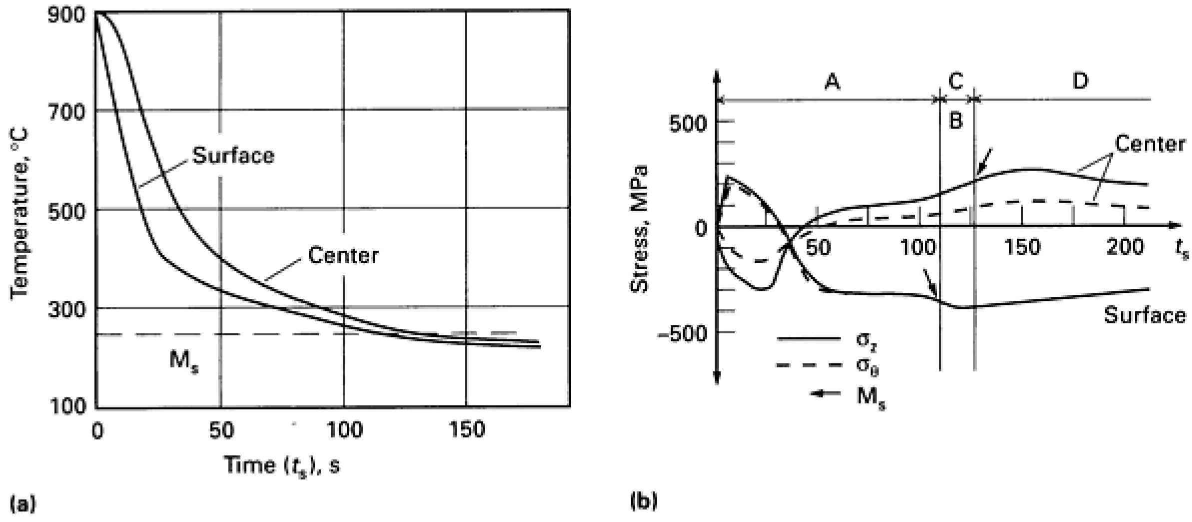

Fig. 25 Temperatures (a) and calculated stresses (b) in a long 0.6 wt% C low-alloy steel cylinder with 50 mm (2 in.) diameter quenched in 20 °C (70 °F) oil. In region A, the temperature is above M_s; in region D, it is below M_s. In region C, B, the temperature is above M_s at the center, but below M_s at the surface. σ_z, axial stress; $\sigma\theta$, tangential stress. Source: Ref 39

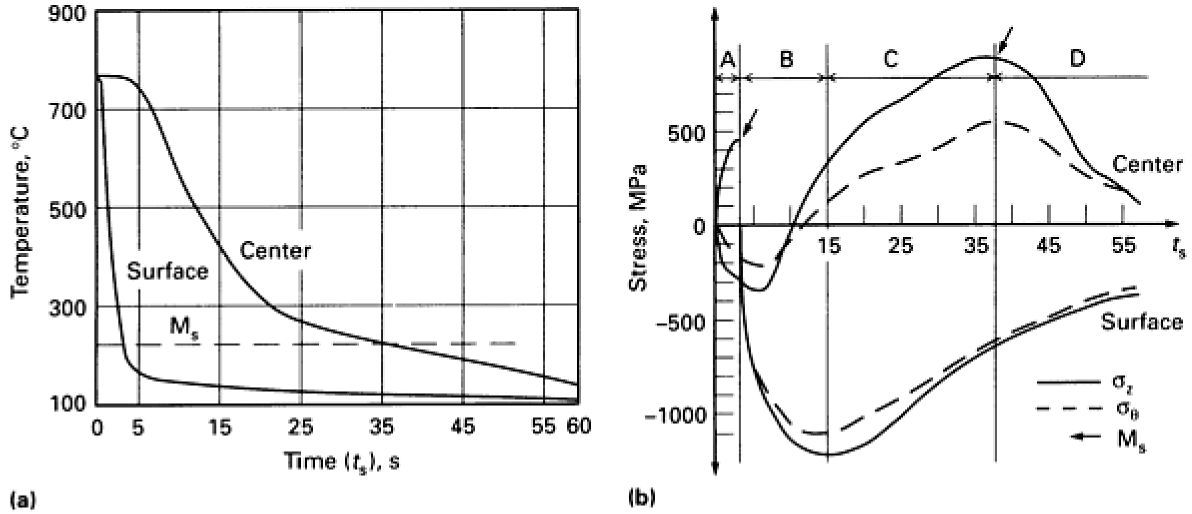

Fig. 26 Same type of diagram for the same steel and cylinder as in Fig. 25, but the specimen is quenched in 20 °C (70 °F) water. The final microstructure is completely martensitic. Source: Ref 39

In these calculations, the transformation plasticity was not considered. Figure 27 shows that it is important to include this effect in order to obtain the best agreement with measured residual stress values.

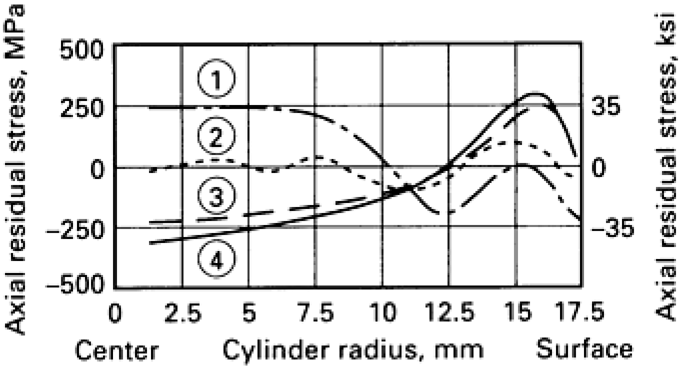

Fig. 27 Calculated residual axial stress profiles after martensitic quenching of a 0.6 wt% C low-alloy steel in 20 °C (70 °F) water. Curve 1: the effect of internal stresses on the kinetics of martensitic transformation. Curve 2: calculated without stress/transformation interactions. Curve 3: calculated with transformation plasticity alone. Curve 4: calculated with both stress and transformation effects considered. Source: Ref 36

Another series of calculations has been made to study the effect of cylinder diameter and cooling medium on residual stresses in 1045 steel. In the case of oil, ferrite-pearlite mixtures are formed; during water quenching, martensite and bainite are also formed. Figure 28 shows the stress development during water quenching. The 10 mm (0.4 in.) diameter cylinder starts to transform to martensite at the surface and the transformation front moves gradually inward resulting in a typical tensile stress at the surface. The large-diameter cylinders first transform to ferrite-pearlite at intermediate radii and then to martensite at the surface. This causes two stress minima seen in the dashed curves in Fig. 28(a), (b), and (c). The final residual stress is compressive at the surface and tensile in the core. Good agreement was obtained with x-ray stress measurements in several cases, as well as with older mechanically measured data. The dependence on specimen diameter and quenching medium is summarized in Fig. 29. The difference between oil and water quenching decreases with increasing diameter.

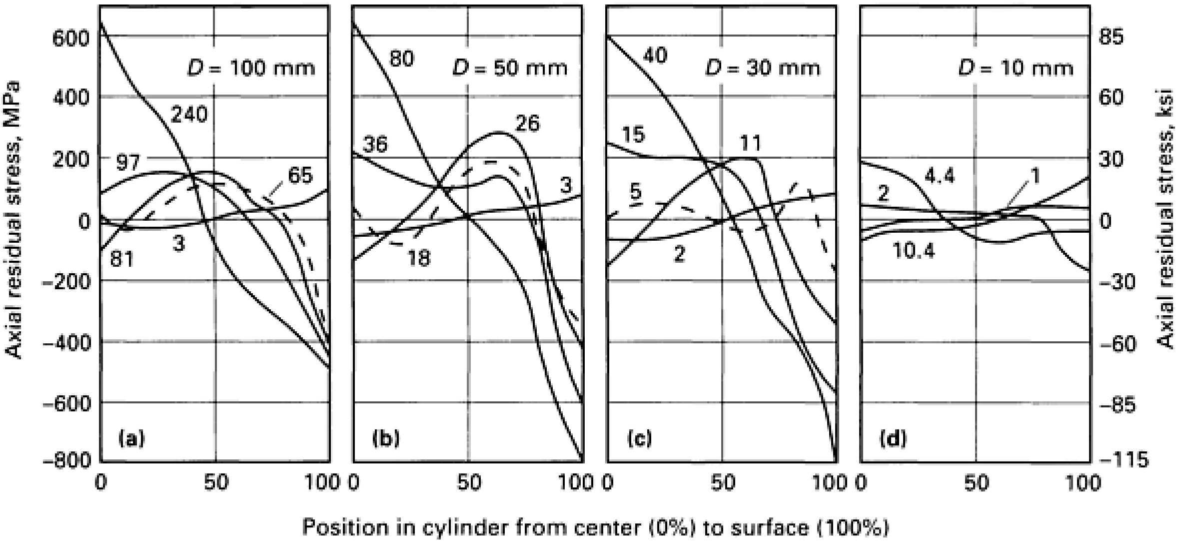

Fig. 28 Axial residual stress distributions for various AISI 1045 steel cylinder diameters, *D*, at selected times (in seconds) after the start of quenching from 850 °C (1560 °F) in 20 °C (70 °F) water. The final microstructure of the 10 mm (0.4 in.) diameter cylinder is completely martensitic, while the others have a ferritic-pearlitic core. Source: Ref 40

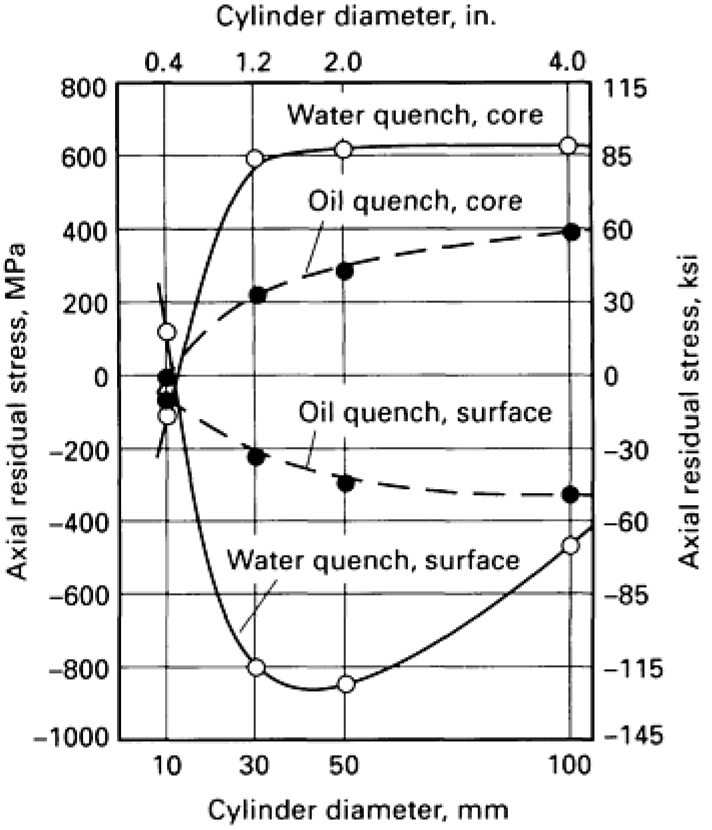

Fig. 29 The dependence of axial residual stresses on cylinder diameter. Same steel as in Fig. 28. The core is martensitic for 10 mm (0.4 in.) diameter, but ferritic-pearlitic for larger diameters. Source: Ref 40

Case hardening (that is, carburizing and quenching) is a rather complicated process. During the carburizing stage at about 900 °C (1650 °F), carbon diffuses into the steel from the surrounding environment, most often as a gas mixture. The carburizing takes several hours, and usually the temperature is lowered 50 to 100 °C (90 to 180 °F) for about one hour before quenching to reduce the risk of distortion. It is reasonable to assume that the material is stress-free when the quenching takes place.

Figure 30 shows the development of the residual stresses during the case hardening of a 17 mm (0.70 in.) diameter cylinder with a carburizing depth of 1 mm (0.04 in.). The onset of martensite formation can clearly be seen below the surface where, due to the combination of temperature and carbon content, the M_s is first attained. The transformation to martensite then moves toward the surface and the transformation to bainite moves toward the core. The transformation of austenite at the surface occurs very late and some retained austenite remains. The residual stress is first tensile at the surface due to thermal effects. The stress is shifted in the compressive direction where the martensite has formed, and simultaneously the tensile stresses are increased near the surface in the untransformed austenite as a compensating effect. Under these conditions, the hard and brittle martensite is never exposed to tensile stresses.

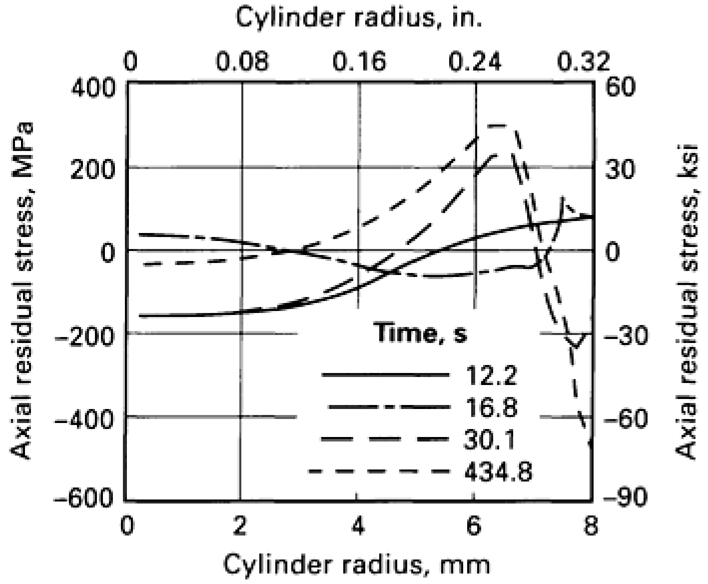

Fig. 30 Calculated axial residual stress for various times following the start of quenching after carburizing a 17 mm (0.70 in.) diameter cylinder made of AISI 3138 steel. Source: Ref 41

The final residual stress distribution has its minimum slightly below the surface. This is due to the presence of retained austenite near the surface. The position of the residual stress minimum occurs approximately at 50 to 60% of the total case depth corresponding to a carbon concentration at a position where the case carbon content is 0.5 wt% C. Below the hardened case, the residual stress may show a tensile peak.

This type of computer prediction can give good agreement with experimentally measured residual stress distributions (Fig. 31). The observed tensile stress at the surface is due to the presence of a soft pearlitic layer caused by the slight internal oxidation of the alloying elements chromium and molybdenum, which has reduced the hardenability of the surface layer. This reduction in hardness can be included in the calculations by adding a transformation diagram relevant to this surface layer (Ref 42).

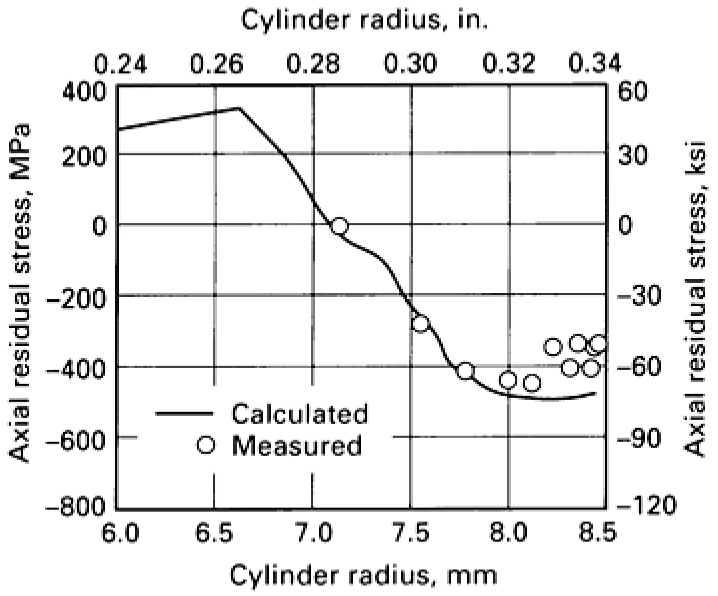

Fig. 31 Calculated and measured axial residual stress for a 17 mm (0.70 in.) diameter cylinder made of AISI 3138 steel. Source: Ref 41

With access to a good computer model, the effect of a number of variables, such as increased base carbon content, different cooling medium, and higher or lower base hardenability, can be studied. Increased base carbon content does not affect the magnitude of compressive stress significantly but the tensile peak below the case disappears. A more intense cooling medium like water instead of oil changes the compressive residual stress value to a higher value of 600 MPa (87 ksi) compared to 500 MPa (73 ksi), but does not increase the depth of the compressed layer.

Induction hardening is more complicated than carburizing. Both the heating stage as well as the cooling stage have been calculated (Ref 43). Static, or single-shot induction hardening, can be distinguished from progressive induction hardening. Using the single-shot method, a multiturn coil totally surrounds the area to be hardened; using the progressive technique, the workpiece and a single-turn coil are moved relative to each other. The single-shot method is more readily calculated and will be described here.

To calculate the heating during induction hardening, the magnetic field equation must be solved and the magnetic permeability, μis determined. A function fitted to experimental curves is:

$$m = \frac{a}{b + H} + c \qquad \textbf{(Eq 7)}$$

where a, b, and c are constants and *H* is the magnetic field strength. The electrical resistivity must also be determined as a function of temperature and phases present.

Quenching by a water spray requires experimental data for the corresponding heat-transfer function. For the description of the transformation to austenite from the starting structure, an isothermal diagram for heating (ITh diagram) is needed. To describe the transformation behavior during the subsequent cooling, an IT diagram representative of a short austenitizing time is necessary. The austenitizing time during induction hardening is normally less than one minute. This means that carbide dissolution has little time to take place, and therefore the type and distribution of carbides in the starting structure are important. It is well known that structures with fine carbides harden to greater depths than structures with coarse carbides.

Calculated values for single-shot induction hardening of a 4140 steel specimen are shown in Fig. 32. Experimentally measured residual stresses for the same steel are compared with the calculated values in Fig. 33. In Fig. 32(a), the evolution of the temperature with time at different depths is shown. It is clearly seen that the heating rate decreases at the Curie temperature and that the transformation to austenite absorbs heat (constant temperature at the surface between 10 and 20 s). A brief air cooling step is followed by water spraying. The final martensite distribution is shown in Fig. 32(b). The evolution of the stress versus depth at different times and stress versus time for different depths is shown in Fig. 32(c) and (d), respectively. At the outset, the stress becomes compressive in the heated zone, but is shifted in the tensile direction when the austenite formation sets in. Only the axial stress component is shown in Fig. 32 and 33.

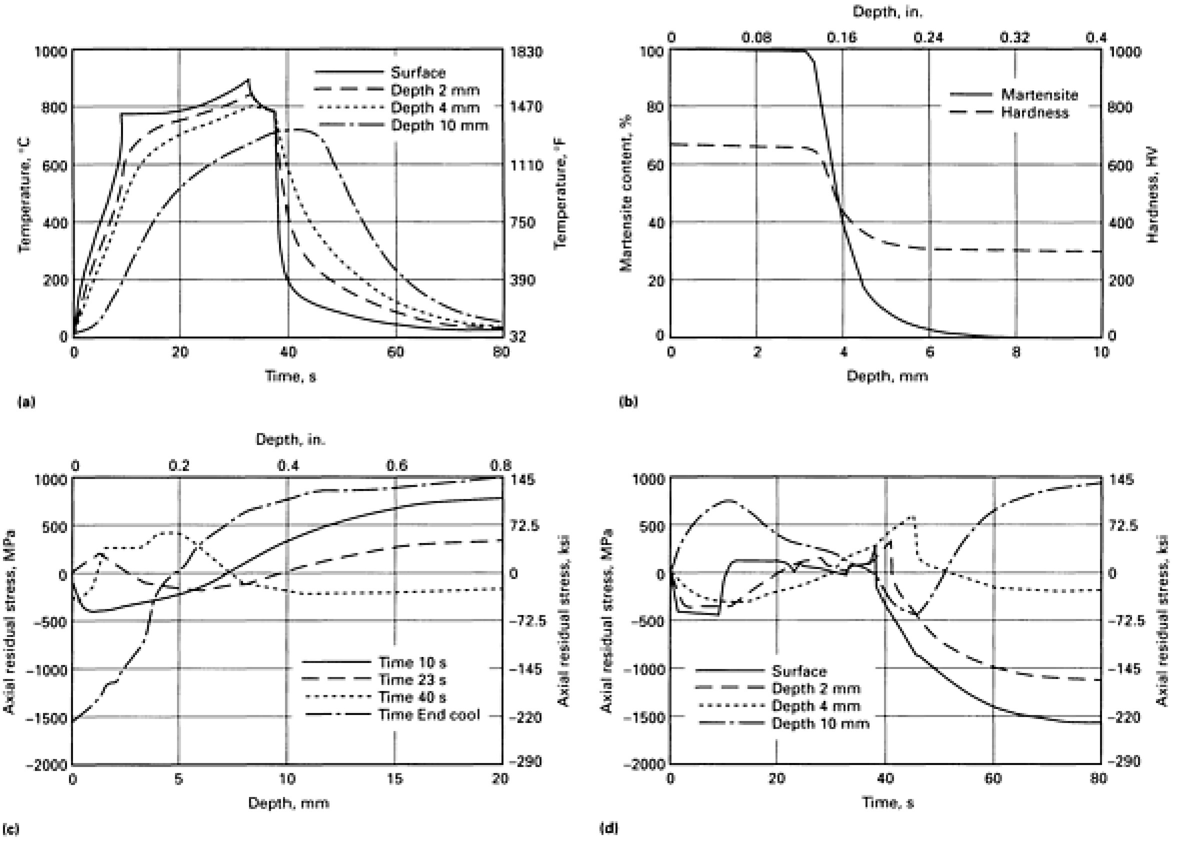

Fig. 32 Calculated values for single-shot induction hardening of a 40 mm (1.6 in.) diameter cylinder made of AISI 4140 steel. Induction frequency: 300 kHz. (a) Temperature versus time for different depths. (b) The final martensite and hardness distributions. (c) Axial residual stress versus depth at different times. (d) Axial residual stress versus time for different depths. Source: Ref 43

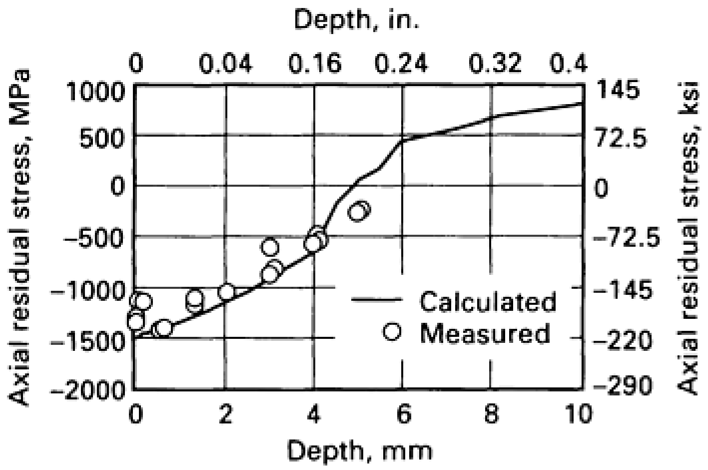

Fig. 33 Calculated and experimental axial residual stress after induction hardening versus depth for a 40 mm (1.6 in.) diameter steel specimen made of AISI 4140 steel. Source: Ref 43

The computer predictions are reasonably good as can be seen in Fig. 33. The experimental data show a smaller compressive stress at the surface than is predicted. The effect of variables such as the quenching medium and the ITh diagram has also been taken into consideration. Figure 34(a) shows how the hardening depth is increased when the transformation to austenite at elevated temperature occurs more easily. The different transformation rates can be due to different steel compositions or to different prior microstructures of the same steel. The cooling is rapid enough to transform all austenite that has formed to martensite and the residual stress distribution is only affected slightly as shown

in Fig. 34(b). If the water spray is replaced by oil quenching, the calculation shows that the magnitude of the compressive stress peak is reduced while the hardening depth is the same because the depth of austenitization is the same.

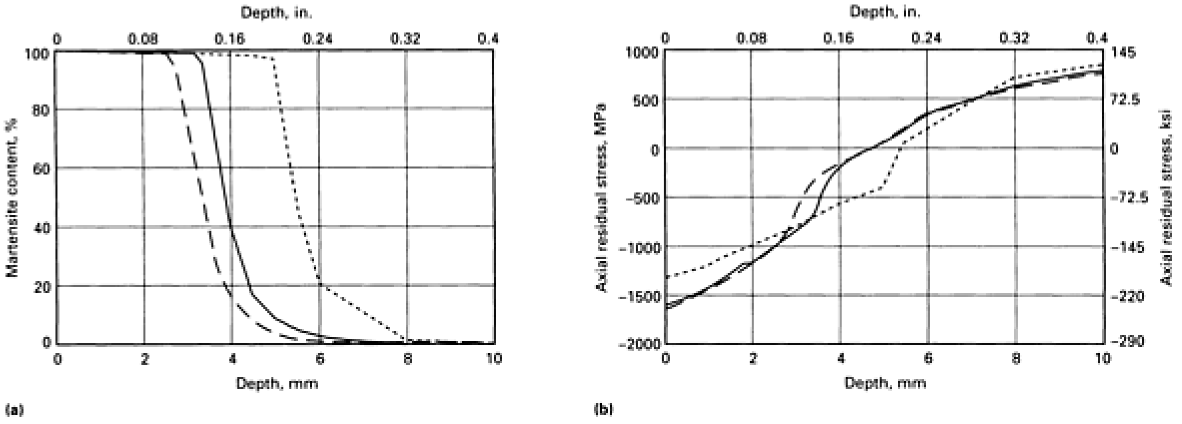

Fig. 34 Calculated values of martensite distribution and residual stress after induction hardening of a cylinder with a 40 mm (1.6 in.) diameter. The solid curve is calculated using the ITh diagram in Fig. 4, and the two others are hypothetical displacements of this diagram to shorter and longer times, respectively. This can illustrate the effect of different prior microstructures or different steel compositions. (a) Final martensite distribution. (b) Axial residual stress profiles for the three cases in (a). Source: Ref 43

Cracking and Distortion due to Hardening. There is a risk for cracking of a workpiece if large tensile stresses, transient or residual, are combined with the presence of a brittle microstructure (particularly martensite). Thermal stresses during cooling generally increase with the size of a workpiece. For phase transformation-induced stresses, geometric dimension, hardenability of the steel, and quench intensity interact in a complicated manner as has been described in earlier paragraphs. However, as a general rule it holds that the use of a more efficient cooling medium, for example, water as compared to oil, will lead to larger stresses as demonstrated in Fig. 25, 26, and 29. The presence of geometric stress raisers increases the risk of cracking.

Figure 22 indicates that tensile stresses are present at the surface when the surface transformation to martensite is complete and the core transformation is in progress. As such, there is the risk of surface cracking. However, it is shown in Fig. 25 and 26 that through hardening does not necessarily lead to tensile stresses at the surface. In case hardening, surface cracking is not to be expected (see Fig. 30, 31, and 33).

Large tensile stresses in the core at lower temperatures may lead to center cracks even if the microstructure is not martensitic. Figure 29 shows that such a situation exists for larger diameter cylinders with a martensitic surface and a ferritic-pearlitic core. Case hardening may also lead to core cracking.

Hardening is usually accompanied by distortion of a workpiece. The degree of distortion depends on the magnitude of the residual stresses. Hardening procedures that minimize transient and residual stresses are beneficial as well as the use of fixtures (press hardening). Distortion can also occur during tempering or annealing due to release of residual stresses or phase transformations during tempering as described previously in this article.

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Introduction

HARDENABILITY STEELS, or H-steels, offer a wide range of mechanical properties that depend on the development of tempered martensite after quenching and tempering. Typical room-temperature properties of quenched and tempered steels can vary as follows:

- Hardness values of 130 to 700 HV (30 kgf load)
- Tensile strengths of 400 to 2000 MPa (58 to 290 ksi)
- Yield strengths of 300 to 1800 MPa (43 to 261 ksi)
- Elongation of 8 to 28% in 50 mm (2 in.)

This broad range of properties depends on the maximum (as-quenched) hardness and the degree of softening (tempering) after quenching.

The maximum (100% martensite) hardness of heat-treated steel depends primarily on the carbon content (Table 1), until carbon levels reach about 0.50 wt%. Above 0.50 wt%, carbon has little effect on hardness but does improve hardenability. Alloying elements have little effect on the maximum hardness that can be developed in steel, but they profoundly affect the depth to which this maximum hardness can be developed in a part of specific size and shape. Thus, for a specific application, one of the first decisions to be made is what carbon level is required to obtain the desired hardness. The next step is to determine what alloy content will give the proper hardening response in the section size involved. This is not to imply that tempered martensitic steels are alike in every respect, regardless of composition, because the alloy content is responsible for differences in the preservation of strength at elevated temperatures; in abrasion resistance; in resistance to corrosion; and even, to a certain extent, in toughness. However, the similarities are sufficiently marked to permit reasonably accurate predictions of mechanical properties from hardness rather than from composition, thereby justifying the emphasis on hardenability as the most important function of the alloying elements. The basic effects of alloying elements on hardening are described in the article "Principles of Heat Treating of Steels" in this Volume.

Table 1 Steel hardness for various carbon contents and percentages of martensite for some low-alloy steels

Carbon, %	Rockwell C hardness (HRC) with martensite contents of:

	50%	**80%**	**90%**	**95%**	**99.9%**
0.18	31	35	37.5	39	43
0.23	34	37.5	40.5	42	46
0.28	36.5	40.5	43	44.5	49
0.33	39	43.5	46.5	48.5	52
0.38	42	46	49	51	54
0.43	44	48	51	53.5	57
0.48	46.5	52	54	57	60

Source: *Metals Handbook*, 1948 Edition

This article is primarily concerned with computer-assisted prediction of steel hardening and hardenability as a function of heat treatment parameters. In this regard, the two main measures of steel hardening are the Jominy end-quench hardenability curves and the continuous cooling transformation (CCT) curves. The intended focus is to outline the uses and limitations of computer modelling for the prediction of steel hardness profiles after quenching. Quantitative modelling of properties after tempering is also briefly discussed in this article and in the article "Computerized Properties Prediction and Technology Planning in Heat Treatment of Steels" in this Volume.

When considering any quantitative prediction of steel hardening, it is important to first recognize the inherent limitations of even well-established empirical data such as Jominy end-quench hardenability curves. For example, Fig. 1 and 2 show sets of Jominy curves selected from a large international set for 8620 carburizing steels and deep-hardening 4140 automotive steels of almost the same nominal composition and grain size (Ref 1). Such discrepancies could be attributed to incorrectly reported chemistry, careless test procedures, and/or unreported or uncontrolled process variables. Likewise, CCT curves also conceal comparable empirical errors because fractions transformed and cooling histories are incompletely determined or ambiguous, and these deficiencies can be expressed alternatively as an uncertainty in the time scale of the superposed cooling curves of factors reaching as high as four (Ref 2, 3). Notwithstanding the empirical difficulties, it is our aim to illustrate that sufficiently quantitative predictions can be attained so as to sustain reliable selection, improved quality control, cost optimization, on-line decision-making, and reduction of costly testing.

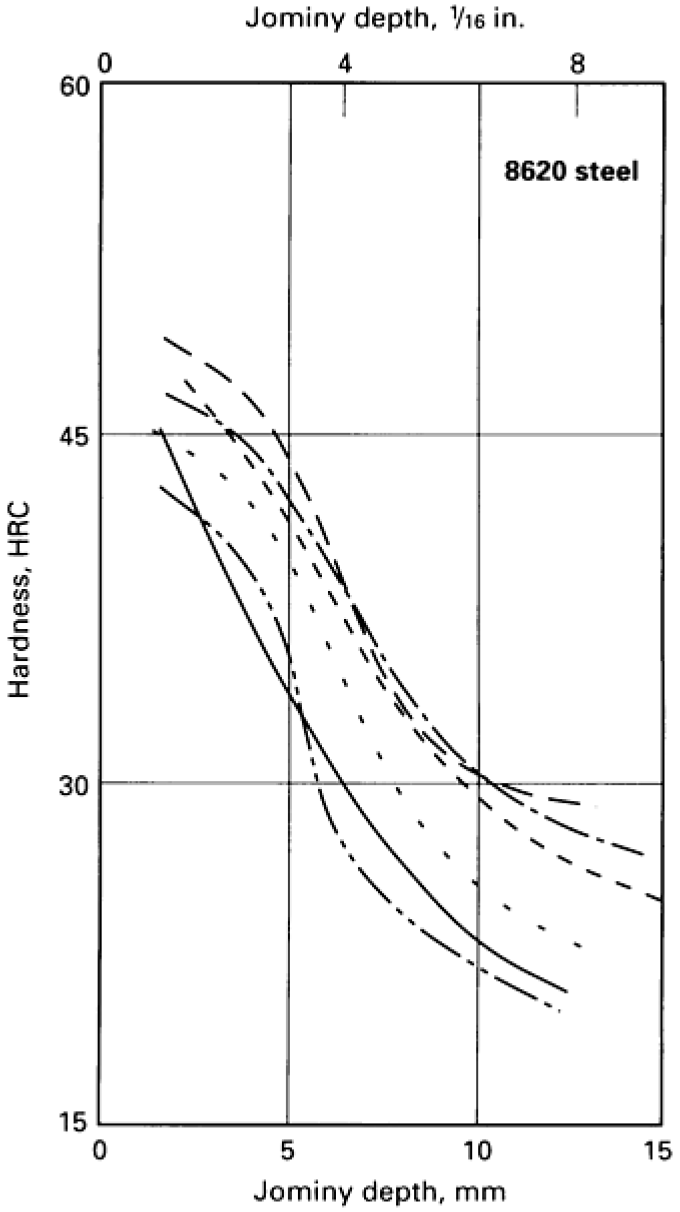

Fig. 1 Summary of reported Jominy tests by several laboratories on an SAE 8620 steel of approximately the same composition and grain size. Source: Ref 1

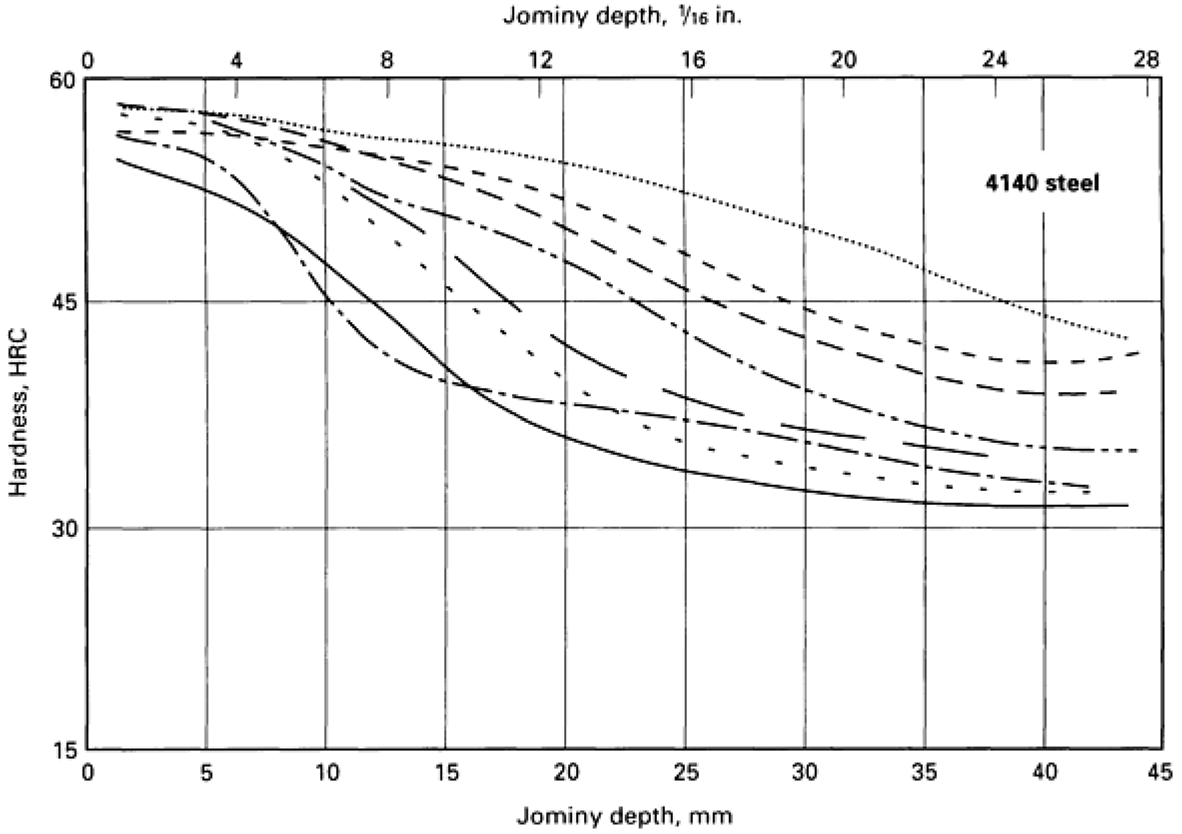

Fig. 2 Summary of reported Jominy tests by several laboratories on a 4140 steel of approximately the same composition and grain size. Source: Ref 1

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Relationship between IT, CCT, and Jominy Curves

Jominy curves and CCT curves are closely related as indicated in Fig. 3 for a eutectoid steel (Ref 4). Here the CCT curve has been derived from the isothermal transformation (IT) diagram by one of the methods to be described later. This construction gives more than a hint as to how one might proceed to develop a mechanical property predictor for arbitrary shapes and quench media from a fundamental theory of isothermal transformation (Ref 5, 6, 7). Figure 4 presents a schematic description of a recent semi-empirical, finite element computer program (Ref 8) which claims to predict the full course of a continuous cooling transformation, including the development of residual stresses and dilatation. This illustrates the complex interplay of thermal and deformation physics, multicomponent thermodynamics, and phase transformation kinetics which relates a room-temperature stress and hardness distribution to the geometry, thermal treatment, and chemistry of a part. Other programs for predicting residual stresses after quenching are discussed in the articles "Principles of Heat Treating of Steels" and "Computerized Properties Prediction and Technology Planning in Heat Treatment of Steels" in this Volume.

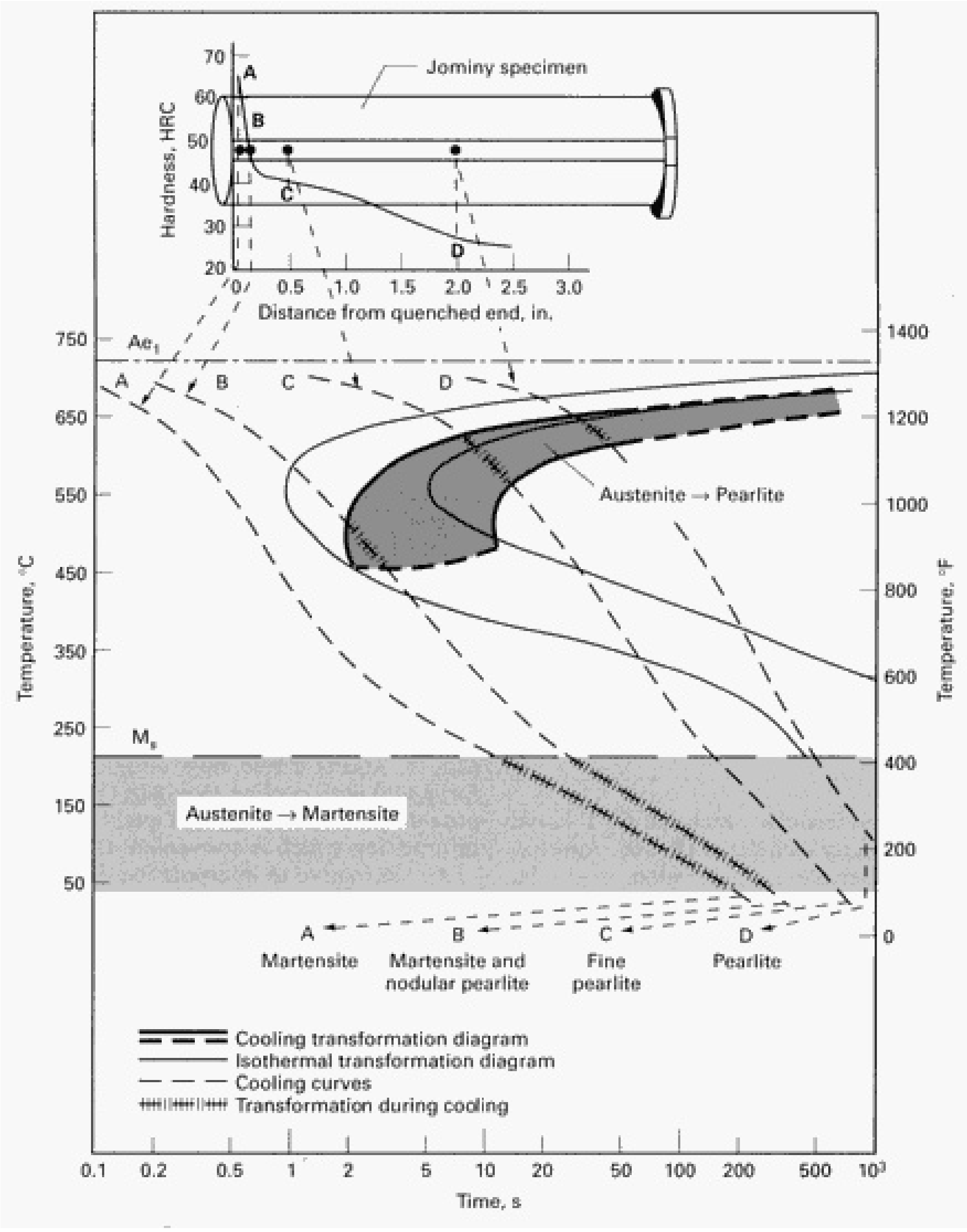

Fig. 3 Relationship of CCT (heavy lines) and IT (light lines) diagrams of eutectoid steel. Four cooling rates from different positions on a Jominy end-quench specimen are superimposed on the CCT diagram. Source: Ref 4

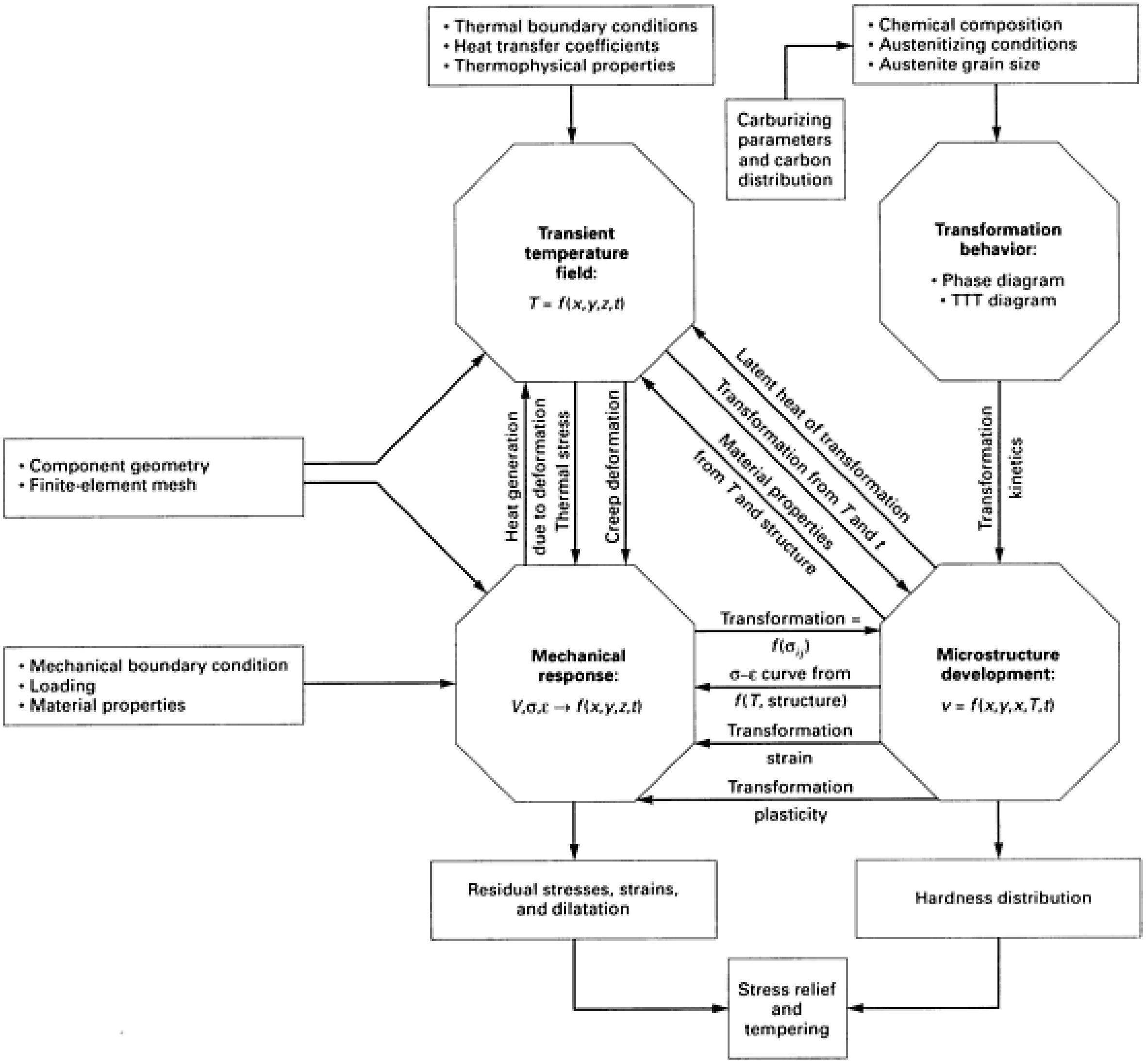

Fig. 4 General system overview of a program to predict the thermomechanical behavior of low-alloy steels. Source: Ref 8

The key assumption in this kind of development is that an IT prediction, empirically calibrated against a metallographic data set, defines an integrating factor over time and temperature through which the CCT curve can be directly calculated (Ref 9). Approximately equivalent information could be drawn from a large empirical set of CCT diagrams suitably interpolated and adjusted for varying geometry and cooling histories. The shape of CCT curves depends on the detailed shape of the cooling curves for the part being considered and therefore on the nature of the quenchant.

Unlike an IT diagram (Fig. 5), a CCT diagram is only unique to a particular composition and grain size if in the measurement the cooling rate at every depth in the test specimen was constant (Ref 9). It is at best a very crude approximation to apply a universal CCT diagram evaluated with constant cooling rates to a particular part by superposing natural or approximately exponential cooling curves upon the diagram. Newton's law of cooling, which applies to many fluid quenching or air-cooling situations, exhibits such decelerated or exponential cooling.

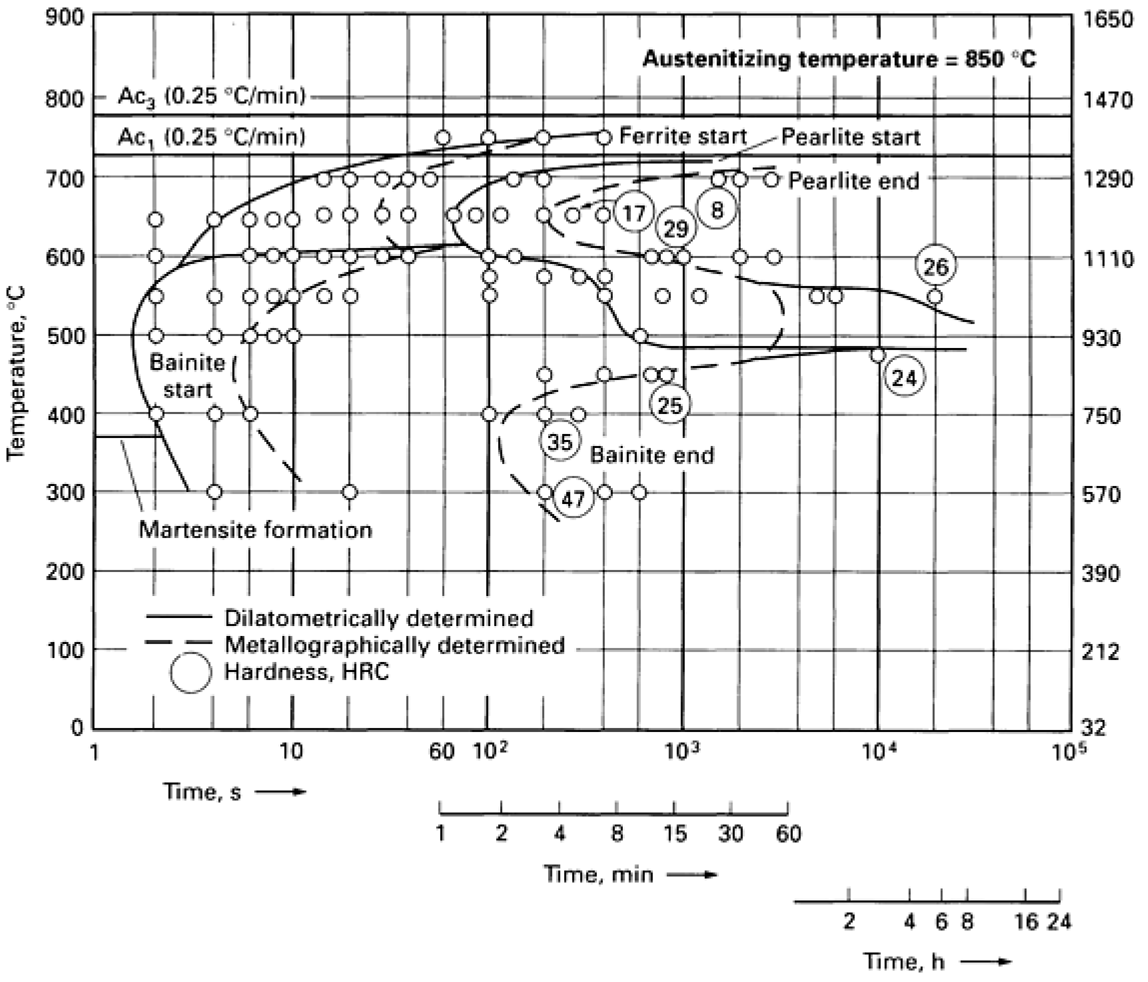

Fig. 5 Comparison of IT diagram for steel with German designation 42 CrMo 4 (0.38% C, 0.99% Cr, and 0.16% Mo) determined by dilatometry (dashed lines) and metallography (continuous lines). Source: Ref 4

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Quantitative Aspects of IT and CCT Curves

This section examines in detail the empirical and theoretical record for defining quantitative information on IT and CCT curves. This could be made part of an "expert" system, since probabilistic judgments based on ancillary subjective

information also play an essential part in quality control and design. Expansion of the system to deal with carburizing, tempering, and related processes is briefly discussed in subsequent sections of this article.

The international set of experimental CCT curves consists of some 1000 diagrams of highly varying quality. The smallest and most definitive set has been determined by precision metallography of sequentially quenched specimens according to natural cooling regimes (Ref 10). The largest set has been determined by dilatometry at mostly constant cooling rates (Ref 2, 3) with a necessary ambiguity in interpretation as to relative volume fraction of constituents (compare Fig. 5). Another less definitive set has been obtained by substituting hardness testing for metallography after sequential quenching (Ref 4). A rather complete compendium of sources is given in Ref 3, and in Ref 4, p 105 and 106. The simplest of information systems would be a complete compilation of the CCT curve subsets in computer memory, and upon specification of a new composition and grain size, each subset would be searched for close chemical correspondence; then three or more diagrams possessing cautionary statements would be presented graphically for inspection. In principle, interpolation formulas could also be developed for more explicit access. Atkins shows how outputs can be formatted with cooling rate data (Ref 11) to provide practical design and quality control information which is convenient (Fig. 6).

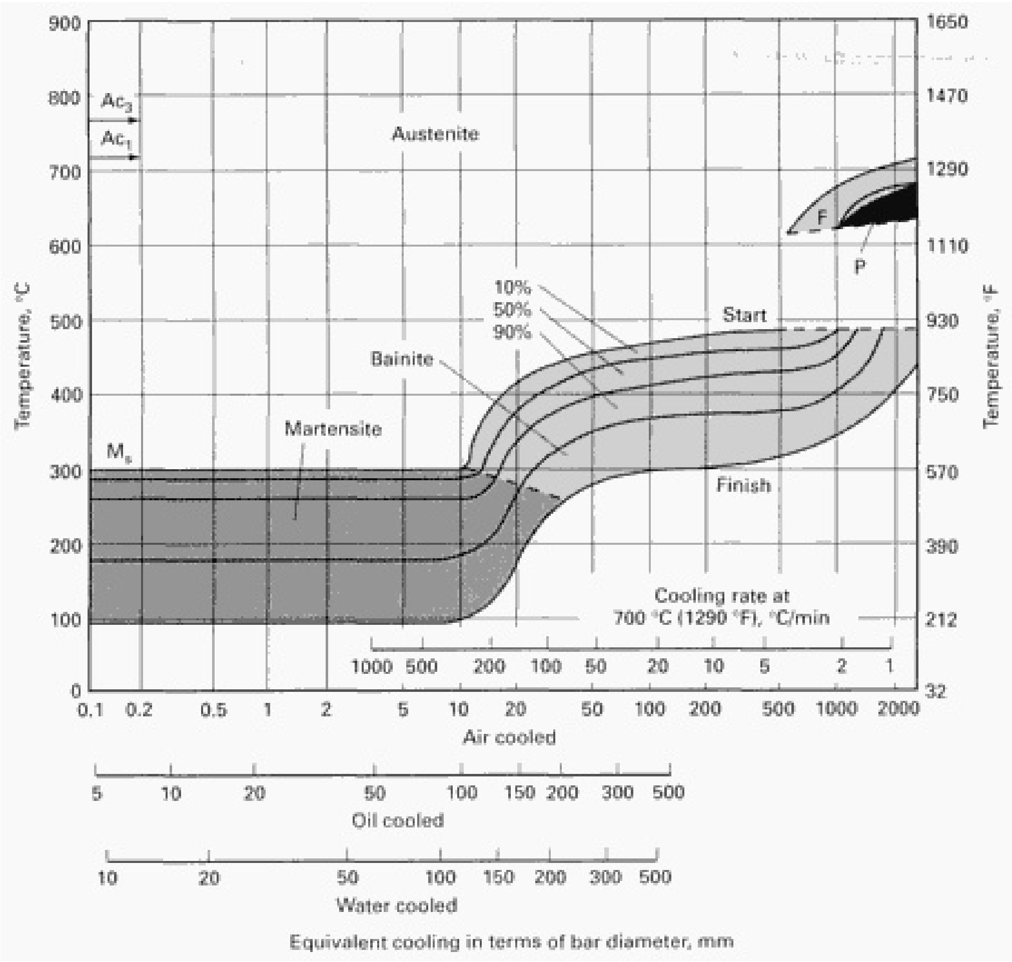

Fig. 6 CCT diagram for an alloy steel with 0.40% C, 1.50% Ni, 1.20% Cr, and 0.30% Mo, plotted as a function of bar diameter. Steel was austenitized at 850 °C (1560 °F); previous treatment: rolling, then softening at 650 °C (1200 °F). Source: Ref 4

An alternative to interpolation on a complete data set is to systematize a part or all of the data of a self-consistent subset according to linear regression formulas. A nonproprietary set of this kind has been developed by Creusot-Loire (Ref 3) in France based on approximately 200 dilatometrically determined, mainly constant cooling rate diagrams. Note that such a small data set can at best effectively span a matrix of 3 carbon levels, 3 manganese levels, 2 Si levels, 3 Ni levels, 2 Cr levels, 2 Mo levels, and one grain size ($3 \times 3 \times 2 \times 3 \times 2 \times 2 \times 1 = 216$) which falls far short of a precision analysis. As described in the following discussion on the Creusot-Loire system, the addition of two theoretical approximations ameliorates the situation somewhat. Here the interest is in room-temperature microstructure and hardness of low-alloy steels. It was found to be sufficient to systematize the data set by recording critical cooling rates at 700 °C (1300 °F) (or the average between 500 to 800 °C, or 930 to 1470 °F) for selected percentages of martensite, bainite, and pearlite-ferrite

(Fig. 7) and expressing these through linear regression analysis as a function of composition and austenitizing temperature. Relative volume fractions according to cooling rates are then found by interpolation and hardnesses through empirical formulas and a law of mixtures. Eleven numerical formulas are involved in the predictive algorithm. The numerical system recommended by the author is described below in "The Creusot-Loire Systematization of CCT Curves."

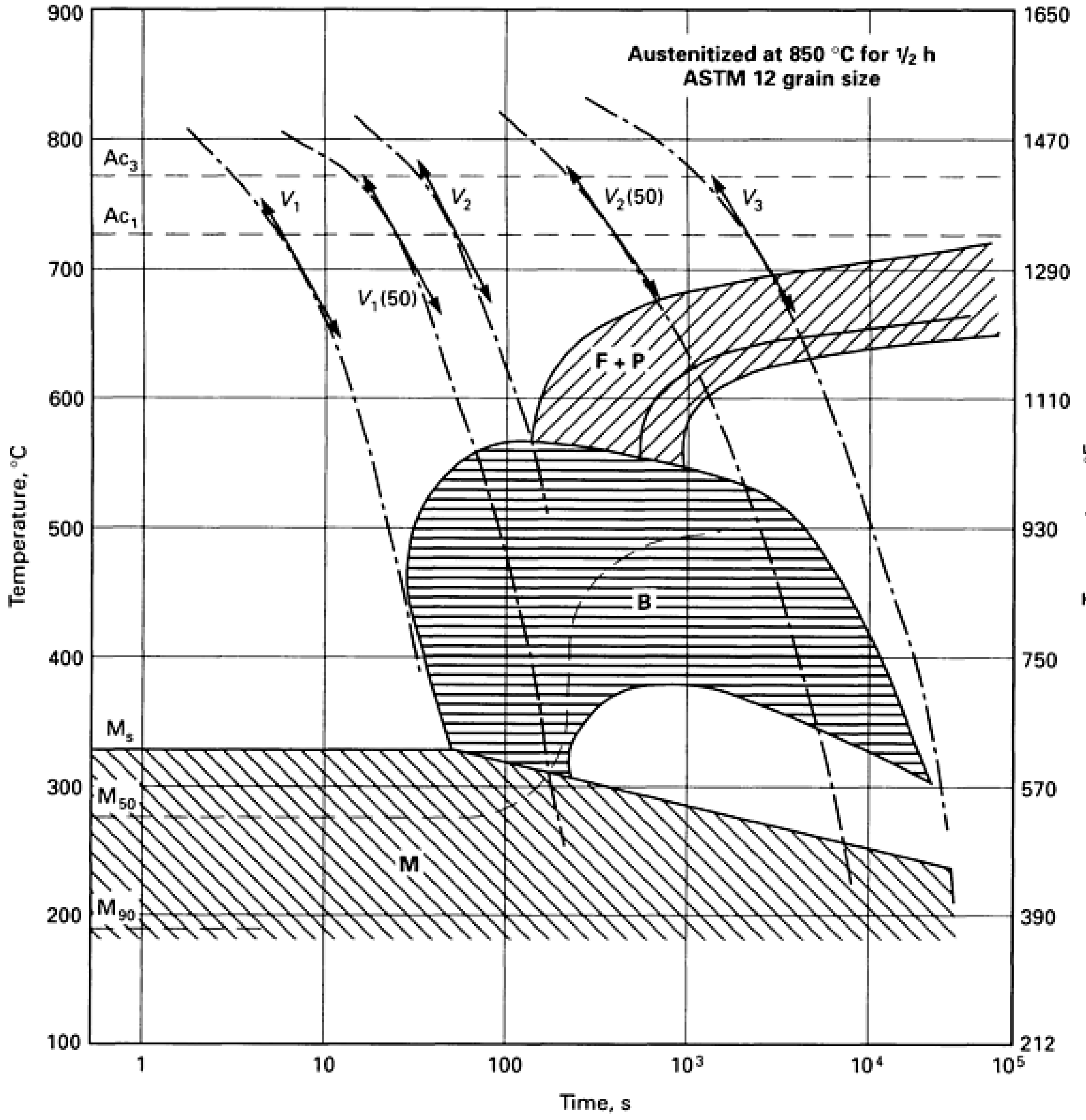

Fig. 7 CCT diagram showing critical cooling curves of 30 NC11 steel (0.32% C, 0.3% Mn, 0.2% Si, 0.008% S, 0.017% P, 2.95% Ni, 0.69% Cr, 0.10% Mo, 0.31% Cu, 0.056% As). Source: Ref 3

Residual Stress Estimates from CCT Curves. If for the purpose of estimating residual stresses (Fig. 4), the data set was systematized to all temperatures and times, at least 40 regression formulas would be required together with a greatly expanded number of interpolation and mixing formulas. (See, for example, some of the references listed in the article "Computerized Properties Prediction and Technology Planning in Heat Treatment of Steels" in this Volume.) However, in view of inconsistencies between techniques and the many independent data sets, an alternative based on systematization of IT curves (Fig. 5) has considerable merit and is explored elsewhere in this article.

The Creusot-Loire systematization of CCT curves involves explicit formulas, which allow the estimation of microstructure and hardness distributions in various shapes, including a Jominy bar. The formulas can be incorporated within an algorithm that is simple and short enough for programming on a quality hand calculator. They are already available in a

user-friendly form within a personal computer software package HAZ CALCULATOR developed by Mat-Weld-Soft of Graz, Austria (Ref 12).

The allowed inputs cover the ranges 0.2 to 0.5% C; Si $\leq$1%; Mn $\leq$2%; Ni $\leq$4%; Cr $\leq$3%; Mo $\leq$1%; V $\leq$0.2% together with the austenitizing temperature (T) and time (t). The latter parameters (T in degrees Kelvin and t in hours) are taken to define a thermally activated grain growth parameter (P_a):

$$P_a^{'} = \left[\frac{1}{T(K)} - \frac{nR}{H_a}\log t(h)\right]^{-1} \quad \textbf{(Eq 1)}$$

or

$$P_a\ (°C) = P'_a - 273$$

which enters the regression analysis along with the composition. All logs are to the base 10, n = 2.303, R = 1.986 as the gas constant, and H_a = 110,000 cal/mole as the activation enthalpy. There are eight critical cooling velocities V_i (in °C/h), which as log V_i have been linearly regressed against compositions in wt% and P_a. The logarithmic term reflects the usual convenient time normalization for plotting IT or CCT curves and has roughly the same combinatory effect as Grossmann multiplying factors in hardenability calculations. These two qualitative devices greatly increase the effectiveness of performing linear regression analysis on what is in fact a highly nonlinear and empirically sparse manifold. The formulas are:

$$\log V_1 = 9.81\text{-}4.62\text{C}\text{-}1.05\text{Mn}\text{-}0.54\text{Ni}\text{-}0.5\text{Cr}\text{-}0.66\text{Mo}\text{-}0.00183P_a \quad \textbf{(Eq 2)}$$

$$\log V_1(10) = 8.76\text{-}4.04\text{C}\text{-}0.96\text{Mn}\text{-}0.49\text{Ni}\text{-}0.58\text{Cr}\text{-}0.97\text{Mo}\text{-}0.0010P_a \quad \textbf{(Eq 3)}$$

$$\log V_1(50) = 8.50\text{-}4.13\text{C}\text{-}0.86\text{Mn}\text{-}0.57\text{Ni}\text{-}0.41\text{Cr}\text{-}0.94\text{Mo}\text{-}0.0012P_a \quad \textbf{(Eq 4)}$$

$$\log V_2 = 10.17\text{-}3.80\text{C}\text{-}1.07\text{Mn}\text{-}0.70\text{Ni}\text{-}0.57\text{Cr}\text{-}1.58\text{Mo}\text{-}0.0032P_a \quad \textbf{(Eq 5)}$$

$$\log V_2(90) = 10.55\text{-}3.65\text{C}\text{-}1.08\text{Mn}\text{-}0.77\text{Ni}\text{-}0.61\text{Cr}\text{-}1.49\text{Mo}\text{-}0.0040P_a \quad \textbf{(Eq 6)}$$

$$\log V_2(50) = 8.74\text{-}2.23\text{C}\text{-}0.86\text{Mn}\text{-}0.56\text{Ni}\text{-}0.59\text{Cr}\text{-}1.60\text{Mo}\text{-}0.0032P_a \quad \textbf{(Eq 7)}$$

$$\log V_3(90) = 7.51\text{-}1.38\text{C}\text{-}0.35\text{Mn}\text{-}0.93\text{Ni}\text{-}0.11\text{Cr}\text{-}2.31\text{Mo}\text{-}0.0033P_a \quad \textbf{(Eq 8)}$$

$$\log V_3 = 6.36\text{-}0.43\text{C}\text{-}0.49\text{Mn}\text{-}0.78\text{Ni}\text{-}0.26\text{Cr}\text{-}0.38\text{Mo}\text{-}0.0019P_a\text{-}2\sqrt{Mo} \quad \textbf{(Eq 9)}$$

where the smallest rate for 100% martensite is V_1; the rate for 90% martensite-10% bainite is $V_1(90)$; the rate for 50% martensite-50% bainite is $V_1(50)$; the smallest rate for no ferrite-pearlite is V_2; the rate for 90% bainite-10% ferrite-pearlite is $V_2(90)$; the rate for 50% bainite-50% ferrite-pearlite is $V_2(50)$; the rate for 90% ferrite-pearlite-10% bainite is $V_3(90)$; and the largest rate for 100% ferrite-pearlite is V_3. Note that all but V_2 give a unique volume fraction of the three designated constituents, so a law of mixtures for hardnesses is easily programmed (see below). In this odd case it is easy to interpolate the volume percents of bainite at log V_2 from log $V_2(90)$ and log $V_1(50)$, yielding an estimate of the bainite and martensite phase fractions at log V_2. Table 2 gives the computed critical cooling rates and microstructure for an 8620 carburizing steel of composition in wt%, 0.20C-1Mn-0.5Ni-0.5Cr-0.2Mo.

Table 2 Computed critical cooling rates and microstructure for an 8620 steel

Austenitization parameter, P_a = 917(°C - 1 h)

Critical cooling rates		**Microstructure, %**		
***v*(°C/h)**	**log *v***	**M**	**B**	**F + P**
321,067	5.507	100	0	0
222,017	5.346	90	10	0
108,658	5.036	50	50	0
28,565	4.456	10	90	0
12,177	4.086	0	90	10
4,035	3.606	0	50	50
754	2.877	0	10	90
352	2.547	0	0	100

Note: In the SAE-AISI designation the last two numbers refer to the weight percent of carbon in hundredths (that is, 20 $\equiv$ 0.2%) while the first two or three numbers refer to the alloy class (for example, Cr-Mo-Ni).

Supposing now that for a given part either the mean cooling rate $\dot{T} = dT/dt$ between 800 °C (1470 °F) and 500 °C (930 °F) is known as a function of depth *x* or the inverse function (x):

$$x = x(\dot{T}) \quad \textbf{(Eq 10)}$$

is known, and then the substitutions

$$\dot{T} = V_i \quad \textbf{(Eq 11)}$$

associate an explicit microstructure with a given depth profile. The empirical regression formulas for Vickers hardness (HV) versus composition and cooling rate developed by Creusot-Loire for martensite (M), bainite (B), and ferrite-pearlite (FP) are:

$$HV_M = 127 + 949C + 27Si + 11Mn + 8Ni + 16Cr + 21 \log \dot{T} \quad \textbf{(Eq 12)}$$

$$HV_B = 323 + 185C + 330Si + 153Mn + 65Ni + 144Cr + 191Mo + (89 + 53C - 55Si - 22Mn - 10Ni - 20Cr - 33Mo) \log \dot{T} \quad \textbf{(Eq 13)}$$

$$HV_{FP}=42+223C + 53Si + 30Mn + 13Ni + 7Cr + 19Mo + (10-19Si + 4Ni + 8Cr + 130V) \log \dot{T} \qquad \textbf{(Eq 14)}$$

Graphs in the form of Eq 10 are given for bars and plates subject to different quench media (Fig. 8 and 9) so an estimation of hardness distributions can be obtained in a more general context.

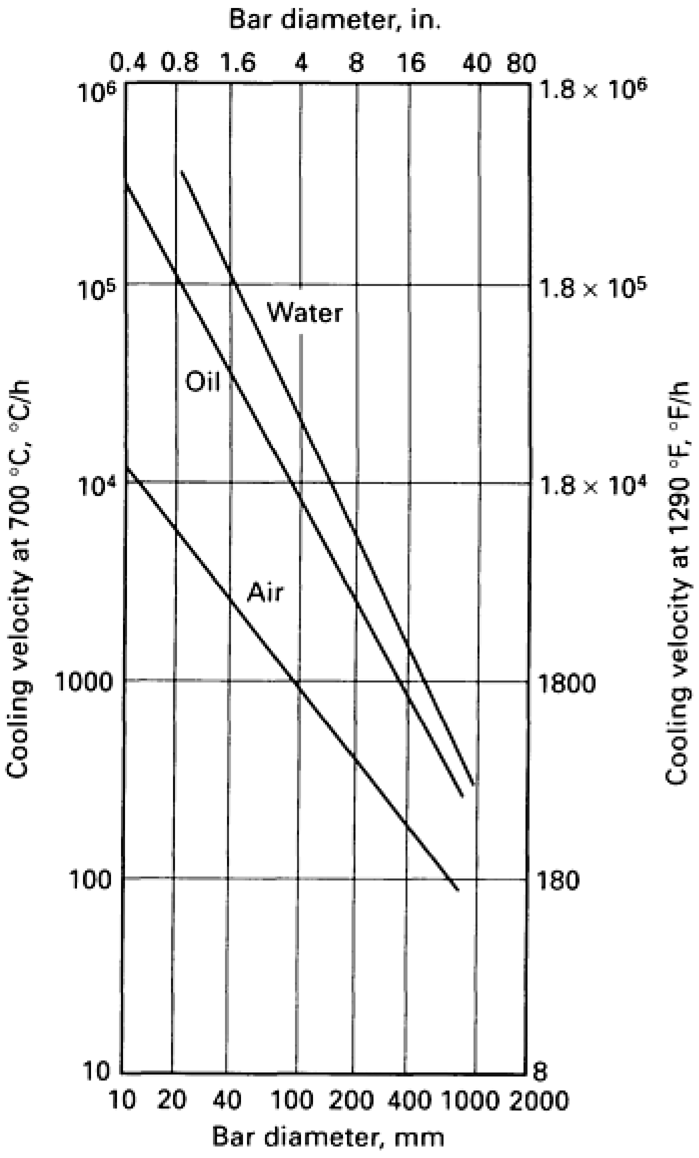

Fig. 8 Cooling rate at the center of bars cooled in air, water, or oil as a function of diameter. Source: Ref 13

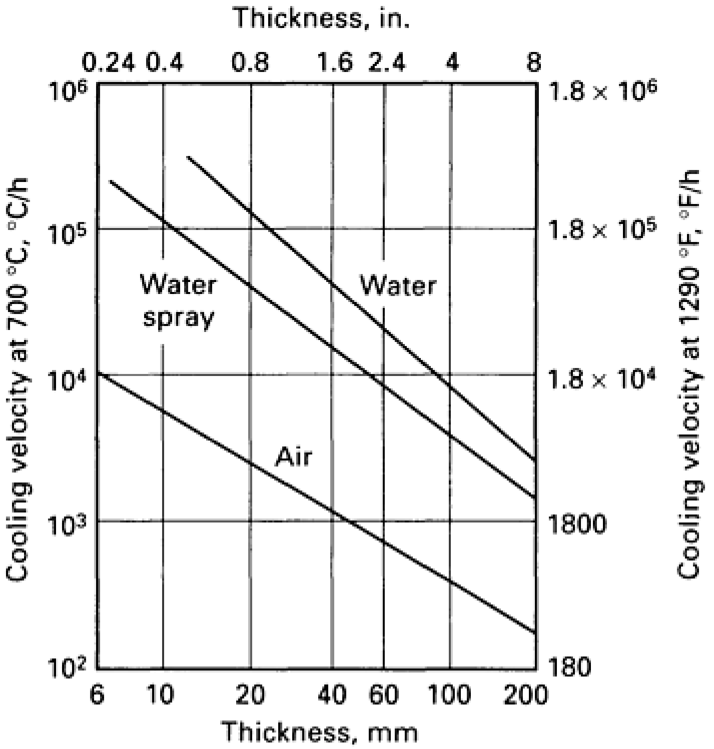

Fig. 9 Cooling rates at center of plates in air, and water, as a function of thickness. Source: Ref 13

Table 3 shows center hardness versus diameter of a water quenched rod of the 8620 composition introduced above. This was derived by a program which incorporated Eq 10, 11, 12, 13, 14 and Fig. 8 together with a weighted summation rule for hardnesses according to Table 1 and linear interpolations of log *V* between critical values (see also Fig. 10).

Table 3 Water-quenched 8620 bar center line hardness as a function of diameter

d, mm	Hardness, HV	*d*, mm	Hardness, HV
10	473	100	252
20	455	150	225
30	401	300	193
40	356	400	184
50	323	500	179
75	277		

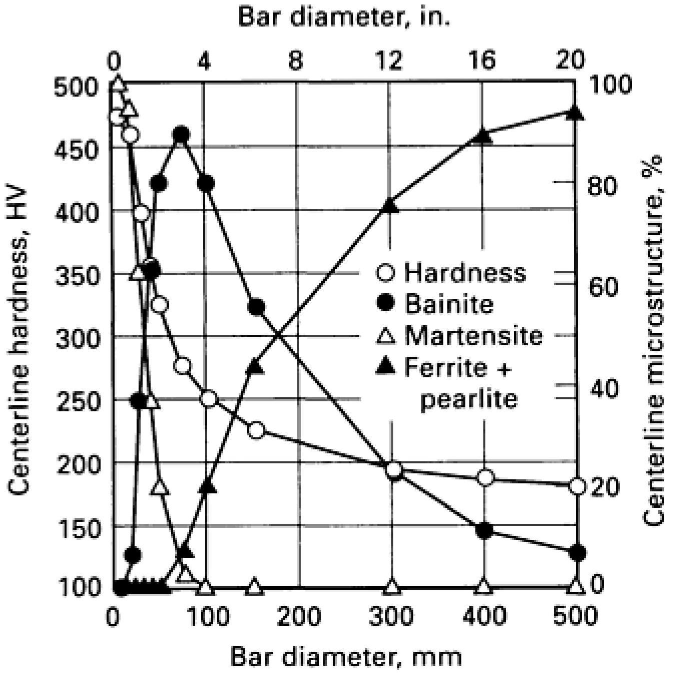

Fig. 10 Center-line hardness and microstructure of water-quenched 8620-type steel bar as predicted by the Creusot-Loire formulas. Composition inputs: 0.2% C, 1% Mn, 0.5% Ni, 0.5% Cr, 0.2% Mo

A quite effective Jominy curve predictor has been developed along these lines using the appropriate form of Eq 10 (see the section on Jominy curves). The main limitation of this methodology lies in its emphasis on room-temperature hardnesses and microstructures, which precludes residual stress calculations.

CCT Curves Derived from IT Curves. Isothermal transformation diagrams (Fig. 5) are deemed to be more accurate and definitive than CCT diagrams since most are micrographically determined under reproducible thermal conditions and the volumetric distribution of products is not nearly so complicated. The data set is smaller since preparation of the diagrams by metallography is expensive, and to the technologist they apply directly only to a few heat treatment processes like austempering; however, it is nonetheless adequate for calibrating nucleation and growth formulas which have an established theoretical basis. As with CCT curves the set could be stored in its entirety for selective recall along with appropriate interpolation rules. More economically, a typical IT curve for fraction transformed X (as in Fig. 5) can be fitted to a Johnson-Mehl nucleation and growth formula (Ref 14, 15) of the form:

$$X = 1 - \exp(-bt^n) \quad \textbf{(Eq 15)}$$

Reference 15 pertains to work on eutectoid steels in Germany, expressing the coefficients b and n as smooth functions of composition and temperature through curve-fitting on a set of 5 steels from the Atlas zur Wärmebehandlung der Stähle (Ref 16). A similar procedure has been used by Hildenwall and Ericsson in Sweden (see the article "Principles of Heat Treating of Steels" in this Volume). Following the suggestion of Kennon (Ref 17), Sakamoto *et al.* (Ref 18) have fitted C-curves for ferrite start, pearlite start and finish, and bainite start and finish to the relevant part of the U.S. Steel compendium (Ref 19, 20) involving the composition ranges, C = 0.06 to 0.79%, Si < 2.1%, Mn = 0.2 to 1.9%, Ni < 3.5%, Cr < 0.2%, Mo < 0.8%, and Cu < 1.5%. Intermediate volume fractions are also interpolated according to a logarithmic formula which is equivalent to Eq 15.

The author and coworkers have reported a predictor for IT curves based on rigorous Fe-C-X thermodynamics (which is accessible as multicomponent phase diagrams, and isothermal phase transformation kinetics for ferrite, pearlite, and bainite) and have calibrated this to the U.S. Steel compendium with a few adjustable parameters (Ref 7). While it is quantitatively similar to the method of Sakamoto *et al.*, it accounts for explicit synergistic alloying effects. Volume fractions also terminate at finite times (compare with Eq 15), and intermediate volume fractions are inherently defined. It is this procedure which underlies the comprehensive system described in Fig. 4. All three procedures have been offered in

elaborate detail in the open literature and limited space precludes repetition here. If the aim is for comprehensiveness, one of the two procedures based on the U.S. Steel Atlas is recommended.

A martensite start (M_s) formula, as for example given by Andrews (Ref 21), completes an information set that is capable of giving good estimates of entire CCT diagrams. The applicability of these procedures is limited to what has been previously designated by AISI-SAE as hardenability steels (H-steels) with alloying ranges 0.15 to 0.65% C, 0 to 0.4% Si, 0.4 to 2% Mn, 0 to 5% Ni, 0 to 1.8% Cr, 0 to 0.5% Mo. All the simple formulas fail outside these ranges because of the complicating effects of alloy carbides. Obviously, the software must be automatically disabled when the concentration inputs extend beyond the acceptable or proven ranges. As already noted, it is assumed that an integrating or weighting factor can be found for the time until each fraction (X) transformed. The best estimate of this quantity is generally agreed to be equal to the isothermal time $_{IT}(X)$ until a fixed X transformed so that along a given cooling curve (Ref 9):

$$\int_{T_{Ac3}}^{TCCT(X)} \frac{dt}{t_{IT}} = \int_{T_{Ac3}}^{TCCT(X)} \frac{dT}{t_{IT}(dT/dt)} = 1 \qquad \textbf{(Eq 16)}$$

where it is understood that the solution of the integral equation, T_{CCT}, together with the corresponding time on the selected cooling curve, gives one point on the CCT curve which is then designated by $_{CCT}(X)$. Although Eq 16, which is variously known as the *Scheil* or *Avrami Rule,* is more general (Ref 9), it is helpful to contemplate steady state growth of pearlite colonies at velocity V from a state of nucleation site saturation at time zero where the dimension l of a colony is simply:

$$l = \nu\ _{IT} \qquad \textbf{(Eq 17)}$$

Substituting this on the left of Eq 16, the unit value of this integral is confirmed for fixed X (or l) irrespective of the path of integration. The term after the first equal expression in Eq 16 is the more convenient one, because the independent variable, T, corresponds directly to the temperature limits. When a given cooling curve generates mixed structures such as ferrite-bainite or pearlite-bainite, Eq 16 evidently requires a detailed interpolative algorithm (Ref 7). Not surprisingly, there is some consensus that this procedure becomes quantitatively more successful as the steels became leaner.

Grange and Kieffer (Ref 22) have offered a useful approximation to the Scheil-Avrami Rule which represents a geometric method of conversion of IT to CCT diagrams. Here the integral (Eq 16) is evaluated by changing the Ae_3 limit to the cooling curve temperature of intersection T_{IT} on the X curve, and averaging the integrand, so that:

$$\frac{t_{CCT}(T_m) - t_{IT}(T_{IT})}{1/2[t_{IT}(T_m) + t_{CCT}(T_m)]} = 1 \qquad \textbf{(Eq 18)}$$

where T_m is the unknown on the cooling curve at $_{CCT}$. This can be found graphically by trial and error as indicated in Fig. 11 or by computer as described by Markowitz and Richman (Ref 23).

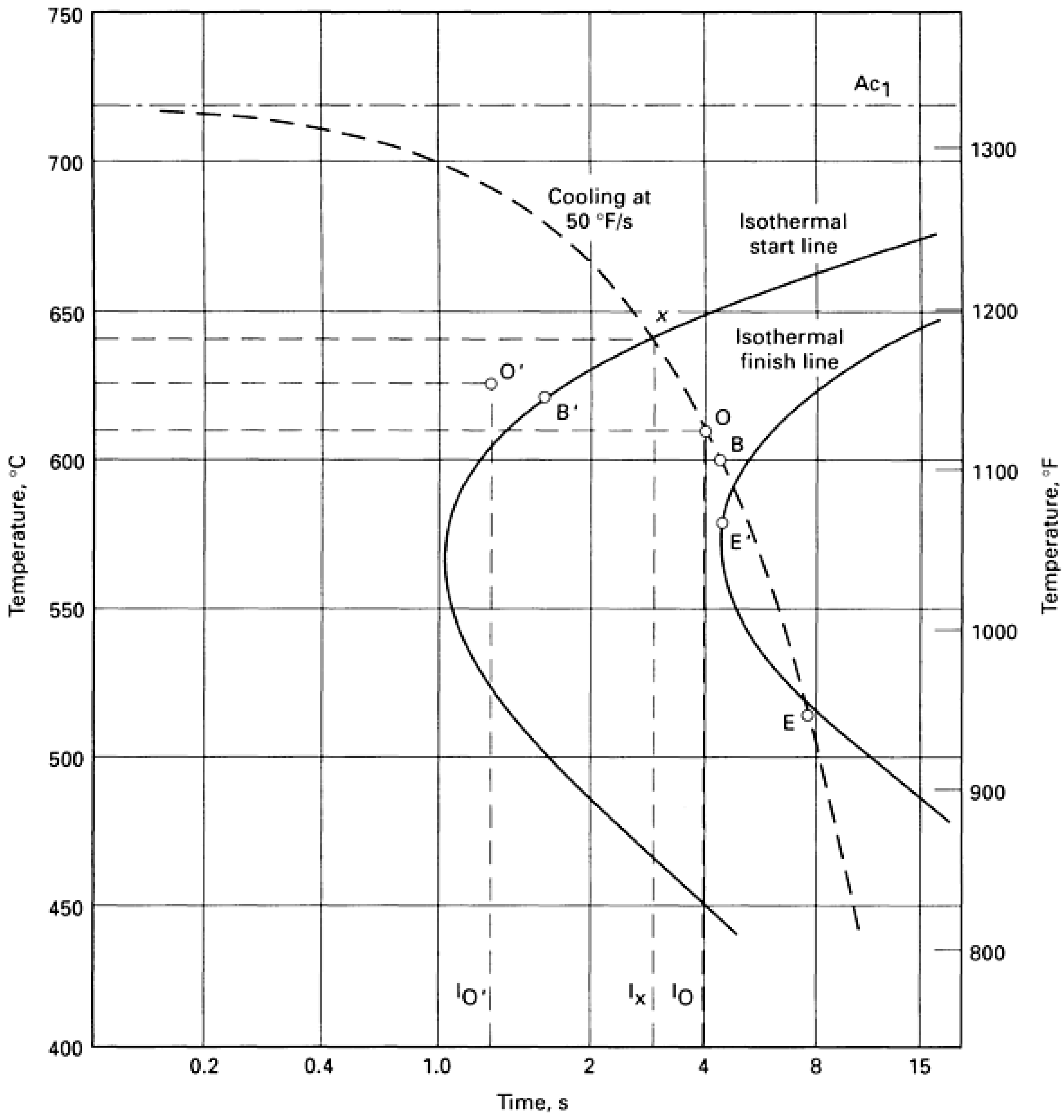

Fig. 11 A portion of the IT diagram for a plain carbon eutectoid steel, illustrating the graphical construction for obtaining the CCT diagram. In accordance with Eq 18, the time $_{CCT}$ at the unknown temperature (T_m) minus the time at *x* must equal the mean of $_{CCT}$ and that on the IT line at T_m.

The existence of an IT-to-CCT transformation procedure raises the question as to whether the process can be inverted. The answer is positive, as Eq 18 implies. This provides a basis for converting CCT curves (which are evaluated for natural, exponential-like cooling conditions) to those for constant cooling rates which are universal (Ref 9). This could be used to rationalize the international CCT data set for greater self-consistency and comprehensiveness and thus expand the knowledge base of an empirical system.

The precision of the various procedures for generating IT and CCT curves has often, and properly been criticized in the literature (Ref 4, 24), but what is being offered here is the art of the possible. It is generally sufficient in this kind of modelling to get all of the broad functional dependencies correct, and then, when the highest precision is demanded, to make empirical amendments.

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The Jominy Hardenability Data Set

The historical definition of "hardenability" as the "relative ability of steels to be deep-hardened" has various quantitative measures such as "ideal critical diameter" (D_I), or the depth of the Jominy inflection point (where the inflection point often corresponds to 50% martensite). It is clearly understood that hardenability is unique to a given steel composition and grain size. The effects of shape and cooling rates are another matter, as discussed below and in the article "Principles of Heat Treating of Steels" in this Volume. All dissolved alloying element additions (with the possible exception of cobalt) and grain size increase the hardenability. Sulfur decreases hardenability slightly by reducing the soluble manganese.

The measure which has been adopted almost universally is the Jominy end-quench hardenability test (Ref 25, 26, 27 and Fig. 3, 12). Given an alloy and its Jominy curve, there is no ambiguity concerning the end hardness value, which corresponds to fully hardened martensite of the given composition. The hardness for different martensite fractions depends on carbon content (Table 1), and data such as in Table 1 can be used to choose reference points during the

formulation of specifications of hardenability for steels of different carbon contents (Ref 28). With such relations of hardness to martensite, the steepness of a Jominy curve at the inflection point (50% martensite) is also of interest, because it relates to the intensity of internal stresses and to distortion. Together with the inflection point or mean depth of hardening there are at least four important pieces of information contained in a Jominy curve. Because the test is acceptably, if not ideally, reproducible (Fig. 13 and 14; Ref 25 and 29) under controlled conditions, and because it is informative and relatively economical, it is not surprising that the Jominy test has become the standard of the industry.

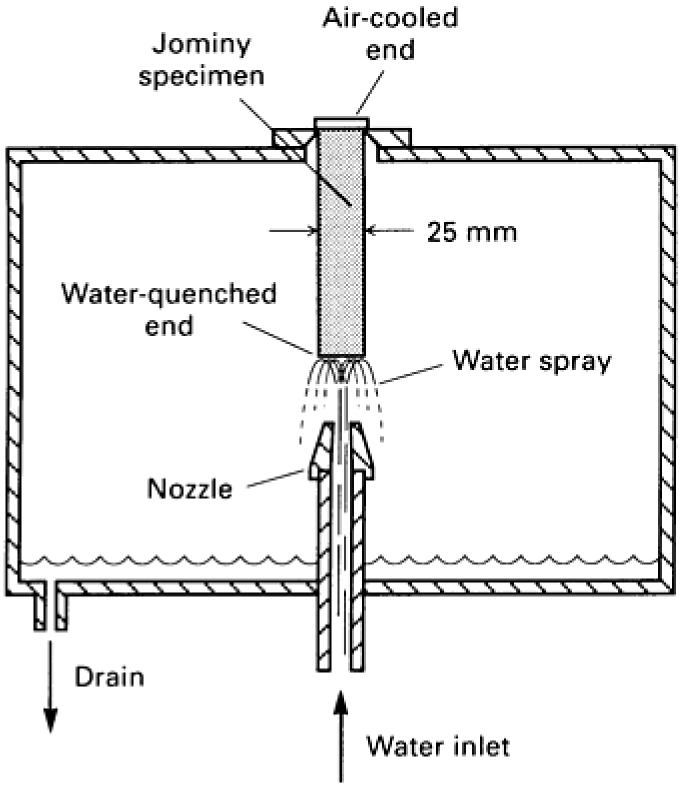

Fig. 12 Hardening procedure for Jominy end-quench specimen

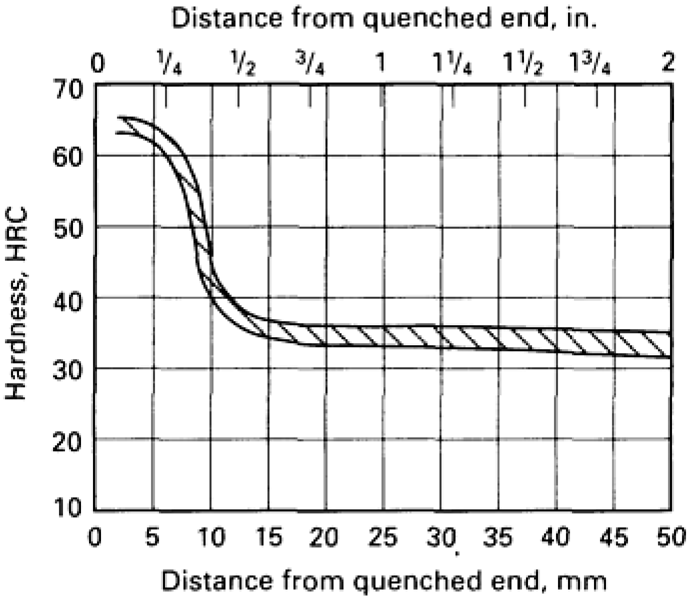

Fig. 13 Reproducibility of Jominy test by nine laboratories on one heat of 4068 steel. Source: Ref 25

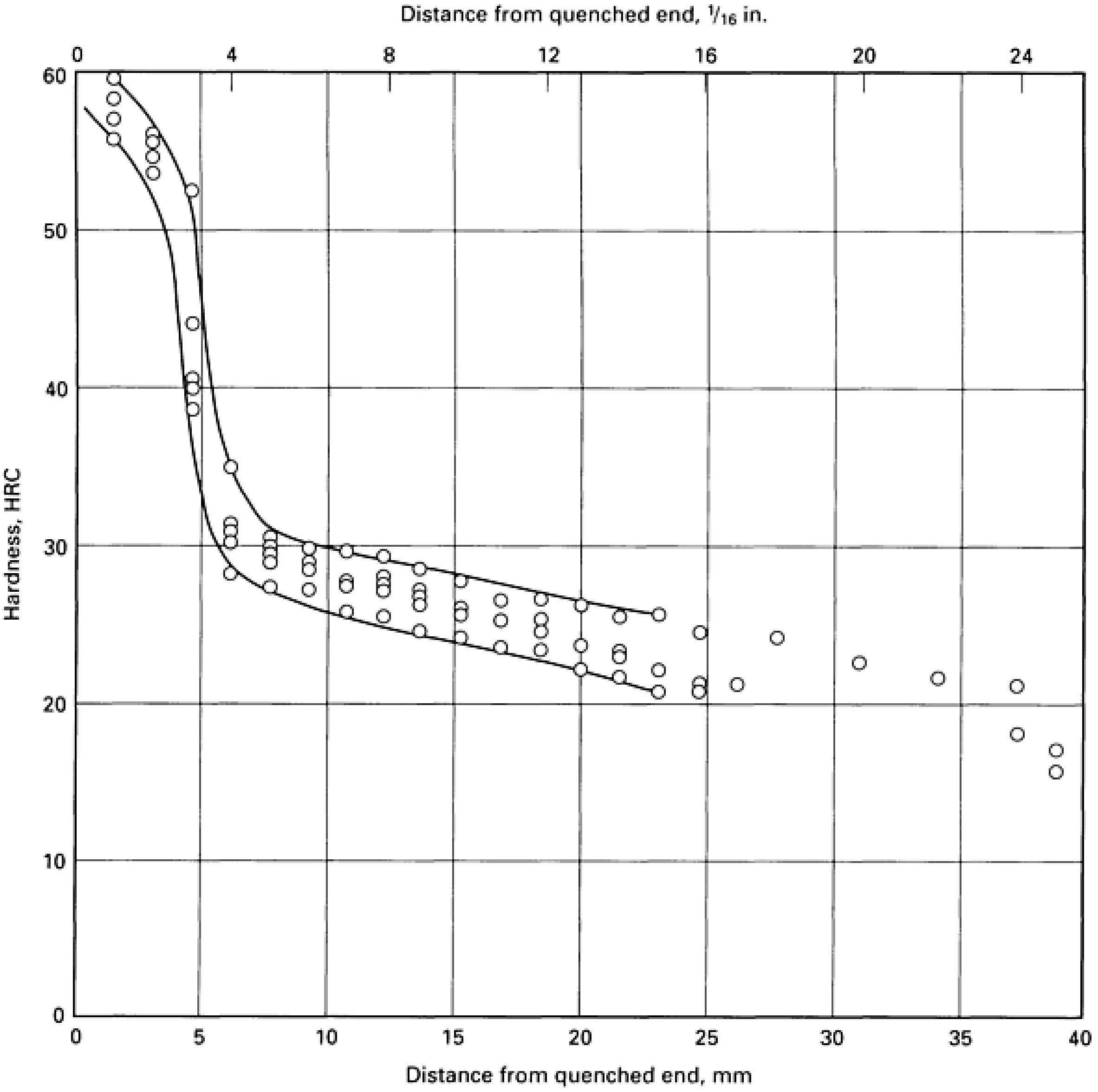

Fig. 14 Scatter band illustrating reproducibility between different organizations using standard Jominy system. Source: Ref 29

The main objectionable feature of the test lies in its impractical shape and quench configuration. Radially quenched bars are by far the most common configuration, a fact which was recognized in earlier test procedures. Unfortunately, to ascertain a unique hardenability measure such as the "ideal critical diameter" (D_I), it is necessary to examine an uneconomically large set of samples. One is therefore forced to conjecture, and hopefully establish the existence of a unique correlation between a Jominy measure (such as the inflection point) and D_I.

What are the grounds for expecting such a correlation which is independent of composition? The justification, which is far from rigorous, lies in the Lamont transformations (Ref 30, Fig. 15), that are based on an idealized but rigorous heat transfer model involving constant thermal conductivities k and surface heat transfer coefficients C as expressed in the Russell tables. They are prepared by numerical integration of the appropriate differential equations for heat transfer (Ref 31). It is assumed that for all low-alloy steels the main indices of phase partitioning are established near 700 °C (1300 °F) so that locations of equal cooling rates at 700 °C (1300 °F) will possess the same room-temperature structures (Fig. 7). The Carney empirical correlation (Ref 32) of Fig. 16 relating Jominy 50% martensite points (interpreted as the inflection point) to D_I (50% martensite at the center) should correspond roughly to the imposition of an infinite severity of quench ($H = \infty$) as indicated in the Lamont transformation of Fig. 15. The agreement here is an encouraging confirmation of the conjecture.

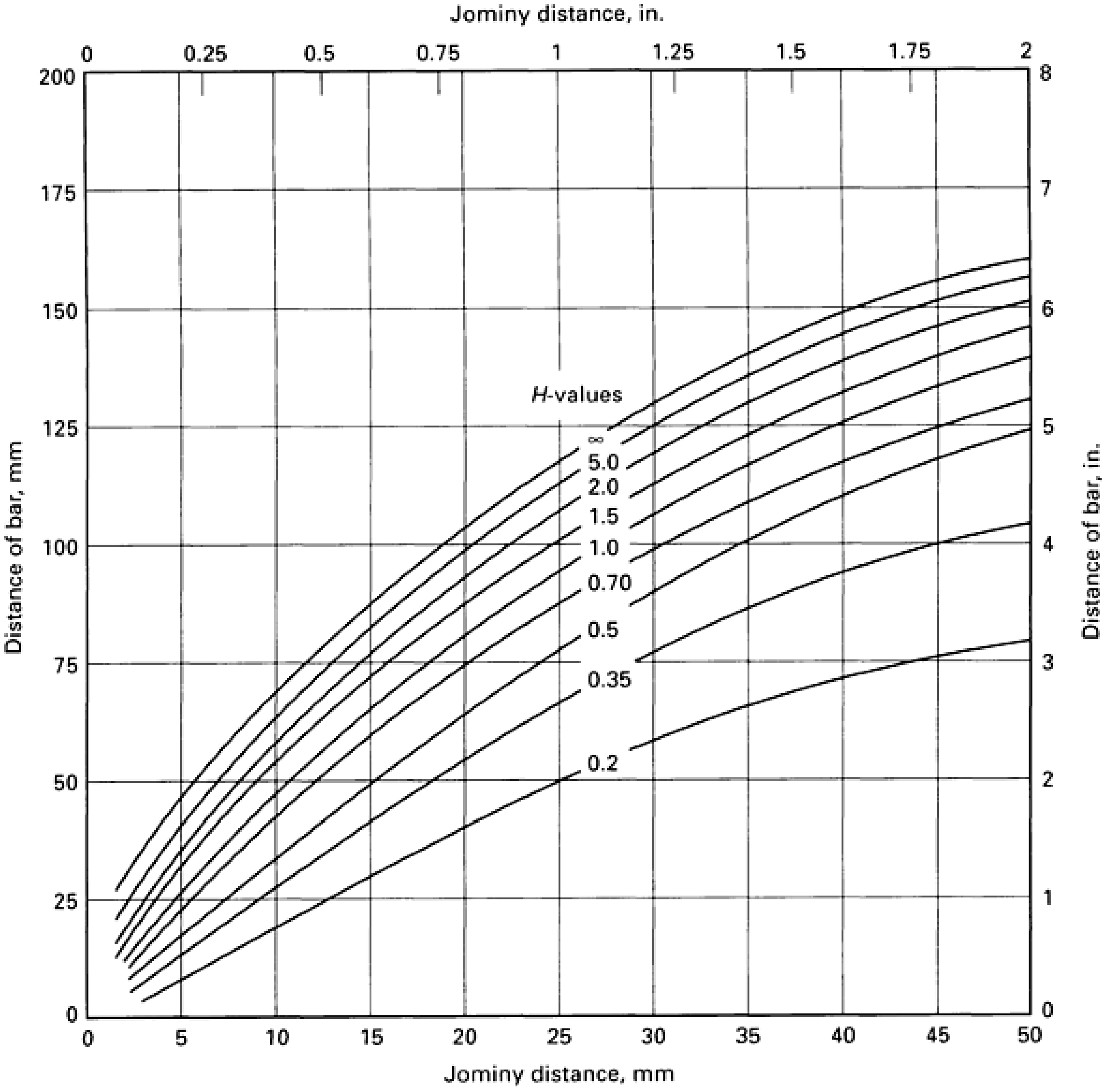

Fig. 15 Curves showing correlation of quench severity (expressed as Grossmann *H*-values) for Jominy specimens. The diagrams apply to points situated at a distance of one-tenth a radius (0.1 *R*) from the center of a round bar. Source: Ref 30

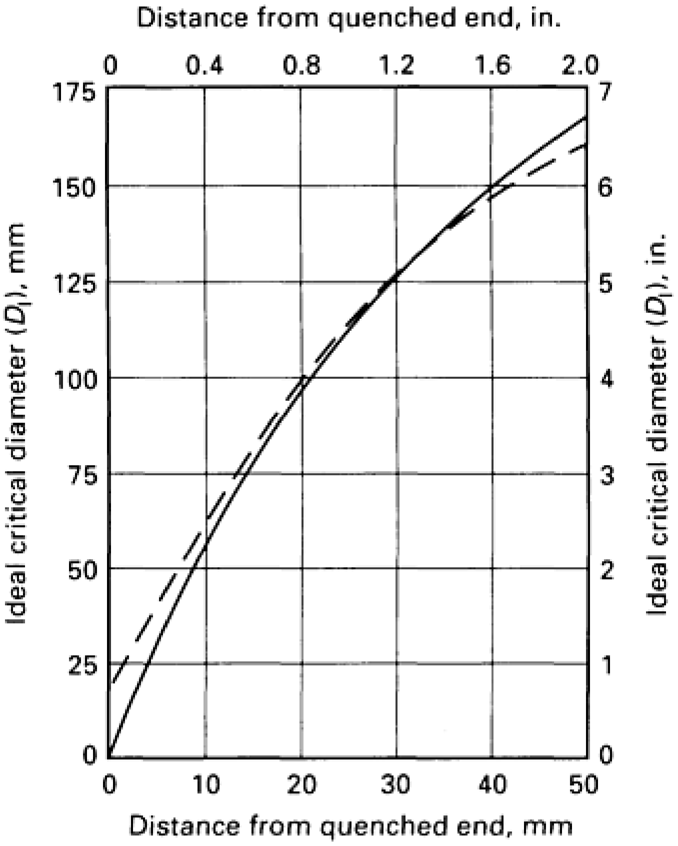

Fig. 16 Results from two similar studies showing the correlation between ideal critical diameter (D_I) and the distance to 50% martensite on an end-quench bar. Source: Ref 32

As Fig. 13 and 14 show, experimental reproducibility of hardness at a fixed Jominy depth near the inflection point of an H-steel in controlled tests can typically be ±6 HRC. It should be appreciated that the actual observed or predicted values of the hardness value at the inflection point are of very little intrinsic interest to the quality control officer or the heat treater. Rather, it is the upper or lower limits of surface (J1) and core (J32) hardness, the "half-hardness" *location*, and the slope of the hardness curve at this location which represent valuable information.

The foregoing comments pertain mainly to shallow and medium hardening steels. Focusing upon deeper hardening steels such as 4340 (Fig. 17), the idea of a Jominy depth of hardening becomes rather indefinite. Even though determination of D_I from an experimental set of critical diameters (*D*) remains a valid concept, this test option for deep hardening steels is not considered for cost reasons. The specification and interpretation problem in this case is not strongly associated with the shape of the curve, but with the extreme sensitivity of the hardnesses to the austenitizing temperature and time actually used in the Jominy test. To a lesser extent this is also true for low-alloy steels. This problem arises from the fact that the higher carbon hardenable steels are invariably hypereutectoid and therefore possess a substantial volume fraction of very unstable, undissolved carbides in the as-rolled condition. The quality control officer and heat treater should be critical of both the hardenability specifications and the experimental Jominy curves received for such grades. On the positive side, the heat treater should be cognizant of the flexibility afforded by minor variations in the austenitizing temperature.

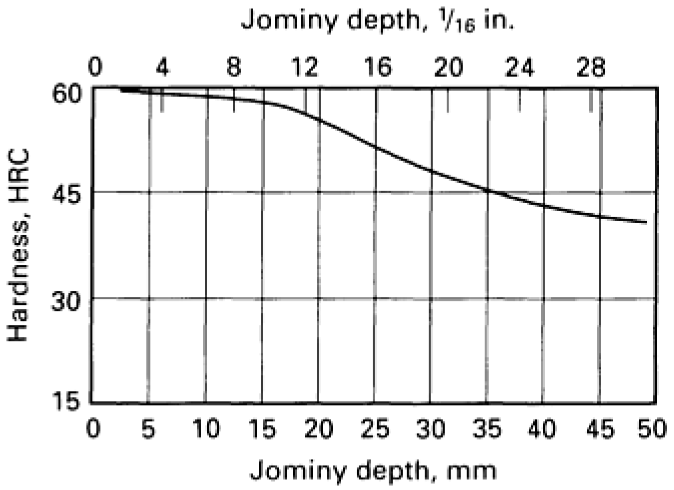

Fig. 17 Typical Jominy curve for a high hardenability (4340) steel. Source: Ref 1

The precision and reproducibility of the Jominy test is appreciably worse than indicated thus far. The test is a complex procedure which is carried out in most laboratories as though it were routine. Although the ASTM specification A 255-89 is highly specific, there are many instances whereby significant deviations from the specified practice are not preventable within the most disciplined laboratory situations. There are often five levels of uncoordinated servicing involved in the completion of the test: sampling, chemical analysis, heat treating, grinding, and hardness testing. The expectation of random and systematic errors, even when staff discipline is optimal, is obviously high and this is reflected in the strictly controlled reproducibility tests of Fig. 13 and 14 compiled by Jominy (Ref 25) and Brown (Ref 29). Such expectations led Caterpillar Tractor to undertake the regular auditing of the laboratory procedures of all of their suppliers and to establish their own specifications for test procedures (Ref 33). In England, others have been equally critical of routine Jominy testing (Ref 29, 34). To illustrate once more, Fig. 1 and 2 show a worldwide collection of Jominy curves for grades 8620 and 4140 of nearly the same reported individual chemistries and grain sizes. The scatter here reflects not only the exigencies of inadequate test procedures, but also the variations in melt shop practices which determine the inclusion content and therefore the effective grain size. The question is raised whether a carefully calibrated predictor might have advantages over routine, unaudited testing.

Prediction of Jominy Hardenability. This section gives alternatives to the set of Grossmann factors offered annually for many years in the June issue of *Metal Progress* and which are now included in the Appendices to ASTM Code A255-89 and SAE Standard J406. Such general systematizations run counter to the common intelligence that a different set of factors is required for each narrow class of steels (Ref 33, 35).

As with CCT diagrams a large compendium of observed Jominy curves spanning the composition and grain size range of interest can be stored. This can be accessed according to a composition and grain size input by near-matching to produce an empirically expected Jominy curve. At least one major steel producer proceeds in this way. The pitfalls in this methodology have been made evident by data sets such as those shown in Fig. 1 and 2. The methodology is computationally inefficient.

The development of linear regression formulas to a set of hardnesses corresponding to selected Jominy depths has been widely explored. This can be fairly effective for a single grade provided the data set densely covers the chemistry limits and hardness bands (Ref 29, 34). Such formulas, however, cannot be used outside of this single grade context (Ref 34), so comprehensive information or "expert" systems based on such procedures are inherently inflexible and exaggerated. However, producers or users of a limited number of grades may find this appropriate as an alternative to grade-selected Grossmann factors.

A comprehensive, if relatively crude system has been given for the HRC distribution in a Jominy bar by Just (Ref 36) who developed a universal Jominy curve shape in terms of penetration "E" in sixteenths of an inch and linearly regressed the coefficients for the weight percents of all of the constituents except carbon. As a consequence of the observed trends, carbon is accorded a square root rather than linear dependence. The main data set is taken as the center-line of the SAE-

AISI bands at the mean chemical composition specifications. The resulting formula for Rockwell C hardnesses (HRC) as a function of depth (4-25 sixteenths of an inch), independent of grain size, is:

$$\begin{aligned} J4\text{-}25 = {} & 98\sqrt{C} - 0.025E^2\sqrt{C} + 20Cr \\ & + 6.4Ni + 19Mn + 34Mo + 28V \\ & - 24\sqrt{E} + 2.86E - 7 \end{aligned} \quad \textbf{(Eq 19)}$$

Regression to 37 steels from the U.S. Steel Atlas, for which ASTM grain sizes A are given, yields the similar formula:

$$\begin{aligned} & J4\text{-}40 \\ & = 88\sqrt{C} - 0.0135E^2\sqrt{C} + 19Cr \\ & + 6.3Ni + 16Mn + 35Mo + 5Si - 0.82A \\ & - 20\sqrt{E} + 2.11E - 2 \end{aligned} \quad \textbf{(Eq 20)}$$

Together these suggest a more general composite formula:

$$\begin{aligned} & J4\text{-}32 \\ & = 98\sqrt{C} - 0.025E^2C + 20Cr + 6.4Ni \\ & + 19Mn + 34Mo + 28V + 5Si - \\ & 24\sqrt{E} + 2.86E - 0.82A - 1 \end{aligned} \quad \textbf{(Eq 21)}$$

The quenched end hardness (depth 0) is given empirically by:

$$J0 = 60\sqrt{C} + 20 \quad \textbf{(Eq 22)}$$

The combination of Eq 21 and 22 can be evaluated by hand-held calculators. Just also offers regression formulas which take into account higher powers of carbon-alloy interactions, but it is by no means clear that the rather subjective data set formulation justifies this extra sophistication. On the other hand, his partition of the data set into case-hardening and strongly hardenable steels seems justified, so the special formulas offered will probably improve on the predictive capabilities of Eq 21 in context. This methodology has been favorably tested by Jernkontorets in Sweden (Ref 35) and *in the general context* is expected to give better Jominy curves than those generated by slide rules or tables based on Grossmann multiplying factors (Ref 35) for the alloys 0.1 to 0.6% C, 0 to 1% Si, 0 to 2% Mn, 0 to 5% Ni, 0 to 2% Cr, 0 to 0.5(%Mo + %V). On the other hand, precise curve shapes are not expected to be reproduced.

As already indicated, the systematization of CCT diagrams due to Creusot-Loire is also a sound foundation for predicting Jominy curves (Ref 3, 13). For a Jominy specimen an explicit expression for Eq 10 is obtained by inverting the Timken estimate (Ref 37):

$$\dot{T} \text{ (in °C/h)} = 2.1298 \times 10^{26} \exp[-46.6254x^{0.03}] \quad \textbf{(Eq 23)}$$

where x is in sixteenths of an inch. Figure 18 shows a typical calculation of a Jominy curve based on this and the Creusot-Loire equation in relation to a typical observation. Any of the foregoing procedures can be calibrated to the user's data set by the simple device of a dummy correction to the carbon input and grain size parameter.

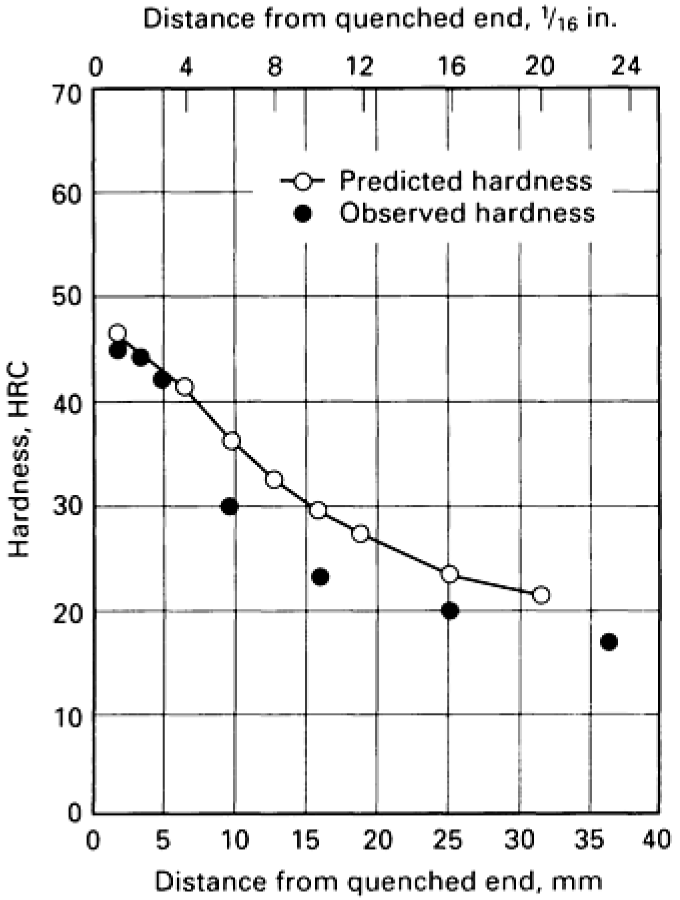

Fig. 18 Observed and predicted Jominy curve for the 8620-type steel of Fig. 10. Composition inputs (0.2% C, 1% Mn, 0.5% Cr, and 0.2% Mo) for the program has manganese slightly above the range for 8620 steel (0.7 to 0.9% Mn).

Evidently the set of TTT curves systematized by the Sakamoto *et al.* (Ref 18) or the Kirkaldy *et al.* (Ref 7) methods can be converted to CCT curves via the Scheil-Avrami Rule and room-temperature volume fractions and hardnesses can be calculated for various shapes, sizes, and cooling regimes, including the Jominy configuration. Accuracies comparable to those obtained by the Creusot-Loire method are undoubtedly obtainable.

None of the foregoing methods is capable of predicting in any generality the detailed shapes of the full range of Jominy curves because of the smoothing by averaging or the approximations and inherent errors in the various subsidiary formulas, such as for cooling rates and hardnesses. The proprietary system developed by Kirkaldy *et al.* (Ref 6) overcomes this defect by classifying the Jominy curves of steels into ten shape categories and correcting a data-based universal shape predictor accordingly. The Jominy inflection point depth is predicted directly from operations on theoretically systematized TTT-CCT start curves as above, and this and the shapes are calibrated against approximately 1000 well-characterized Jominy curves from an industry-provided set. It can be further calibrated to the user's data set, guaranteeing predictions at every Jominy point to a root mean square better than 2 HRC Operating in its most general format, all of the SAE-AISI and EX-Steel bands are generated to good precision. On the other hand, this predictive device offers only limited information about microstructure.

Relative Reliability of Jominy Measurements and Predictions (Ref 1). At this point, the question is raised as to whether calibrated predictors have reached the stage where chemistry-based outputs can be relied upon for decision-making by both the producer and user of hardenability steels. Although a number of corporations have already made a positive decision in this respect, the following statistical analysis compares the relative reliability of Jominy measurements and predictions (Ref 1).

An ideal Jominy hardness curve is defined by J_n where n designates the indentation location. The J_n curve is obtained by a precise Jominy measurement (per ASTM specification) on a forged bar which is sampled so as to best represent the performance of heats (or partial heats) of a particular grade from the user's point of view. A J'_n value will represent the

Jominy curve reported for an actual sample (which may or may not correspond to the ideal specification) and J''_n will represent the predicted Jominy curve based on the measured chemistry and grain size of a standard melt or bar sample. The formula which predicts J''_n has previously been calibrated to a large random set (N > 10; preferably 30) of measured Jominy curves (of form J_n or J'_n) from extended production or laboratory runs which span the expected or known production run band. It is therefore statistically established as a reliable average.

We now ask the question as to the respective expected deviations of J'_n and J''_n from J_n (the presumed actual) in application to a single heat. Regarding J''_n the first errors to consider are random and systematic chemical errors. Modern procedures and technology together with the expected chemical laboratory discipline allow the assignment of a zero systematic error and a random chemistry error (σ_c) less than 1 HRC. Secondly, the calibration errors (σ_n) must be considered. Ideally the calibrations would be based on a J_n set of N samples where N > 10. Figures 13 and 14 and our experience suggest that σ_n < 4 HRC would be typical, so the predictive error on a single heat would be $\sigma_n \div \sqrt{N-1}$ from this cause. There are random and systematic errors σ_0 and δ_0 due to the hardenability factors which are not represented by the chemistry. These are primarily systematic errors arising from plant or vessel practice and inadequate control of inclusions. Assuming a well-controlled standard practice, δ_0 will be stationary over long periods of time and thus eliminated from the predictor error by the calibration. The residual random error is estimated as $\sigma_0 \leq 1$ HRC. Finally, for conservatism, a random sampling error (σ_s) of 1 HRC and a systematic sampling error (δ_s) are introduced, which are assumed to be eliminated through the calibration. The net maximum predictive error for a single heat is accordingly:

$$e_n = \sqrt{s_c^2 + s_0^2 + s_s^2 + s_n^2/(N-1)} < \sqrt{1+1+1+16/10} = 2.2 HRC \qquad \textbf{(Eq 24)}$$

This figure, as an upper limit at an n location on the steep portions of the Jominy curve, is in complete accord with our general experience. It should be appreciated that if hardenability predictions are being taken seriously the principals will pay close attention to the quality of the input data sets, J_n.

Regarding J'_n, which pertains to routine Jominy testing, the situation is highly variable from producer to producer (Fig. 1 and 2). Under strictly controlled trials, such as in Fig. 13 and 14, on the steep portions of the curves, $_n$ generally exceeds 3 HRC and can be as high as 6 HRC. In routine testing, where there are often systematic errors as well, these values may be expected to be even higher, therefore, properly calibrated predictors offer a strong advantage over testing in routine applications (compare 6 HRC with ε_n in Eq 24). A properly calibrated hardenability formula will also anticipate the results of a check test at every hardness point better than an actual Jominy test. Thus, if spot testing for recalibration is maintained to allow for possible long-term changes in the systematic errors, or if standard practice is rigid enough to prevent such changes, confidence can be placed in a calibrated prediction formula based on final melt or bar chemistry.

Application of Jominy Predictors. In many cases decisions on the release of heats for rolling and/or delivery are now made on the basis of prediction from bar or melt-down chemistry alone. As such, a comprehensive formula, which is accurately calibrated to a grade range and a particular plant practice, can be used within this context. However, prior austenite grain size must be considered since, unlike chemistry as a hardenability determinant, it is not routinely reported.

Prior austenite grain size usually becomes an adjustable parameter in theoretical or empirical predictors which can be altered for different grades and for local conditions. (In the Creusot-Loire procedure it is estimated by a calculation based on the austenitizing parameter P_a.) This element of the calibration procedure operates on the assumption that typically the effective grain size is repeatable as a consequence of standardized melt shop practices. When standard melt practice is grossly altered through scheduling breaks, nonstandard preheats, refractory defects and/or large changes in unreported residuals (which alter the inclusion count), the effective grain size may change so as to alter detectably the Jominy curves. As a warning here, the modern trend toward cleaner heats necessarily generates larger grain sizes and concomitant hardenability, a result often counteracted by microalloying.

Unscheduled production variations, together with gross errors in the Jominy test procedure, are the sources of what is known as "maverick" heats. These may be recognized when the observed measure lies outside of the calibrated predictor measure by more than 2μ. Upon mandatory retesting with special care, it can be immediately established whether or not the deviation is due to a testing error or other cause. If the latter is the case then we must agree with the common view of producers (Ref 1) that a systematic change in practice should be suspected and identified as the source of the problem.

Through private communication with parties in three countries other than the U.S., it is known that Jominy predictions are being used for release to rolling mills and substituted for tests in both critical and noncritical applications. The

replacement of Jominy testing by equivalent predictions has long been the case with very shallow hardening steels where hardenability testing is difficult or impossible (Ref 1). Great savings can be realized by producers and users by adopting this kind of computer-aided technology.

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Modelling of Post-Hardening Treatments

Predicting the Tempering Characteristics of Quenched Low-Alloy Steels. While the theory of temper softening of martensite is now advanced to the point of accurate predictions (Ref 38), the same cannot be said for mixed structures found at the center of thicker parts. The Creusot-Loire system overcomes this problem through empiricism and a plausible hypothesis that a low-temperature version of the austenitizing grain growth parameter (P_a) designated as (Ref 39):

$$Pc = \left[\frac{1}{T} - \frac{nR}{H_a}.\log\frac{t}{t_0}\right]^{-1} \qquad \textbf{(Eq 25)}$$

controls the coarsening and therefore the hardness of all room-temperature microstructural mixtures. It is claimed that the activation enthalpy H_a = 57,500 cal/mole for carbon steels with Mo < 0.04% and H_a = 100,000 for all steels with Mo > 0.04% with the time unit t_0 = 1 h. The first regression formula pertains to the temperature-time dependence of the deflection or softening point (Fig. 19), that is:

$$10^3/P_c = 1.365 -(0.205C+0.233Mo+0.135V) \qquad \textbf{(Eq 26)}$$

and this relates to the time and temperature of the sharp deflection in Fig. 19. The term $10^3/P_c$ from Eq 25 is also input to hardness formulas for martensite and bainite of the form:

$$HV_M = -74 - 434C - 368Si = 25Mn + 37Ni - 335Mo$$
$$-2235V + \frac{10^3}{P_c}(260 + 616C + 321Si - 21Mn - 35Ni - 11Cr + 352Mo + 2354V) \qquad \textbf{(Eq 27)}$$

and

$$HV_B = 262 + 163C _ 349Si - 64Mn - 6Ni - 186Cr - 458Mo - 857V$$
$$+\frac{10^3}{Pc}(-149 + 43C + 446Si + 79Mn + 16Ni + 196Cr + 498Mo + 1094V) \qquad \textbf{(Eq 28)}$$

and

$$HV_{F-P} = 152 - 493C - 10Mn - 19Mo + \frac{10^3}{Pc}(-37 + 726C + 14Mn + 17Mo) \qquad \textbf{(Eq 29)}$$

The softening of ferrite-pearlite is almost negligible, so the usual rule of mixing can now be employed and the time or temperature dependent process of softening generated. A nomographic summary for a particular steel is given in Fig. 19. For example, none of the structures in French steel 20CND6 contribute softening at 550 °C (1020 °F) for times up to 100 h. On the other hand they all show significant softening after 60 s at 700 °C (1300 °F). Figure 20 shows the computed softening after 1 h at 600 °C (1110 °F) from the center line hardnesses of the alloy recorded in Fig. 10. Generally, the observational validations are impressive (Ref 13).

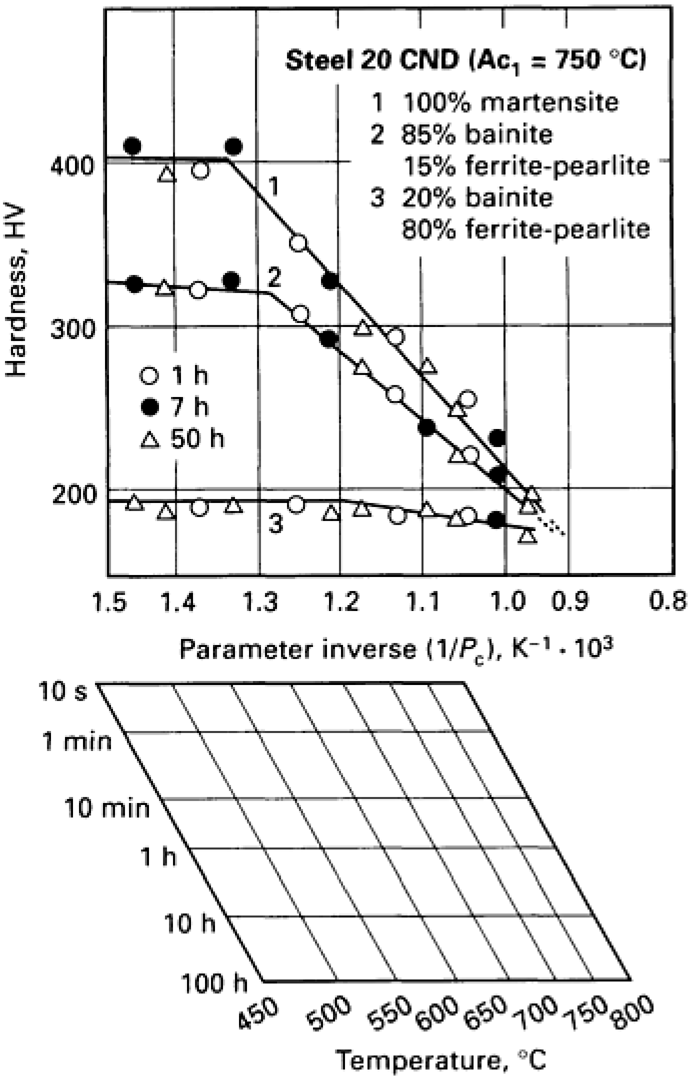

Fig. 19 Hardness variation as a linear function of the inverse of the tempering parameter (P_c) in Eq 25. The activation enthalpy (H_a) was 1 × 10^5 cal/mole. Source. Ref 13

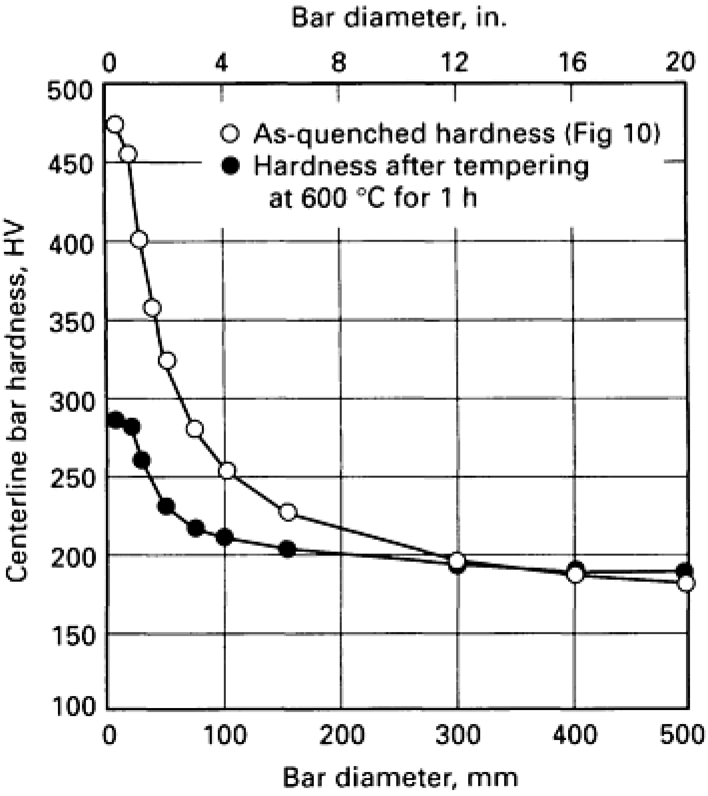

Fig. 20 Hardness after tempering predicted by the Creusot-Loire system for the 8620-type steel composition of Fig. 10

It must be emphasized that the estimates from all the previous formulas are based upon incomplete information pertaining to the original data set and the theoretical bases, and upon inaccurate or incomplete inputs. To achieve predictive precision, all formulas should be calibrated by the user within narrowed contexts and checked against outcomes on a regular basis to remove systematic inadequacies. The best formulas are those with valid functional dependencies which are amenable to easy calibration against historical data, and these will prove to be indispensable within a viable, quantitative information system. The grain size or coarsening parameters and the carbon content which enter into most of the preceding formulas are effective parameters for calibration adjustment.

Elements of a Comprehensive Quantitative Information System for Heat-Treated Low-Alloy Steel Parts. A survey of about thirty international corporations using hardenability and heat treatment software identifies the following cost-saving functions:

- Aid to dispatching heats for rolling or to a particular customer, together with control of inventory
- Diversion of heats to particular sizes and product lines and subsequent rolling schedules
- On-line cost-optimal calculation of alloy vessel and ladle additions to meet hardenability and mechanical specifications. Cost savings of greater than $2/ton have been demonstrated
- Aid in customer service to reduce risks in accepting orders where chemistry and hardenability requirements may not be compatible, to help meet very narrow hardenability specifications, and to suggest alternate steels which meet customer's hardenability requirements
- On-line control in bar and plate heat-treating facilities based on chemistry. A major reduction of rejects has been reported
- Substitution of calculations where possible for costly Jominy and other mechanical testing. Annual savings of $100,000 have been reported for a medium-sized steel-making shop
- Scientific aid to design and development, taking account of mechanical properties and residual stresses
- Development of new hardenable steel grades together with specifications and bands
- Development of a research tool to match hardenability requirements and compositions to stress levels imposed on various components
- Simulation of product heat-treat operations

- Incorporation in a comprehensive material selection program
- Quality control of steel deliveries including their chemistry, hardenability, mechanical properties, and heat-treat response. Auditing incoming heats in relation to received and historical data
- On-line control of heat treatment and multistage gas carburization processes

Modelling of Carburization Response. The chart in Fig. 4 contemplates an accurate predictor which goes beyond the main features of quenching and tempering discussed in this article. In particular, carburization response, residual stresses, and stress relief are areas of further modelling and program complication. Carburization, for example, includes the distribution of carbon content as an additional variable to the basic quench and temper program, which must be adjusted to accommodate hypereutectoid compositions. This obviously increases running time and expands the time scale of the stress-strain calculations. Furthermore, an on-line capability, which accounts for largescale multistage operations, must also take into account atmosphere control and furnace and charge configurations so as to provide a correctly predicted carbon injection level. Research towards this goal is well advanced through the efforts of Stickels (Ref 40) and others.

Prediction of Residual Stress and Distortion. The inclusion of mechanical response to a complex temperature field and variation in chemical composition to allow prediction of internal stresses, strains, and overall dilatation represents the most severe complication because finite element methods must be used. (See the article "Computerized Properties Prediction and Technology Planning in Heat Treatment of Steels" in this Volume for a listing of various finite element analysis programs.)

The preliminary program being investigated by the author and coworkers requires at least one hour running time on a mainframe computer or work station and generates tabular information pertaining to a sample part (the Jominy bar) which consumes approximately 1000 pages of printout. In the latter outcome the modeler must confront the problem of generating too much information for the needs of the average industrial software user. Thus much programming effort and memory must be devoted to aiding the user in selection for brevity and clarity. Figures 21 and 22 are two examples of processed predictions from a finite element analysis program.

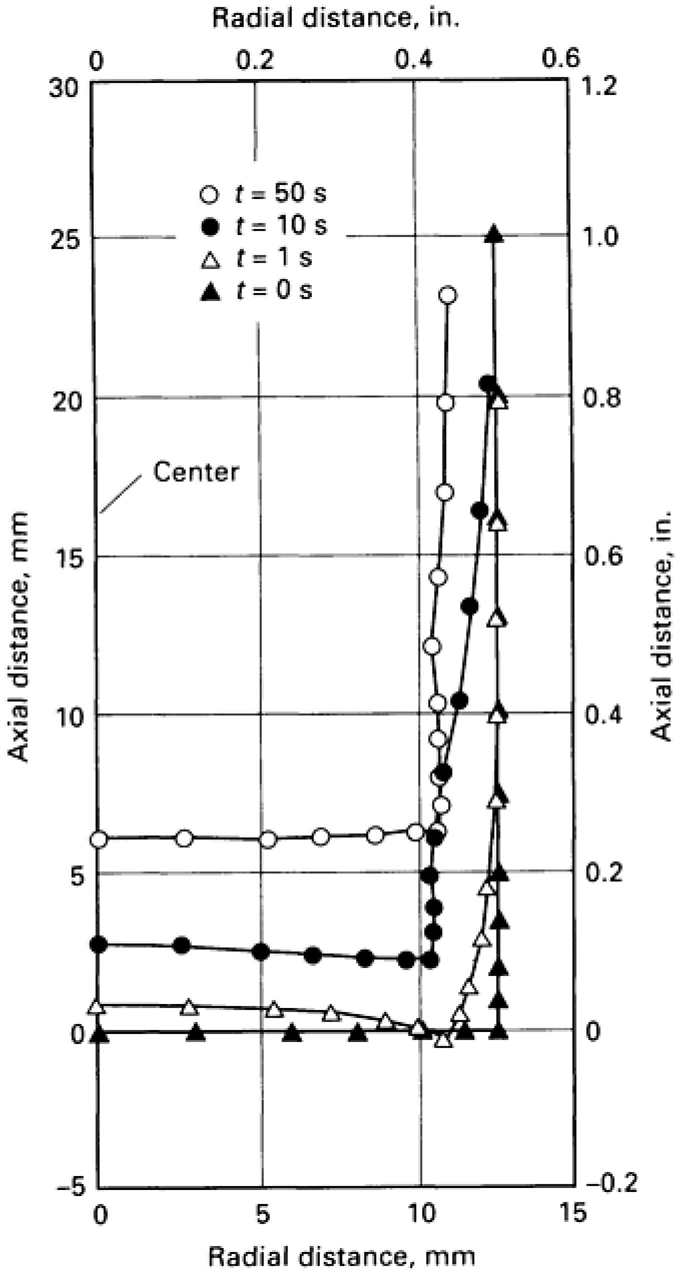

Fig. 21 Finite element analysis of distortion at the quenched end of a Jominy specimen at different cooling times (*t*) for 4140 steel. Node displacements are drawn using a scale factor of 20. Source: Ref 8

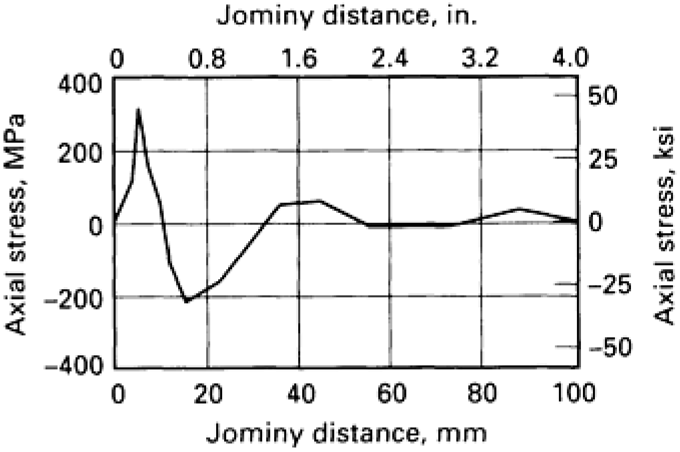

Fig. 22 Predicted residual stress at the surface of a Jominy specimen after cooling. Source: Ref 8

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Stress-Relief Heat Treating of Steel

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Introduction

STRESS-RELIEF HEAT TREATING is used to relieve stresses that remain locked in a structure as a consequence of a manufacturing sequence. This definition separates stress-relief heat treating from postweld heat treating in that the goal of postweld heat treating is to provide, in addition to the relief of residual stresses, some preferred metallurgical structure or properties (Ref 1, 2). For example, most ferritic weldments are given postweld heat treatment to improve the fracture toughness of the heat-affected zones (HAZ). Moreover, austenitic and nonferrous alloys are frequently postweld heat treated to improve resistance to environmental damage.

Stress-relief heat treating is the uniform heating of a structure, or portion thereof, to a suitable temperature below the transformation range (Ac_1 for ferritic steels), holding at this temperature for a predetermined period of time, followed by uniform cooling (Ref 2, 3). Care must be taken to ensure uniform cooling, particularly when a component is composed of variable section sizes. If the rate of cooling is not constant and uniform, new residual stresses can result that are equal to or greater than those that the heat-treating process was intended to relieve.

Stress-relief heat treating can reduce distortion and high stresses from welding that can affect service performance. The presence of residual stresses can lead to stress-corrosion cracking (SCC) near welds and in regions of a component that has been cold strained during processing. Furthermore, cold strain per se can produce a reduction in creep strength at elevated temperatures.

Residual stresses in a ferritic steel cause significant reduction in resistance to brittle fracture. In a material that is not prone to brittle fracture, such as an austenitic stainless steel, residual stresses can be sufficient to provide the stress necessary to promote SCC even in environments that appear to be benign (Ref 4).

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Sources of Residual Stress

There are many sources of residual stress; they can occur during processing of the material from ingot to final product form (Ref 4, 5). Residual stresses can be generated during rolling, casting, or forging; during forming operations such as shearing, bending, drawing, and machining; and during fabrication, in particular, welding. Residual stresses are present whenever a component is stressed beyond its elastic limit and plastic flow occurs. Additional information on residual stresses can be found in the article "Defects and Distortion in Heat-Treated Parts" in this Volume.

Bending a bar during fabrication at a temperature where recovery cannot occur (cold forming, for example) will result in one surface location containing residual tensile stresses, whereas a location 180° away will contain residual compressive stresses (Ref 6).

Quenching of thick sections results in high residual compressive stresses on the surface of the material. These high compressive stresses are balanced by residual tensile stresses in the internal areas of the section (Ref 7).

Grinding is another source of residual stresses; these can be compressive or tensile in nature, depending on the grinding operation. Although these stresses tend to be shallow in depth, they can cause warping of thin parts (Ref 8).

Welding. The cause of residual stresses that has received the most attention in the open literature is welding. The residual stresses associated with the steep thermal gradient of welding can occur on a macroscale over relatively long distances (reaction stresses) or can be highly localized (microscale) (Fig. 1). Welding usually results in localized residual stresses that approach levels equal to or greater than the yield strength of the material at room temperature.

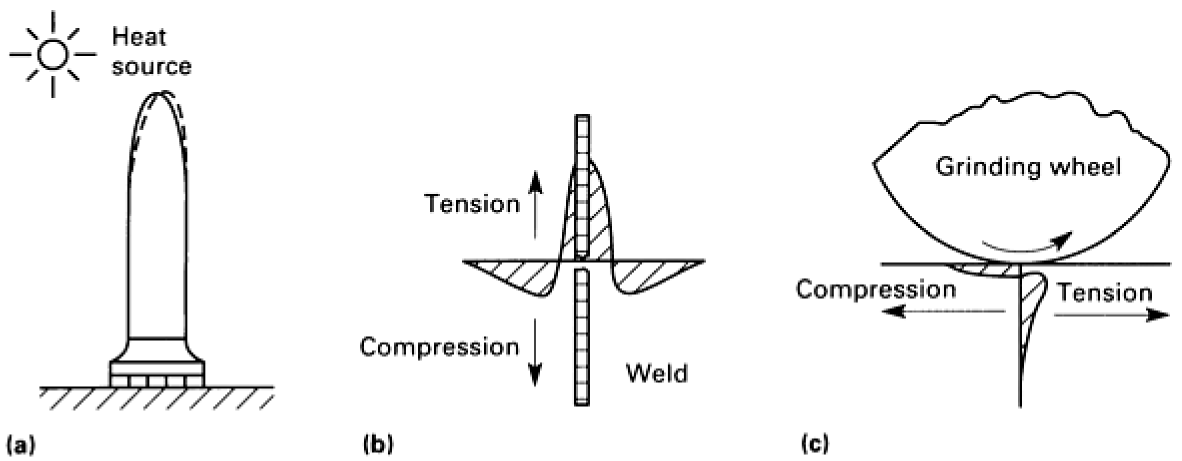

Fig. 1 Examples of the causes of residual stresses: (a) Thermal distortion in a structure due to heating by solar radiation. (b) Residual stresses due to welding. (c) Residual stresses due to grinding. Source: Ref 4

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Alleviation of Residual Stresses

A number of factors influence the relief of residual stresses, including level of stress, permissible (or practicable) time for their relief, temperature, and metallurgical stability.

Time-Temperature Factors. The relief of residual stresses is a time-temperature-related phenomenon (Fig. 2), parametrically correlated by the Larson-Miller equation:

$$\text{Thermal effect} = T(\log t + 20)10^{-3} \qquad \textbf{(Eq 1)}$$

where T is temperature (Rankin), and t is the time in hours. It is evident in Fig. 2 that similar relief of residual stresses can be achieved by holding a component for longer periods at a lower temperature. For example, holding a piece at 595 °C (1100 °F) for 6 h provides the same relief of residual stress as heating at 650 °C (1200 °F) for 1 h.

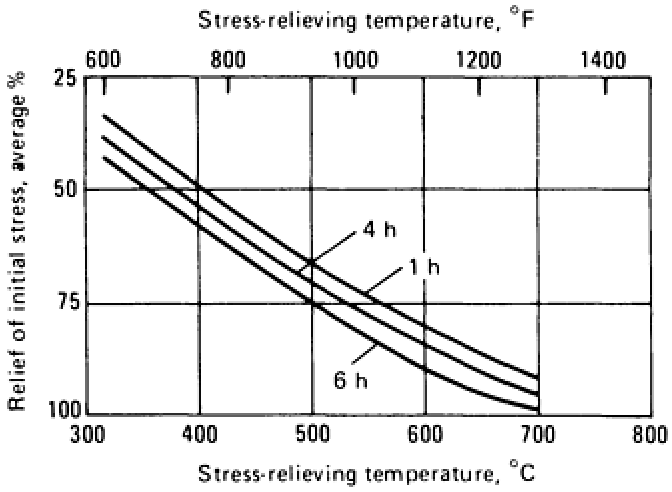

Fig. 2 Relationship between time and temperature in the relief of residual stresses in steel. Source: Ref 3

Alloy Considerations. Relief of residual stresses represents typical stress-relaxation behavior, in which the material undergoes microscopic (sometimes even macroscopic) creep at the stress-relief temperature. Creep-resistant materials, such as the chromium-bearing low-alloy steels and the chromium-rich high-alloy steels, normally require higher stress-relief heat-treating temperatures than conventional low-alloy steels. Typical stress-relief temperatures for low-alloy ferritic steels are between 595 and 675 °C (1100 and 1250 °F). For high-alloy steels, these temperatures may range from 900 to 1065 °C (1650 to 1950 °F).

For high-alloy steels, such as the austenitic stainless steels, stress relieving is sometimes done at temperatures as low as 400 °C (750 °F). However, at these temperatures, only modest decreases in residual stress are achieved. Residual stresses can be significantly reduced by stress-relief heat treating those austenitic materials in the temperature range from 480 to 925 °C (900 to 1700 °F). At the higher end of this range, nearly 85% of the residual stresses may be relieved. Stress-relief heat treating in this range, however, may result in sensitizing susceptible material. This metallurgical effect can lead to SCC in service (Ref 9). Frequently, solution-annealing temperatures of about 1065 °C (1950 °F) are used to achieve a reduction of residual stresses to acceptably low values.

Some copper alloys may fail by SCC due to the presence of residual stresses. These stresses are usually relieved by mechanical or thermal stress-relief treatments. Stress-relief heat treating tends to be favored because it is more controllable, less costly, and also provides a degree of dimensional stability. Stress-relief heat treating of copper alloys is usually carried out at relatively low temperatures, in the range from 200 to 400 °C (390 to 750 °F) (Ref 5).

Resistance of a material to the reduction of its residual stresses by thermal treatment can be estimated with a knowledge of the influence of temperature on its yield strength. Figure 3 provides a summary of the yield strength to temperature relationship for three generic classes of steels. The room-temperature yield strength of these materials provides an excellent estimate of the level of localized residual stress that can be present in a structure. To relieve the residual stress requires that the component be heated to a temperature where its yield strength approaches a value that corresponds to an acceptable level of residual stress. Holding at this temperature can further reduce the residual stress through the reduction of strain due to creep. Uniform cooling after residual-stress heat treating is mandatory if these levels of residual stress are to be maintained.

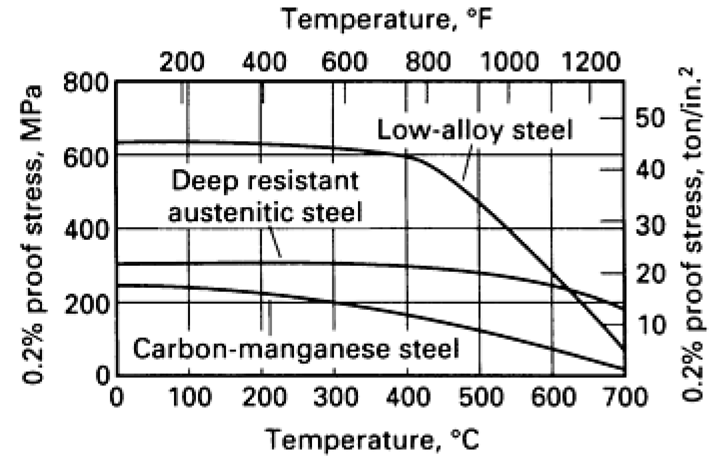

Fig. 3 Variation of the yield strength with temperature for three generic classes of steel. Source: Ref 10

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Normalizing of Steel

Revised by Thomas Ruglic, Hinderliter Heat Treating, Inc.

Introduction

NORMALIZING OF STEEL is a heat-treating process that is often considered from both thermal and microstructural standpoints. In the thermal sense, normalizing is an austenitizing heating cycle followed by cooling in still or slightly agitated air. Typically, the work is heated to a temperature about 55 °C (100 °F) above the upper critical line of the iron-iron carbide phase diagram, as shown in Fig. 1; that is, above Ac_3 for hypoeutectoid steels and above A_{cm} for hypereutectoid steels. To be properly classed as a normalizing treatment, the heating portion of the process must produce a homogeneous austenitic phase (face-centered cubic, or fcc, crystal structure) prior to cooling. Figure 2 compares the time-temperature cycle of normalizing to that of full annealing. Typical normalizing temperatures for many standard steels are given in Table 1.

Table 1 Typical normalizing temperatures for standard carbon and alloy steels

Grade	Temperature[a]	
	°C	°F
Plain carbon steels		
1015	915	1675
1020	915	1675
1022	915	1675
1025	900	1650
1030	900	1650
1035	885	1625
1040	860	1575
1045	860	1575
1050	860	1575
1060	830	1525
1080	830	1525
1090	830	1525
1095	845	1550
1117	900	1650
1137	885	1625
1141	860	1575
1144	860	1575
Standard alloy steels		
1330	900	1650
1335	870	1600
1340	870	1600
3135	870	1600
3140	870	1600
3310	925	1700
4027	900	1650
4028	900	1650
4032	900	1650
4037	870	1600
4042	870	1600
4047	870	1600
4063	870	1600
4118	925	1700
4130	900	1650
4135	870	1600
4137	870	1600
4140	870	1600
4142	870	1600
4145	870	1600
4147	870	1600
4150	870	1600
4320	925	1700
4337	870	1600
4340	870	1600
4520	925	1700
4620	925	1700
4621	925	1700
4718	925	1700

Grade	Temperature[a]	
	°C	°F
4720	925	1700
4815	925	1700
4817	925	1700
4820	925	1700
5046	870	1600
5120	925	1700
5130	900	1650
5132	900	1650
5135	870	1600
5140	870	1600
5145	870	1600
5147	870	1600
5150	870	1600

Grade	Temperature[a]	
	°C	°F
5155	870	1600
5160	870	1600
6118	925	1700
6120	925	1700
6150	900	1650
8617	925	1700
8620	925	1700
8622	925	1700
8625	900	1650
8627	900	1650
8630	900	1650
8637	870	1600
8640	870	1600

Grade	Temperature[a]	
	°C	°F
8642	870	1600
8645	870	1600
8650	870	1600
8655	870	1600
8660	870	1600
8720	925	1700
8740	925	1700
8742	870	1600
8822	925	1700
9255	900	1650
9260	900	1650
9262	900	1650
9310	925	1700

Grade	Temperature[a]	
	°C	°F
9840	870	1600
9850	870	1600
50B40	870	1600
50B44	870	1600
50B46	870	1600
50B50	870	1600
60B60	870	1600
81B45	870	1600
86B45	870	1600
94B15	925	1700
94B17	925	1700
94B30	900	1650
94B40	900	1650

(a) Based on production experience, normalizing temperature may vary from as much as 27 °C (50 °F) below, to as much as 55 °C (100 °F) above, indicated temperature. The steel should be cooled in still air from indicated temperature.

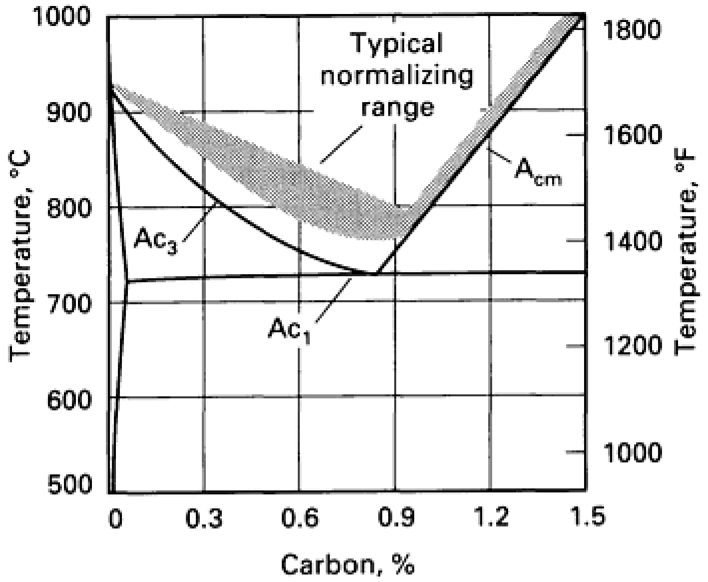

Fig. 1 Partial iron-iron carbide phase diagram showing typical normalizing range for plain carbon steels

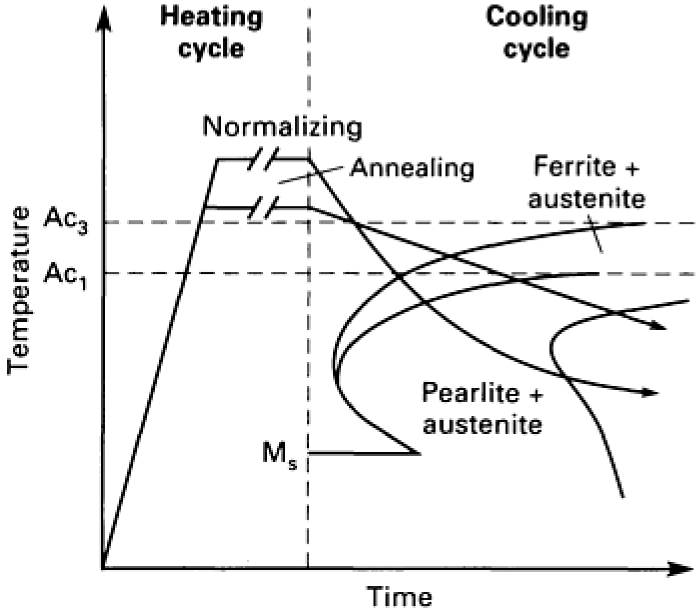

Fig. 2 Comparison of time-temperature cycles for normalizing and full annealing. The slower cooling of annealing results in higher temperature transformation to ferrite and pearlite and coarser microstructures than does normalizing. Source: Ref 1

Normalizing is also frequently thought of in terms of microstructure. The areas of the microstructure that contain about 0.8% C are pearlitic (lamellae of ferrite and iron carbide). The areas that are low in carbon are ferritic (body-centered cubic, or bcc, crystal structure). In hypereutectoid steels, proeutectoid iron carbide first forms along austenite grain boundaries. This transformation continues until the carbon level in the austenite reaches approximately 0.8%, at which time a eutectoid reaction begins as indicated by the formation of pearlite. Air-hardening steels are excluded from the class of normalized steels because they do not exhibit the normal pearlitic microstructure that characterizes normalized steels.

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Applications of Normalizing Based on Steel Classification

A broad range of ferrous products can be normalized. All of the standard low-carbon, medium-carbon, and high-carbon wrought steels can be normalized, as well as many castings. Many steel weldments are normalized to refine the structure within the weld-affected area. Austenitic steels, stainless steels, and maraging steels either cannot be normalized or are not usually normalized. Tool steels are generally annealed by the steel supplier.

The purpose of normalizing varies considerably. Normalization may increase or decrease the strength and hardness of a given steel in a given product form, depending on the thermal and mechanical history of the product. Actually, the functions of normalizing may overlap with or be confused with those of annealing, hardening, and stress relieving. Improved machinability, grain-structure refinement, homogenization, and modification of residual stresses are among the reasons normalizing is done. Homogenization of castings by normalizing may be done in order to break up or refine the dendritic structure and facilitate a more even response to subsequent hardening. Similarly, for wrought products, normalization can help reduce banded grain structure due to hot rolling, as well as large grain size or mixed large and small grain size due to forging practice. The details of normalizing treatments applied to three typical production parts are given in Table 2, which also lists the reasons for normalizing and gives some of the mechanical properties obtained in the normalized and tempered condition. Comparisons of typical hot-rolled or annealed mechanical properties versus typical normalized properties are presented in Table 3.

Table 2 Typical applications of normalizing and tempering of steel components

Part	Steel	Heat treatment	Properties after treatment	Reason for normalizing
Cast 50 mm (2 in.) valve body, 19 to 25 mm ($\frac{3}{4}$ to 1 in.) in section thickness	Ni-Cr-Mo	Full annealed at 955 °C (1750 °F), normalized at 870 °C (1600 °F), tempered at 665 °C (1225 °F)	Tensile strength, 620 MPa (90 ksi); 0.2% yield strength, 415 MPa (60 ksi); elongation in 50 mm, or 2 in., 20%; reduction in area, 40%	To meet mechanical-property requirements
Forged flange	4137	Normalized at 870 °C (1600 °F), tempered at 570 °C (1060 °F)	Hardness, 200 to 225 HB	To refine grain size and obtain required hardness
Valve-bonnet forging	4140	Normalized at 870 °C (1600 °F) and tempered	Hardness, 220 to 240 HB	To obtain uniform structure, improved machinability, and required hardness

Table 3 Properties of selected carbon and alloy steels in the hot-rolled, normalized, and annealed conditions

AISI grade[a]	Condition or treatment	Tensile strength		Yield strength		Elongation[b], %	Reduction in area, %	Hardness, HB	Izod impact strength	
		MPa	ksi	MPa	ksi				J	ft · lbf
1015	As-rolled	420	61	315	46	39.0	61	126	111	82
	Normalized at 925 °C (1700 °F)	425	62	325	47	37.0	70	121	115	85

AISI grade[a]	Condition or treatment	Tensile strength		Yield strength		Elongation[b], %	Reduction in area, %	Hardness, HB	Izod impact strength	
		MPa	ksi	MPa	ksi				J	ft · lbf
	Annealed at 870 °C (1600 °F)	385	56	285	41	37.0	70	111	115	85
1020	As-rolled	450	65	330	48	36.0	59	143	87	64
	Normalized at 870 °C (1600 °F)	440	64	345	50	35.8	68	131	118	87
	Annealed at 870 °C (1600 °F)	395	57	295	43	36.5	66	111	123	91
1022	As-rolled	505	73	360	52	35.0	67	149	81	60
	Normalized at 925 °C (1700 °F)	485	70	360	52	34.0	68	143	117	87
	Annealed at 870 °C (1600 °F)	450	65	315	46	35.0	64	137	121	89
1030	As-rolled	550	80	345	50	32.0	57	179	75	55
	Normalized at 925 °C (1700 °F)	525	76	345	50	32.0	61	149	94	69
	Annealed at 845 °C (1550 °F)	460	67	345	50	31.2	58	126	69	51
1040	As-rolled	620	90	415	60	25.0	50	201	49	36
	Normalized at 900 °C (1650 °F)	595	86	370	54	28.0	55	170	65	48
	Annealed at 790 °C (1450 °F)	520	75	350	51	30.2	57	149	45	33
1050	As-rolled	725	105	415	60	20.0	40	229	31	23
	Normalized at 900 °C (1650 °F)	750	109	430	62	20.0	39	217	27	20
	Annealed at 790 °C (1450 °F)	635	92	365	53	23.7	40	187	18	13
1060	As-roIled	815	118	485	70	17.0	34	241	18	13
	Normalized at 900 °C (1650 °F)	775	113	420	61	18.0	37	229	14	10

AISI grade[a]	Condition or treatment	Tensile strength		Yield strength		Elongation[b], %	Reduction in area, %	Hardness, HB	Izod impact strength	
		MPa	ksi	MPa	ksi				J	ft · lbf
	Annealed at 790 °C (1450 °F)	625	91	370	54	22.5	38	179	11	8
1080	As-rolled	965	140	585	85	12.0	17	293	7	5
	Normalized at 900 °C (1650 °F)	1015	147	525	76	11.0	21	293	7	5
	Annealed at 790 °C (1450 °F)	615	89	380	55	24.7	45	174	7	5
1095	As-rolled	965	140	570	83	9.0	18	293	4	3
	Normalized at 900 °C (1650 °F)	1015	147	505	73	9.5	14	293	5	4
	Annealed at 790 °C (1450 °F)	655	95	380	55	13.0	21	192	3	2
1117	As-rolled	490	71	305	44	33.0	63	143	81	60
	Normalized at 900 °C (1650 °F)	470	68	305	44	33.5	54	137	85	63
	Annealed at 860 °C (1575 °F)	430	62	285	41	32.8	58	121	94	69
1118	As-rolled	525	76	315	46	32.0	70	149	109	80
	Normalized at 925 °C (1700 °F)	475	69	315	46	33.5	66	143	103	76
	Annealed at 790 °C (1450 °F)	450	65	285	41	34.5	67	131	107	79
1137	As-rolled	625	91	380	55	28.0	61	192	83	61
	Normalized at 900 °C (1650 °F)	670	97	400	58	22.5	49	197	64	47
	Annealed at 790 °C (1450 °F)	585	85	345	50	26.8	54	174	50	37
1141	As-rolled	675	98	360	52	22.0	38	192	11	8
	Normalized at 900 °C (1650 °F)	710	103	405	59	22.7	56	201	53	39

AISI grade[a]	Condition or treatment	Tensile strength		Yield strength		Elongation[b], %	Reduction in area, %	Hardness, HB	Izod impact strength	
		MPa	ksi	MPa	ksi				J	ft · lbf
	Annealed at 815 °C (1500 °F)	600	87	355	51	25.5	49	163	34	25
1144	As-rolled	705	102	420	61	21.0	41	212	53	39
	Normalized at 900 °C (1650 °F)	670	97	400	58	21.0	40	197	43	32
	Annealed at 790 °C (1450 °F)	585	85	345	50	24.8	41	167	65	48
1340	Normalized at 870 °C (1600 °F)	835	121	560	81	22.0	63	248	92	68
	Annealed at 800 °C (1475 °F)	705	102	435	63	25.5	57	207	71	52
3140	Normalized at 870 °C (1600 °F)	890	129	600	87	19.7	57	262	54	40
	Annealed at 815 °C (1500 °F)	690	100	420	61	24.5	51	197	46	34
4130	Normalized at 870 °C (1600 °F)	670	97	435	63	25.5	60	197	87	64
	Annealed at 865 °C (1585 °F)	560	81	360	52	28.2	56	156	62	46
4140	Normalized at 870 °C (1600 °F)	1020	148	655	95	17.7	47	302	23	17
	Annealed at 815 °C (1500 °F)	655	95	420	61	25.7	57	197	54	40
4150	Normalized at 870 °C (1600 °F)	1160	168	740	107	11.7	31	321	12	9
	Annealed at 815 °C (1500 °F)	730	106	380	55	20.2	40	197	24	18
4320	Normalized at 895 °C (1640 °F)	795	115	460	67	20.8	51	235	73	54
	Annealed at 850 °C (1560 °F)	580	84	430	62	29.0	58	163	110	81
4340	Normalized at 870 °C (1600 °F)	1280	186	860	125	12.2	36	363	16	12
	Annealed at 810 °C (1490 °F)	745	108	475	69	22.0	50	217	52	38

AISI grade[(a)]	Condition or treatment	Tensile strength		Yield strength		Elongation[(b)], %	Reduction in area, %	Hardness, HB	Izod impact strength	
		MPa	ksi	MPa	ksi				J	ft · lbf
4620	Normalized at 900 °C (1650 °F)	570	83	365	53	29.0	67	174	135	98
	Annealed at 860 °C (1575 °F)	510	74	370	54	31.3	60	149	94	69
4820	Normalized at 860 °C (1580 °F)	760	110	485	70	24.0	59	229	110	81
	Annealed at 815 °C (1500 °F)	685	99	460	67	22.3	59	197	94	69
5140	Normalized at 870 °C (1600 °F)	795	115	475	69	22.7	59	229	38	28
	Annealed at 830 °C (1525 °F)	570	83	295	43	28.6	57	167	41	30
5150	Normalized at 870 °C (1600 °F)	870	126	530	77	20.7	59	255	31	23
	Annealed at 825 °C (1520 °F)	675	98	360	52	22.0	44	197	26	19
5160	Normalized at 860 °C (1575 °F)	960	139	530	77	17.5	45	269	11	8
	Annealed at 815 °C (1495 °F)	725	105	275	40	17.2	31	197	10	7
6150	Normalized at 870 °C (1600 °F)	940	136	615	89	21.8	61	269	35	26
	Annealed at 815 °C (1500 °F)	665	97	415	60	23.0	48	197	27	20
8620	Normalized at 910 °C (1675 °F)	635	92	360	52	26.3	60	183	100	74
	Annealed at 870 °C (1600 °F)	540	78	385	56	31.3	62	149	115	83
8630	Normalized at 870 °C (1600 °F)	650	94	430	62	23.5	54	187	95	70
	Annealed at 845 °C (1550 °F)	565	82	370	54	29.0	59	156	95	70
8650	Normalized at 870 °C (1600 °F)	1025	149	690	100	14.0	45	302	14	10
	Annealed at 795 °C (1465 °F)	715	104	385	56	22.5	46	212	30	22

AISI grade[a]	Condition or treatment	Tensile strength		Yield strength		Elongation[b], %	Reduction in area, %	Hardness, HB	Izod impact strength	
		MPa	ksi	MPa	ksi				J	ft · lbf
8740	Normalized at 870 °C (1600 °F)	930	135	605	88	16.0	48	269	18	13
	Annealed at 815 °C (1500 °F)	695	101	415	60	22.2	46	201	41	30
9255	Normalized at 900 °C (1650 °F)	930	135	580	84	19.7	43	269	14	10
	Annealed at 845 °C (1550 °F)	775	112	490	71	21.7	41	229	10	7
9310	Normalized at 890 °C (1630 °F)	910	132	570	83	18.8	58	269	119	88
	Annealed at 845 °C (1550 °F)	820	119	440	64	17.3	42	241	79	58

(a) All grades are fine grained except for those in the 1100 series, which are coarse grained

(b) In 50 mm or 2 in.

Figure 3 shows that high-carbon steels with large amounts of pearlite have high transition temperatures and therefore will fail in a brittle manner even well above room temperature. On the other hand, low-carbon steels have subzero transition temperatures and are quite tough at room temperature (Ref 1).

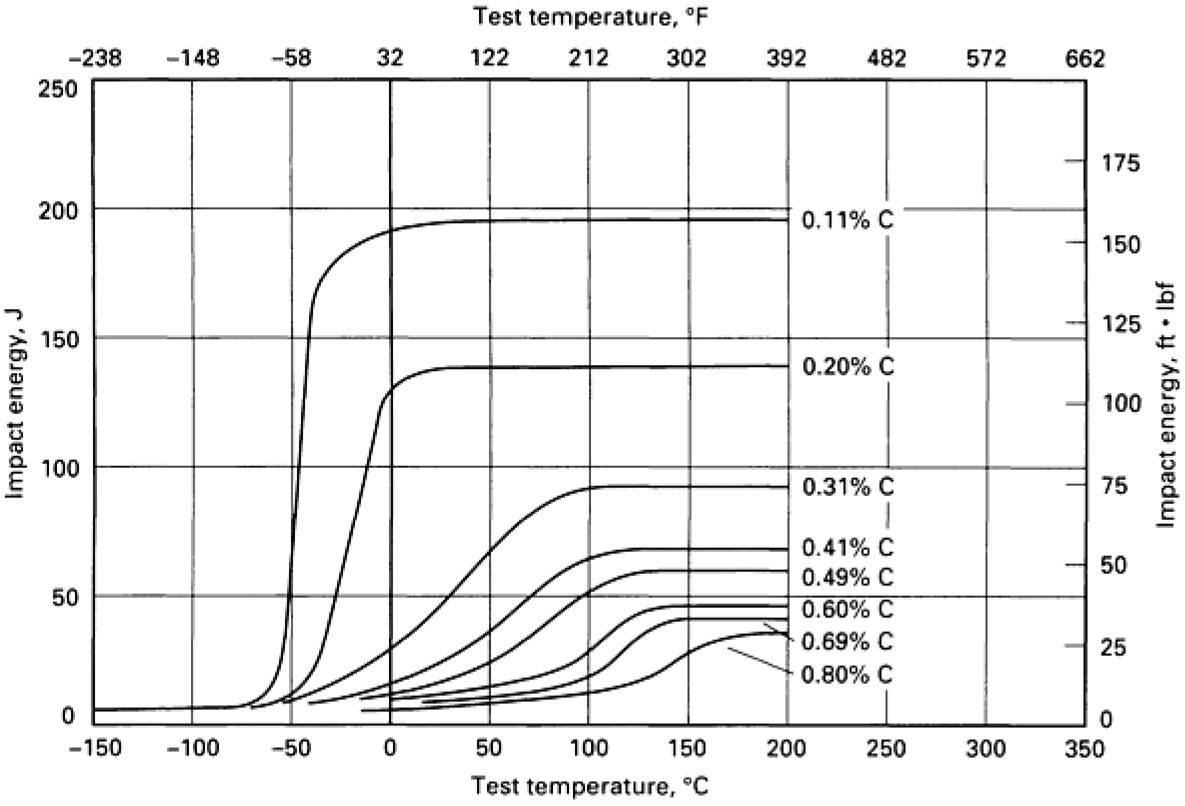

Fig. 3 Change in impact transition curves with increasing pearlite content in normalized carbon steels. Source: Ref 1

Depending on the mechanical properties required, normalizing may be substituted for conventional hardening when the size or shape of the part is such that liquid quenching might result in cracking, distortion, or excessive dimensional changes. Thus, parts that are of complex shape or that incorporate sharp changes in section may be normalized and tempered, provided that the properties obtained are acceptable.

The rate of heating generally is not critical for normalizing; on an atomic scale, it is immaterial. In parts having great variations in section size, however, thermal stress can cause distortion.

Time at temperature is critical only in that it must be sufficient to cause homogenization. Sufficient time must be allowed for solution of thermodynamically stable carbides, or for diffusion of constituent atoms. Generally, time sufficient for complete austenitization is all that is required. One hour at temperature, after the furnace recovers, per inch of part thickness, is considered to be standard. Parts often can be austenitized adequately in much less time (with a saving of energy). In cases where normalizing is done to homogenize segregated structures, longer times may be required.

The rate of cooling significantly influences both the amount of pearlite and the size and spacing of the pearlite lamellae. At higher cooling rates, more pearlite forms, and the lamellae are finer and more closely spaced. Both the increased amount of pearlite and the greater fineness of the pearlite result in higher strength and higher hardness. Conversely, lower cooling rates result in softer parts. The effect of mass on hardness (via its effect on cooling rate) is illustrated by the data in Table 4. In any part having both thick and thin sections, the potential exists for variations in cooling rate, and thus for variations in strength and hardness as well. This can also increase the probability of distortion or even cracking. Cooling rate sometimes is enhanced with fans to increase strength and hardness of parts or to decrease the time required, following the furnace operation, for sufficient cooling of parts to permit convenient handling.¨

Table 4 Effect of mass on hardness of normalized carbon and alloy steels

Grade	Normalizing temperature	Hardness, HB, for bar with diameter, mm (in.), of

	°C	°F	13($\frac{1}{2}$)	25(1)	50(2)	100(4)
Carbon steels, carburizing grades						
1015	925	1700	126	121	116	116
1020	925	1700	131	131	126	121
1022	925	1700	143	143	137	131
1117	900	1650	143	137	137	126
1118	925	1700	156	143	137	131
Carbon steels, direct-hardening grades						
1030	925	1700	156	149	137	137
1040	900	1650	183	170	167	167
1050	900	1650	223	217	212	201
1060	900	1650	229	229	223	223
1080	900	1650	293	293	285	269
1095	900	1650	302	293	269	255
1137	900	1650	201	197	197	192
1141	900	1650	207	201	201	201
1144	900	1650	201	197	192	192
Alloy steels, carburizing grades						
3310	890	1630	269	262	262	248
4118	910	1670	170	156	143	137

Grade	Normalizing temperature		Hardness, HB, for bar with diameter, mm (in.), of			
	°C	°F	13($\frac{1}{2}$)	25(1)	50(2)	100(4)
4320	895	1640	248	235	212	201
4419	955	1750	149	143	143	143
4620	900	1650	192	174	167	163
4820	860	1580	235	229	223	212
8620	915	1675	197	183	179	163
9310	890	1630	285	269	262	255
Alloy steels, direct-hardening grades						
1340	870	1600	269	248	235	235
3140	870	1600	302	262	248	241
4027	905	1660	179	179	163	156
4063	870	1600	285	285	285	277
4130	870	1600	217	197	167	163
4140	870	1600	302	302	285	241
4150	870	1600	375	321	311	293
4340	870	1600	388	363	341	321
5140	870	1600	235	229	223	217
5150	870	1600	262	255	248	241
5160	855	1575	285	269	262	255

Grade	Normalizing temperature		Hardness, HB, for bar with diameter, mm (in.), of			
	°C	°F	13($\frac{1}{2}$)	25(1)	50(2)	100(4)
6150	870	1600	285	269	262	255
8630	870	1600	201	187	187	187
8650	870	1600	363	302	293	285
8740	870	1600	269	269	262	255
9255	900	1650	277	269	269	269

Note: All data are based on single heats. Source; Ref 2, 3

After parts have cooled uniformly through their cross section to black heat below Ar_1 (the parts are no longer red, as when they were removed from the furnace), they may be water or oil quenched to decrease the total cooling time. In heavy sections, cooling of the center material to black heat may require considerable time. Thermal shock, residual thermally induced stress, and resultant distortions are factors to be considered. The microstructure remains essentially unaffected by the increased cooling rate, provided that the entire mass is below the lower critical temperature, Ar_1, although changes involving precipitates may occur.

Carbon Steels. Table 1 lists typical normalizing temperatures for some standard grades of carbon steel. These temperatures can be interpolated to obtain values for carbon contents not listed.

Steels containing 0.20% C or less usually receive no treatment subsequent to normalizing. However, medium-carbon or high-carbon steels are often tempered after normalizing to obtain specific properties such as a lower hardness for straightening, cold working, or machining. Whether tempering is desirable depends on specific property requirements and not on carbon content and section size requirements. Table 3 presents typical mechanical properties of selected carbon and alloy steels in the hot-rolled, normalized, and annealed conditions. Because of pearlite lamellae and spacing, a low-carbon or medium-carbon steel of thin section may be harder after normalizing than a high-carbon steel of large section size subjected to the same treatment.

Alloy Steels. For alloy steel forgings, rolled products, and castings, normalizing is commonly used as a conditioning treatment before final heat treatment. Normalizing also refines the structures of forgings, rolled products, and castings that have cooled nonuniformly from high temperatures. Table 1 lists typical normalizing temperatures for some standard alloy steels.

Alloy carburizing steels such as 3310 and 4320 usually are normalized at temperatures higher than the carburizing temperature to minimize distortion in carburizing and to improve machining characteristics. Carburizing steels of the 3300 series sometimes are double normalized with the expectation of minimizing distortion; these steels are tempered at about 650 °C (1200 °F) for intervals of up to 15 h to reduce hardness to below 223 HB for machinability. Carburizing steels of the 4300 and 4600 series usually can be normalized to a hardness not exceeding 207 HB and therefore need not be tempered for machinability.

Hypereutectoid alloy steels such as 52100 are normalized for partial or complete elimination of carbide networks, thus producing a structure that is more susceptible to 100% spheroidization in the subsequent spheroidize annealing treatment. The spheroidized structure provides improved machinability and a more uniform response to hardening.

Some alloy grades require more care in heating to prevent cracking from thermal shock. They also require longer soaking times because of lower austenitizing and solution rates. For many alloy steels, rates of cooling in air to room temperature must be carefully controlled. Certain alloy steels are forced-air cooled from the normalizing temperature in order to develop specific mechanical properties. This is a normalizing treatment only in the microstructural sense discussed in the introduction to this article.

References cited in this section

1. G. Krauss, *Steels: Heat Treatment and Processing Principles,* ASM International, 1990
2. *Modern Steels and Their Properties,* 6th ed., Bethlehem Steel Corporation, 1966
3. *Modern Steels and Their Properties,* Handbook 3310, Bethlehem Steel Corporation, Sept 1978

Forgings

When forgings are normalized before carburizing or before hardening and tempering, the upper range of normalizing temperatures is used. However, when normalizing is the final heat treatment, use is made of the lower range of temperatures.

Furnaces. Any appropriately sized furnace may be utilized for normalizing. Furnace type and size will depend upon the specific need. In a continuous furnace, forgings to be normalized are usually placed in shallow pans, and a pusher mechanism at the loading end of the furnace transports the pans through the furnace. Furnace burners located on both sides of the furnace fire below the hearth, and combustion products rise along the walls of the work-zone muffle and exhaust into the roof of the furnace. No atmosphere control is used. Combustion products enter the work zone through ports lining both sides of the entire hearth. A typical furnace is 9 m (30 ft) long and has 18 gas burners (or 9 oil burners) on each side. For purposes of temperature control, such a furnace is divided into three 3 m (10 ft) zones, each having a vertical thermocouple extending into it through the roof of the furnace.

Processing. Small forgings are usually normalized as received from the forge shop. A typical furnace has five pans in each of the three furnace zones. Heating is adjusted so that the work reaches normalizing temperature in the last zone. After passing through the last zone, the pans are discharged onto a cooling conveyor. The work, while still in the pans, is cooled in still air to below 480 °C (900 °F); it is then discharged into tote boxes, where it cools to room temperature. Total furnace time is approximately $3\frac{1}{2}$ h, but during this period the work is held at the normalizing temperature for only 1 h.

Normalizing of large open-die forgings usually is performed in batch-type furnaces pyrometrically controlled to narrow temperature ranges. Forgings are held at the normalizing temperature long enough to allow complete austenitizing and carbide solution to occur (usually one hour per inch of section thickness), and then are cooled in still air.

Axle-Shaft Forging. In forging an axle shaft made of fine-grained 1049 steel, only one end of the forging bar was heated to upset the wheel-flange section. When the part was examined in cross section from the flanged end to the cold end, the metallurgical conditions discussed below were revealed.

The hot-worked flanged area of the axle exhibited a fine-grained structure as a result of the hot working at the forging temperature (approximately 1095 °C, or 2000 °F). However, a section adjacent to the flange, which also had been heated to the forging temperature but which had not been hot worked, exhibited a coarse-grained structure. Nearer the cool end of the shaft, a zone that reached a temperature of about 705 °C (1300 °F) exhibited a spheroidized structure. The cold end of the shaft retained its initial fine grain size throughout the forging operation.

In subsequent operations, this shaft was to be mechanically straightened, machined, and induction hardened. Because of the mixed grain structure, these operations posed several problems. The coarse-grained area adjacent to the flange was extremely weak in the transverse direction, and there was a possibility that fracture would occur if this section were subjected to a severe straightening operation. The spheroidized area would not respond adequately to induction hardening because the solution rate of this type of carbide formation was too sluggish for the relatively rapid rate of induction heating. Furthermore, the mixed metallurgical structure would present difficulties in machining. Consequently, normalizing was required in order to produce a uniformly fine-grained structure throughout the axle shaft prior to straightening, machining, and induction hardening.

Low-Carbon Steel Forgings. In contrast to the medium-carbon axle shaft discussed in the preceding paragraphs, forgings made of carbon steels containing 0.25% C or less are seldom normalized. Only severe quenching from above the austenitizing temperature will have any significant effect on their structure or hardness.

Structural Stability. Normalizing and tempering is also a preferred treatment for promoting the structural stability of low-alloy heat-resistant alloys, such as AMS 6304 (0.45% C, 1% Cr, 0.5% Mo, and 0.3% V), at temperatures up to 540 °C (1000 °F). Wheels and spacer rings used in the cold ends of aircraft gas-turbine engine compressors are typical of parts subjected to such treatment to promote structural stability.

Multiple normalizing treatments are employed to obtain complete solution of all lower-temperature constituents in austenite by the use of high initial normalizing temperatures (for example, 925 °C, or 1700 °F), and to refine final pearlite grain size by the use of a second normalizing treatment at a temperature closer to the Ac_3 temperature (for example, 815 °C, or 1500 °F) without destroying the beneficial effects of the initial normalizing treatment.

Double normalizing is usually applied to carbon and low-alloy steels of large dimension where extremely high forging temperatures have been used (Ref 4). Locomotive-axle forgings made of carbon steel to Association of American Railroads (AAR) Specification M-126, Class F (ASTM A 236, Class F), containing 0.45 to 0.59% C and 0.60 to 0.90% Mn, are double normalized to obtain a uniformly fine grain structure along with other exacting mechanical-property requirements. Forgings made of a low-carbon steel (0.18% C) with 1% Mn intended for low-temperature service are double normalized to meet subzero impact requirements.

Reference cited in this section

4. A.K. Sinha, *Ferrous Physical Metallurgy,* Butterworths, 1989

Bar and Tubular Products

Frequently, the finishing stages of hot-mill operations employed in making steel bar and tube produce properties that closely approximate those obtained by normalizing. When this occurs, normalizing is unnecessary and may even be inadvisable. Nevertheless, the reasons for normalizing bar and tube products are generally the same as those applicable to other forms of steel.

The machinability of steel bars and tubular products depends on a combination of hardness properties and microstructure. For a low-carbon alloy steel, a coarse pearlitic structure obtained by normalizing or annealing maximizes machinability. In the case of medium-carbon alloy steel, a lamellar pearlitic structure obtained by annealing is desirable in order to optimize machinability. For a high-carbon alloy steel, a spheroidized structure lowers the hardness and increases the machinability of the alloy. Prior processing, part configuration, and processing following machining should be taken into consideration when determining the need for annealing or normalization.

In general, annealing improves machinability more than normalization does. Normalizing is used to correct the effects of spheroidization, but the steel bar or tube still needs to be annealed. Multiple anneals and tempering are normally used on only small-diameter parts such as wire gage products. Type 4340 is one of the few steels that is typically delivered to the customer with a normalized heat treatment due to machining specifications standard in the aircraft industry.

Tubes are easier to normalize than bars of equivalent diameter because the lighter section thickness of tubes permits more rapid heating and cooling. These advantages help minimize decarburization and promote more nearly uniform microstructures in tube products.

Furnaces Requirements. Continuous furnaces of the roller-hearth type are widely used for normalizing tube and bar products, especially in long lengths. Batch-type furnaces or other types of continuous furnaces are satisfactory if they provide some means for rapid discharge and separation of the load to permit free circulation of air around each tube as it cools. Continuous furnaces should have at least two zones, one for heating and one for soaking. Cooling facilities should be ample so that uniform cooling can proceed until complete transformation has occurred. If tubes are packed or bundled during cooling from a high temperature, the purpose of normalizing is defeated, and a semiannealed or a tempered product results.

Generally, protective atmospheres are not used in roller-hearth continuous furnaces for normalizing bar or tube products. The scale that forms during normalizing is removed by acid pickling or abrasive blast cleaning.

Castings

In industrial practice, steel castings may be normalized in car-bottom, box, pit, or continuous furnaces. The same heat-treating principles apply to each type of furnace.

Furnace Loading. Furnaces are loaded with castings in such a manner that each casting will receive an adequate and uniform heat supply. This may be accomplished by stacking castings in regular order or by interspersing large and small castings so that load concentration in any one area is not excessive. At normalizing temperatures, the tensile strength of steel is greatly reduced, and heavy unequal sections may become distorted unless bracing and support are provided. Accordingly, small and large castings may be arranged so that they support each other.

Loading Temperature. When castings are charged, the temperature of the furnace should be such that the thermal shock will not cause metal failure. For the higher-alloy grades of steel castings, such as C5, C12, and WC9, a safe furnace temperature for charging is 315 to 425 °C (600 to 800 °F). For lower-alloy grades, furnace temperatures may be as high as 650 °C (1200 °F). For cast carbon steels and low-alloy steels with low carbon contents (low hardenability), castings may be charged into a furnace operating at the normalizing temperature.

Heating. After the furnace has been charged, the temperature is increased at a rate of approximately 225 °C/h (400 °F/h) until the normalizing temperature is reached. Depending on steel composition and casting configuration, a reduction in the rate of heating to approximately 28 to 55 °C/h (50 to 100 °F/h) may be necessary to avoid cracking. Extremely large castings should be heated more slowly to prevent development of extreme temperature gradients.

Soaking. After the normalizing temperature has been reached, castings are soaked at this temperature for a period that will ensure complete austenitization and carbide solution. The duration of the soaking period may be predetermined by microscopic examination of specimens held for various times at the normalizing temperature.

Cooling. After the soaking period, the castings are unloaded and allowed to cool in still air. Use of fans, air blasts, or other means of accelerating the cooling process should be avoided.

Sheet and Strip

Hot-rolled steel sheet and strip (about 0.10% C) are normalized primarily to refine grain size, to minimize directional properties, and to develop desirable mechanical properties. Uniformly fine equiaxed ferrite grains are normally obtained in hot-rolled sheet and strip by finishing the final hot-rolling operation above the upper transformation temperature. However, if part of the hot-rolling operation is performed on steel that has transformed partially to ferrite, the deformed ferrite grains usually will recrystallize and form abnormally coarse-grained patches during the self-anneal induced by coiling or piling at temperatures of 650 to 730 °C (1200 to 1350 °F). Also, relatively thin hot-rolled material, if it is inadvertently finished well below the upper transformation temperature and coiled or piled while it is too cold to self-anneal, may possess directional properties. These conditions are unsuitable for some types of severe press-drawing applications and may be corrected by normalizing.

Normalizing also may be used to develop high strength in alloy steel sheet and strip if the products are sufficiently high in carbon and alloy contents to enable them to transform to fine pearlite or martensite when cooled in air from the normalizing temperature. In general, the hardened material is tempered to attain an optimum combination of strength and ductility. Typical mechanical properties of normalized 4130, modified 4335, and modified 4340 steel sheet are given in Table 5.

Table 5 Typical mechanical properties of normalized alloy steel sheet

Grade	Thickness		Tensile strength		Yield strength[a]		Elongation[b], %	Hardness, HRC
	mm	in.	MPa	ksi	MPa	ksi		

4130	4.9	0.193	835	121	585	85	14	25
4335[(c)]	4.6	0.180	1725	250	1240	180	8	48
4340[(c)]	2.0	0.080	1860	270	1345	195	7	50

(a) At 0.2% offset.

(b) In 50 mm or 2 in.

(c) Modified: 0.40% Mo, 0.20% V

Processing. The normalizing operation consists of passing the sheet or strip through an open, continuous furnace where the material is heated to a temperature approximately 55 to 85 °C (100 to 150 °F) above its upper transformation temperature, 845 to 900 °C (1550 to 1650 °F), thus obtaining complete solution of the original structure with the formation of austenite and then air cooling the material to room temperature.

Furnace Equipment. Normalizing furnaces are designed to heat and cool sheets singly or two in a pile. They are built in the form of long, low chambers and usually comprise three sections: a preheating zone (12 to 20% of the total length); a heating, or soaking, zone (about 40% of the total length); and a cooling zone, which occupies the remaining 40 to 50% of the length.

Heating Arrangements. Normalizing furnaces usually are heated with gas or oil and do not employ protective atmospheres. Therefore, sheets are scaled during heat treatment. Burners are arranged along each side of the heating zone; they usually are above the conveyor, but occasionally are both above and below it. The furnace roof, which is higher in the preheating and soaking zones than in the cooling zone, is usually built in sections. In most furnaces, both the preheating zone and the cooling zone are heated by the hot gases from the heating zone. However, both of these zones may be equipped with burners for more accurate temperature control. Air is excluded by regulating the draft to maintain a slight pressure within all zones.

Conveyor-Type Furnaces. In modern furnaces of the conveyor type (the only type suitable for treating short lengths), sheets are carried through each of the three zones on rotating disks made of heat-resistant alloys. These disks have polished surfaces, which prevent them from scratching the sheets, and are staggered to ensure uniform heating. The disks are mounted on water-cooled shafts, which are driven by variable-speed motors through chains and sprockets or shafts and gears. These furnaces may be up to 2.5 m (100 in.) wide and from 27 to 61 m (90 to 200 ft) long. Fuel consumption is 2.3 to 5.2×10^6 kJ/tonne (2.0 to 4.5×10^6 Btu/ton) of steel treated, and production rates vary from 2.7 to 10.9 tonnes (3 to 12 tons) per hour.

Normalizing in a three-zone conveyor-type furnace equipped with pyrometric controls is a relatively simple operation. If scratching of sheets is to be avoided, the sheets are brought to the charging table and hand laid, one or more at a time, on a rider or conveyor sheet. Heavy sheets are normalized singly, but lighter sheets may be stacked two in a pile. To control heating and retard scaling, single sheets may be laid on a rider sheet and covered with a cover sheet. Sheets are carried by disk-rollers into the preheating zone, where they absorb heat rapidly because of the large temperature differential between the sheets and the interior of the furnace and because of the large surface-to-volume ratio. As the sheets become heated and the temperature differential is reduced, the rate of heat absorption slackens. After traveling $4\frac{1}{2}$ to 6 m (15 to 20 ft), the sheets enter the soaking zone at a temperature several degrees below the normalizing temperature. Heating is completed in the soaking zone, which is maintained at a constant temperature, and sheets are held at the required temperature for a time sufficient to convert the microstructure to austenite before they are passed into the cooling zone. The sheets emerge from the cooling zone at a temperature that can be varied between 150 and 540 °C (300 and 1000 °F), and are conveyed for a short distance on the runout table, where, after being cooled rapidly in air, they are carefully

removed from the rider sheet. The trip through such a furnace is carried out at a uniform speed of 0.03 to 0.10 m/s (5 to 20 ft/min) and requires 5 to 20 min to complete.

Catenary Furnaces. The catenary, or freeloop, type of furnace is designed for continuous normalizing of cold-reduced steel unwound from coils; it does not have rolls or any other type of conveyor for supporting the material passing through the heating zone. The heating zones of catenary furnaces range in length from 6 to 15 m (20 to 50 ft). The preheating and cooling zones usually are shorter than those in conveyor-type furnaces, and for some kinds of work may be omitted entirely. At their exit ends, catenary furnaces may incorporate pickling or other descaling equipment for removing surface oxides formed on the steel during normalizing.

Annealing of Steel

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Introduction

ANNEALING is a generic term denoting a treatment that consists of heating to and holding at a suitable temperature followed by cooling at an appropriate rate, primarily for the softening of metallic materials. Generally, in plain carbon steels, annealing produces a ferrite-pearlite microstructure (Fig. 1). Steels may be annealed to facilitate cold working or machining, to improve mechanical or electrical properties, or to promote dimensional stability. The choice of an annealing treatment that will provide an adequate combination of such properties at minimum expense often involves a compromise. Terms used to denote specific types of annealing applied to steels are descriptive of the method used, the equipment used, or the condition of the material after treatment.

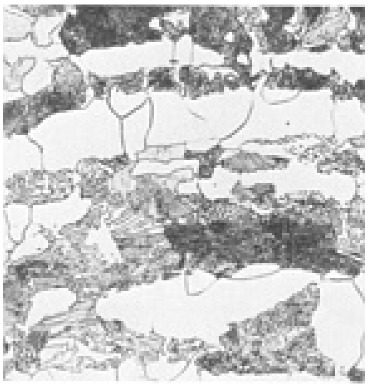

Fig. 1 A fully annealed 1040 steel showing a ferrite-pearlite microstructure. Etched in 4% picral plus 2% nital. 5OO×

Metallurgical Principles

The iron-carbon binary phase diagram (Fig. 2) can be used to better understand annealing processes. Although no annealing process ever achieves true equilibrium conditions, it can closely parallel these conditions. In defining the various types of annealing, the transformation temperatures or critical temperatures are usually used. (See the article "Principles of Heat Treating of Steels" in this Section.)

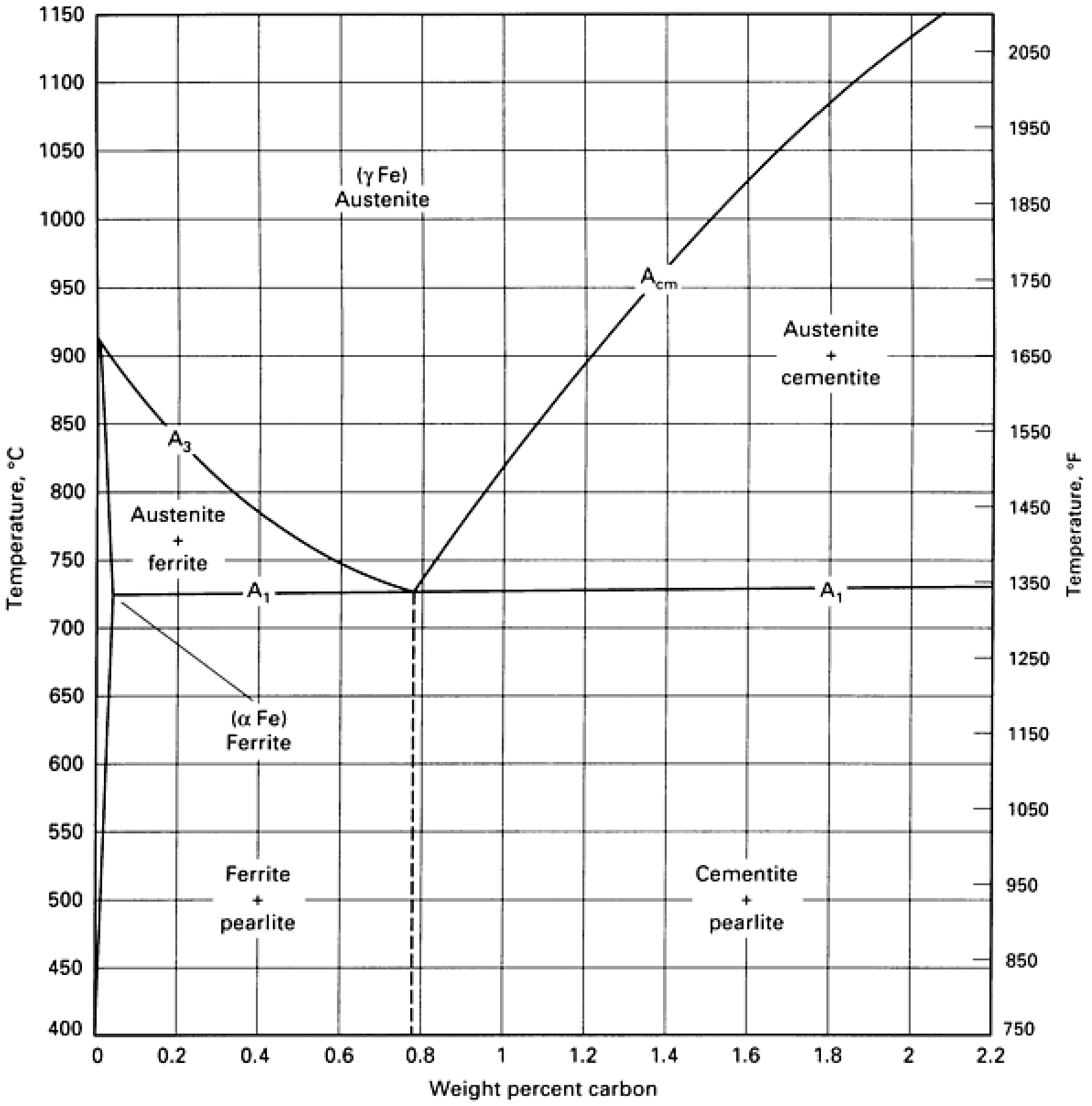

Fig. 2 Iron-carbon binary phase diagram.

Critical Temperatures. The critical temperatures that must be considered in discussing annealing of steel are those that define the onset and completion of the transformation to or from austenite. For a given steel, the critical temperatures depend on whether the steel is being heated or cooled. Critical temperatures for the start and completion of the transformation to austenite during heating are denoted, respectively, by Ac_1 and Ac_3 for hypoeutectoid steels and by Ac_1 and Ac_{cm} for hypereutectoid steels. These temperatures are higher than the corresponding critical temperatures for the start and completion of the transformation from austenite during cooling, which are denoted, respectively, by Ar_3 and Ar_1 for hypoeutectoid steels and by Ar_{cm} and Ar_1 for hypereutectoid steels. (The "c" and "r" in the symbols are derived from the French words *chauffage* for heating and *refroidissement* for cooling.) These critical temperatures converge to the equilibrium values Ae_1, Ae_3, and Ae_{cm} as the rates of heating or cooling become infinitely slow. The positions of the Ae_1, Ae_3, and Ae_{cm} lines are close to the more general (that is, near equilibrium) A_1, A_3, and A_{cm} lines on the iron-carbon binary phase diagram shown in Fig. 2. Various alloying elements markedly affect these critical temperatures. For example, chromium raises the eutectoid temperature, A_1, and manganese lowers it.

It is possible to calculate upper and lower critical temperatures using the actual chemical composition of the steel. The following equations will give an approximate critical temperature for a hypoeutectoid steel (Ref 1):

$$Ac_1(°C) = 723 - 20.7(\% Mn) - 16.9(\%Ni) + 29.1(\%Si) - 16.9(\%Cr)$$
Standard deviation = ± 11.5 °C

$$Ac_3(°C) = 910 - 203\sqrt{\%C} - 15.2(\% Ni) + 44.7(\% Si) + 104(\% V) + 31.5(\% Mo)$$
Standard deviation = ± 16.7 °C

The presence of other alloying elements will also have marked effects on these critical temperatures.

Table 1 provides approximate critical temperatures for selected steels, measured at heating and cooling rates of 28 °C/h (50 °F/h). The equilibrium critical temperatures generally lie about midway between those for heating and cooling at equal rates. Because annealing may involve various ranges of heating and cooling rates in combination with isothermal treatments, the less specific terms A_1, A_3, and A_{cm} are used here in discussing the basic concepts.

Table 1 Approximate critical temperatures for selected carbon and low-alloy steels

Steel	Critical temperatures on heating at 28 °C/h (50 °F/h)				Critical temperatures on cooling at 28 °C/h (50 °F/h)			
	Ac_1		Ac_3		Ar_3		Ar_1	
	°C	°F	°C	°F	°C	°F	°C	°F
1010	725	1335	875	1610	850	1560	680	1260
1020	725	1335	845	1555	815	1500	680	1260
1030	725	1340	815	1495	790	1450	675	1250
1040	725	1340	795	1460	755	1395	670	1240
1050	725	1340	770	1415	740	1365	680	1260
1060	725	1340	745	1375	725	1340	685	1265
1070	725	1340	730	1350	710	1310	690	1275
1080	730	1345	735	1355	700	1290	695	1280
1340	715	1320	775	1430	720	1330	620	1150
3140	735	1355	765	1410	720	1330	660	1220
4027	725	1340	805	1485	760	1400	670	1240

Steel	Critical temperatures on heating at 28 °C/h (50 °F/h)				Critical temperatures on cooling at 28 °C/h (50 °F/h)			
	Ac_1		**Ac_3**		**Ar_3**		**Ar_1**	
	°C	**°F**	**°C**	**°F**	**°C**	**°F**	**°C**	**°F**
4042	725	1340	795	1460	730	1350	655	1210
4130	760	1395	810	1490	755	1390	695	1280
4140	730	1350	805	1480	745	1370	680	1255
4150	745	1370	765	1410	730	1345	670	1240
4340	725	1335	775	1425	710	1310	655	1210
4615	725	1340	810	1490	760	1400	650	1200
5046	715	1320	770	1420	730	1350	680	1260
5120	765	1410	840	1540	800	1470	700	1290
5140	740	1360	790	1450	725	1340	695	1280
5160	710	1310	765	1410	715	1320	675	1250
52100	725	1340	770	1415	715	1320	690	1270
6150	750	1380	790	1450	745	1370	695	1280
8115	720	1300	840	1540	790	1450	670	1240
8620	730	1350	830	1525	770	1415	660	1220
8640	730	1350	780	1435	725	1340	665	1230
9260	745	1370	815	1500	750	1380	715	1315

Reference cited in this section

1. K.W. Andrews, Empirical Formulae for the Calculation of Some Transformation Temperatures, *J. Iron Steel Inst.*, Vol 203, 1965, p 721

Annealing Cycles

In practice, specific thermal cycles of an almost infinite variety are used to achieve the various goals of annealing. These cycles fall into several broad categories that can be classified according to the temperature to which the steel is heated and the method of cooling used. The maximum temperature may be below the lower critical temperature, A_1 (subcritical annealing); above A_1 but below the upper critical temperature, A_3 in hypoeutectoid steels, or A_{cm} in hypereutectoid steels (intercritical annealing); or above A_3 (full annealing).

Because some austenite is present at temperatures above A_1, cooling practice through transformation is a crucial factor in achieving desired microstructure and properties. Accordingly, steels heated above A_1 are subjected either to slow continuous cooling or to isothermal treatment at some temperature below A_1 at which transformation to the desired microstructure can occur in a reasonable amount of time. Under certain conditions, two or more such cycles may be combined or used in succession to achieve the desired results. The success of any annealing operation depends on the proper choice and control of the thermal cycle, based on the metallurgical principles discussed in the following sections.

Subcritical Annealing

Subcritical annealing does not involve formation of austenite. The prior condition of the steel is modified by such thermally activated processes as recovery, recrystallization, grain growth, and agglomeration of carbides. The prior history of the steel is, therefore, an important factor.

In as-rolled or forged hypoeutectoid steels containing ferrite and pearlie, subcritical annealing can adjust the hardnesses of both constituents, but excessively long times at temperature may be required for substantial softening. The subcritical treatment is most effective when applied to hardened or cold-worked steels, which recrystallize readily to form new ferrite grains. The rate of softening increases rapidly as the annealing temperature approaches A_1. Cooling practice from the subcritical annealing temperature has very little effect on the established microstructure and resultant properties. A more detailed discussion of the metallurgical processes involved in subcritical annealing is provided in Ref 2.

lntercritical Annealing

Austenite begins to form when the temperature of the steel exceeds A_1. The solubility of carbon increases abruptly (nearly 1%) near the A_1 temperature. In hypoeutectoid steels, the equilibrium structure in the intercritical range between A_1 and A_3 consists of ferrite and austenite, and above A_3 the structure becomes completely austenitic. However, the equilibrium mixture of ferrite and austenite is not achieved instantaneously. For example, the rate of solution for a typical eutectoid steel is shown in Fig. 3. Undissolved carbides may persist, especially if the austenitizing time is short or the temperature is near A_1, causing the austenite to be inhomogeneous. In hypereutectoid steels, carbide and austenite coexist in the intercritical range between A_1 and A_{cm}; and the homogeneity of the austenite depends on time and temperature. The degree of homogeneity in the structure at the austenitizing temperature is an important consideration in the development of annealed structures and properties. The more homogeneous structures developed at higher austenitizing temperatures tend to promote lamellar carbide structures on cooling, whereas lower austenitizing temperatures in the intercritical range result in less homogeneous austenite, which promotes formation of spheroidal carbides.

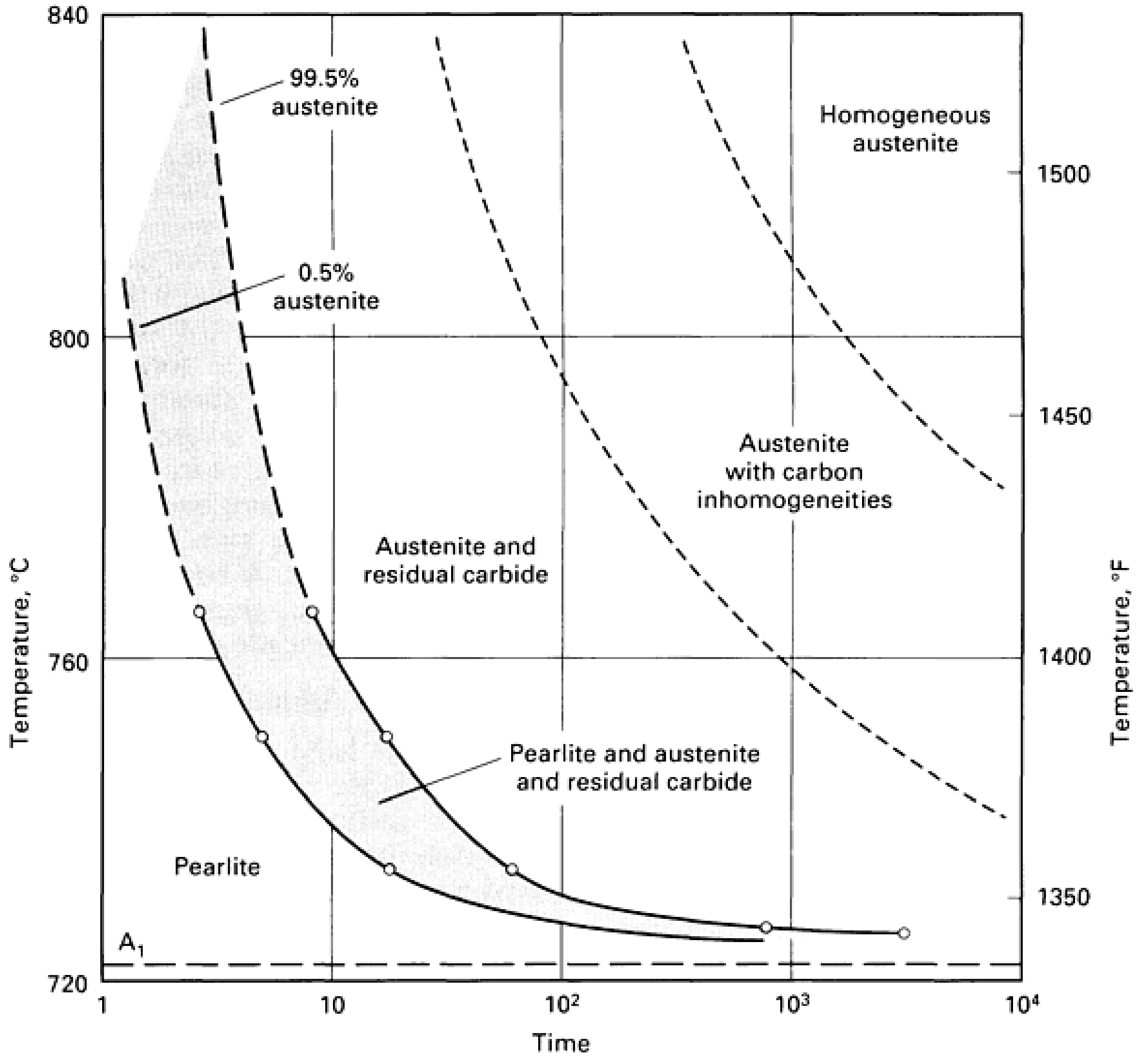

Fig. 3 Austenitizing rate-temperature curves for commercial plain carbon eutectoid steel. Prior treatment was normalizing from 875 °C (1610 °F); initial structure, fine pearlite. First curve at left shows beginning of disappearance of pearlite; second curve, final disappearance of pearlite; third curve, final disappearance of carbide; fourth curve, final disappearance of carbon concentration gradients.

Austenite formed when steel is heated above the A_1 temperature transforms back to ferrite and carbide when the steel is slowly cooled below A_1. The rate of austenite decomposition and the tendency of the carbide structure to be either lamellar or spheroidal depend largely on the temperature of transformation. If the austenite transforms just below A_1, it will decompose slowly. The product then may contain relatively coarse spheroidal carbides or coarse lamellar pearlite, depending on the composition of the steel and the austenitizing temperature. This product tends to be very soft. However, the low rate of transformation at temperatures just below A_1 necessitates long holding times in isothermal treatments, or very slow cooling rates in continuous cooling, if maximum softness is desired. Isothermal treatments are more efficient than slow continuous cooling in terms of achieving desired structures and softness in the minimum amount of time. Sometimes, however, the available equipment or the mass of the steel part being annealed may make slow continuous cooling the only feasible alternative.

As the transformation temperature decreases, austenite generally decomposes more rapidly, and the transformation product is harder, more lamellar, and less coarse than the product formed just below A_1. At still lower transformation temperatures, the product becomes a much harder mixture of ferrite and carbide, and the time necessary for complete isothermal transformation may again increase.

Temperature-time plots showing the progress of austenite transformation under isothermal (IT) or continuous transformation (CT) conditions for many steels have been widely published (Ref 3, 4) and illustrate the principles just

discussed. These IT or CT diagrams may be helpful in design of annealing treatments for specific grades of steel, but their usefulness is limited because most published diagrams represent transformation from a fully austenitized, relatively homogeneous condition, which is not always desirable or obtainable in annealing.

In the continuous annealing process, which is discussed in detail in the following article in this Section, an intercritical annealing practice is used to develop dual-phase and tri-phase microstructures. In this practice, the steel is rapidly cooled from the intercritical temperature. The rapid cooling results in the transformation of the pools of austenite to martensite. The final microstructure consists of islands of martensite in a ferritic matrix. Depending upon the alloy content of the austenite pools and the cooling conditions, the austenite may not fully transform and the microstructure will consist of martensite/retained austenite regions in a ferritic matrix.

Cooling after Full Transformation. After the austenite has been completely transformed, little else of metallurgical consequence can occur during cooling to room temperature. Extremely slow cooling may cause some agglomeration of carbides, and consequently, some slight further softening of the steel, but in this regard such slow cooling is less effective than high-temperature transformation. Therefore, there is no metallurgical reason for slow cooling after transformation has been completed, and the steel may be cooled from the transformation temperature as rapidly as feasible in order to minimize the total time required for the operation.

If transformation by slow continuous cooling has been used, the temperature at which controlled cooling may be stopped depends on the transformation characteristics of the steel. However, the mass of the steel or the need to avoid oxidation are practical considerations that may require retarded cooling to be continued below the temperature at which the austenite transformation ceases.

Effect of Prior Structure. The finer and more evenly distributed the carbides in the prior structure, the faster the rate at which austenite formed above A_1 will approach complete homogeneity. The prior structure, therefore, can affect the response to annealing. When spheroidal carbides are desired in the annealed structure, preheating at temperatures just below A_1 sometimes is used to agglomerate the prior carbides in order to increase their resistance to solution in the austenite on subsequent heating. The presence of undissolved carbides or concentration gradients in the austenite promotes formation of a spheroidal, rather than lamellar, structure when the austenite is transformed. Preheating to enhance spheroidization is applicable mainly to hypoeutectoid steels but also is useful for some hypereutectoid low-alloy steels.

Supercritical or Full Annealing

A common annealing practice is to heat hypoeutectoid steels above the upper critical temperature (A_3) to attain full austenitization. The process is called full annealing. In hypoeutectoid steels (under 0.77% C), supercritical annealing (that is, above the A_3 temperature) takes place in the austenite region (the steel is fully austenitic at the annealing temperature). However, in hypereutectoid steels (above 0.77% C), the annealing takes place above the A_1 temperature, which is the dual-phase austenite-cementite region. Figure 4 shows the annealing temperature range for full annealing superimposed in the iron-carbon binary phase diagram from Fig. 2. In general, an annealing temperature 50 °C (90 °F) above the A_3 for hypoeutectic steels and A_1 for hypereutectoid steels is adequate.

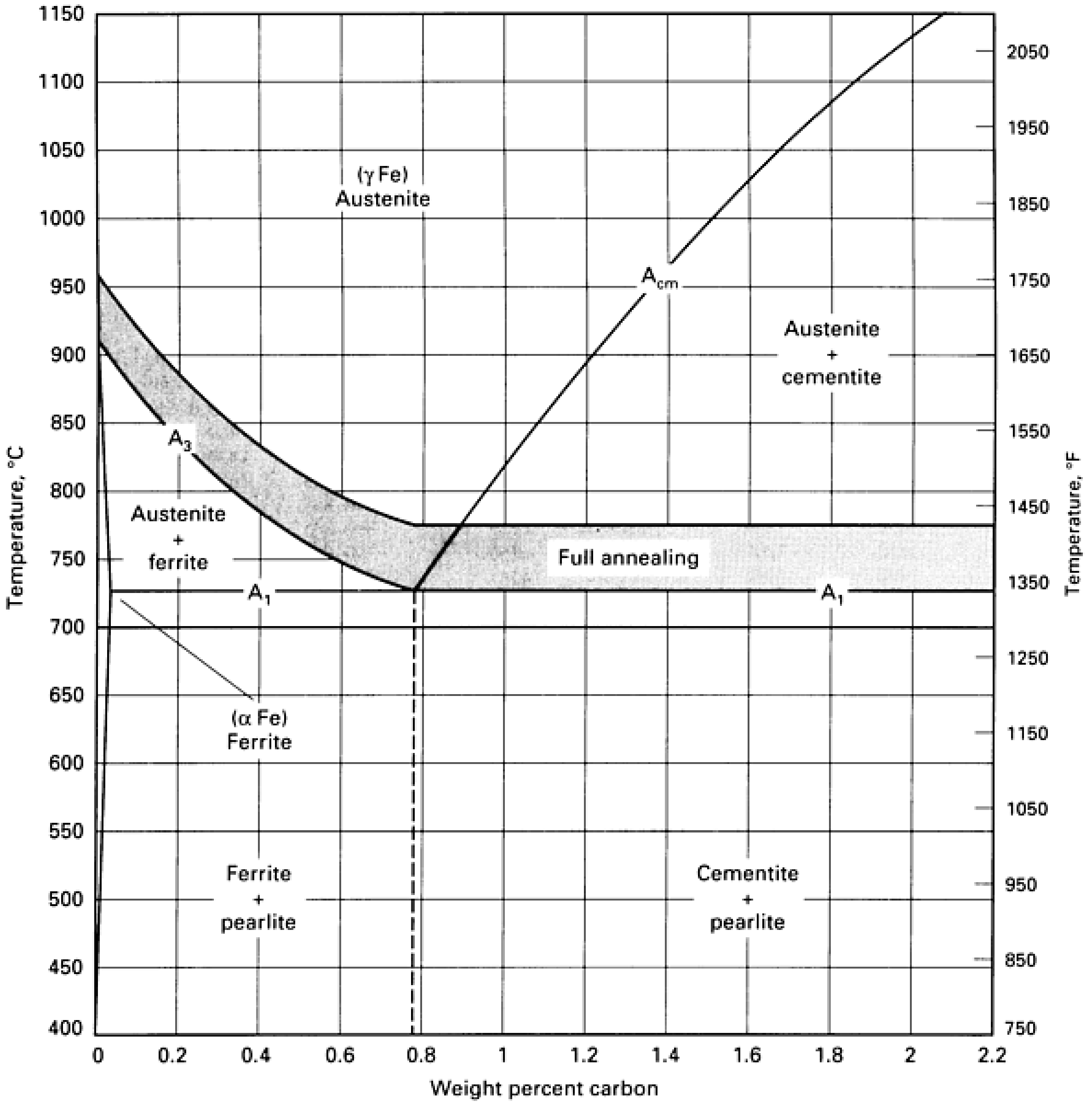

Fig. 4 The iron-carbon binary phase diagram showing region of temperatures for full annealing (Ref 5)

Austenitizing Time and Dead-Soft Steel. Hypereutectoid steels can be made extremely soft by holding for long periods of time at the austenitizing temperature. Although the time at the austenitizing temperature may have only a small effect on actual hardnesses (such as a change from 241 to 229 HB), its effect on machinability or cold-forming properties may be appreciable.

Long-term austenitizing is effective in hypereutectoid steels because it produces agglomeration of residual carbides in the austenite. Coarser carbides promote a softer final product. In lower-carbon steels, carbides are unstable at temperatures above A_1 and tend to dissolve in the austenite, although the dissolution may be slow.

Steels that have approximately eutectoid carbon contents generally form a lamellar transformation product if austenitized for very long periods of time. Long-term holding at a temperature just above the A_1 temperature may be as effective in dissolving carbides and dissipating carbon-concentration gradients as is short-term holding at a higher temperature.

References cited in this section

2. B.R. Banerjee, Annealing Heat Treatments, *Met. Prog.,* Nov 1980, p 59
3. *Atlas of Isothermal Transformation and Cooling Transformation Diagrams,* American Society for Metals, 1977
4. M. Atkins, *Atlas of Continuous Cooling Transformation Diagrams for Engineering Steels,* American Society for Metals, in cooperation with British Steel Corporation, 1980
5. G. Krauss, *Steels: Heat Treatment and Processing Principles,* ASM International, 1989

Guidelines for Annealing

The metallurgical principles discussed above have been incorporated by Payson (Ref 6) into the following seven rules, which may be used as guidelines for development of successful and efficient annealing schedules:

- *Rule 1:* The more homogeneous the structure of the as-austenitized steel, the more completely lamellar will be the structure of the annealed steel. Conversely, the more heterogeneous the structure of the as-austenitized steel, the more nearly spheroidal will be the annealed carbide structure
- *Rule 2:* The softest condition in the steel is usually developed by austenitizing at a temperature less than 55 °C (100 °F) above A_1 and transforming at a temperature (usually) less than 55 °C (100 °F) below A_1
- *Rule 3:* Because very long times may be required for complete transformation at temperatures less than 55 °C (100 °F) below A_1, allow most of the transformation to take place at the higher temperature, where a soft product is formed, and finish the transformation at a lower temperature, where the time required for completion of transformation is short
- *Rule 4:* After the steel has been austenitized, cool to the transformation temperature as rapidly as feasible in order to minimize the total duration of the annealing operation
- *Rule 5:* After the steel has been completely transformed, at a temperature that produces the desired microstructure and hardness, cool to room temperature as rapidly as feasible to decrease further the total time of annealing
- *Rule 6:* To ensure a minimum of lamellar pearlite in the structures of annealed 0.70 to 0.90% C tool steels and other low-alloy medium-carbon steels, preheat for several hours at a temperature about 28 °C (50 °F) below the lower critical temperature (A_1) before austenitizing and transforming as usual
- *Rule 7:* To obtain minimum hardness in annealed hypereutectoid alloy tool steels, heat at the austenitizing temperature for a long time (about 10 to 15 h), then transform as usual

These rules are applied most effectively when the critical temperatures and transformation characteristics of the steel have been established and when transformation by isothermal treatment is feasible.

Reference cited in this section

6. P. Payson, The Annealing of Steel, series, *Iron Age,* June and July 1943; Technical booklet, Crucible Steel Company of America

Annealing Temperatures

From a practical sense, most annealing practices have been established from experience. For many annealing applications, it is sufficient simply to specify that the steel be cooled in the furnace from a designated annealing (austenitizing) temperature. Temperatures and associated Brinell hardnesses for simple annealing of carbon steels are given in Table 2, and similar data for alloy steels are presented in Table 3.

Table 2 Recommended temperatures and cooling cycles for full annealing of small carbon steel forgings

Data are for forgings up to 75 mm (3 in.) in section thickness. Time at temperature usually is a minimum of 1 h for sections up to 25 mm (1 in.) thick; $\frac{1}{2}$ h is added for each additional 25 mm (1 in.) of thickness.

Steel	Annealing temperature		Cooling cycle[a]				Hardness range, HB
			°C		°F		
	°C	°F	From	To	From	To	
1018	855-900	1575-1650	855	705	1575	1300	111-149
1020	855-900	1575-1650	855	700	1575	1290	111-149
1022	855-900	1575-1650	855	700	1575	1290	111-149
1025	855-900	1575-1650	855	700	1575	1290	111-187
1030	845-885	1550-1625	845	650	1550	1200	126-197
1035	845-885	1550-1625	845	650	1550	1200	137-207
1040	790-870	1450-1600	790	650	1450	1200	137-207
1045	790-870	1450-1600	790	650	1450	1200	156-217
1050	790-870	1450-1600	790	650	1450	1200	156-217
1060	790-845	1450-1550	790	650	1450	1200	156-217
1070	790-845	1450-1550	790	650	1450	1200	167-229
1080	790-845	1450-1550	790	650	1450	1200	167-229
1090	790-830	1450-1525	790	650	1450	1200	167-229
1095	790-830	1450-1525	790	655	1450	1215	167-229

(a) Furnace cooling at 28 °C/h (50 °F/h)

Table 3 Recommended annealing temperatures for alloy steels (furnace cooling)

AISI/SAE steel	Annealing temperature		Hardness (max), HB
	°C	°F	
1330	845-900	1550-1650	179
1335	845-900	1550-1650	187
1340	845-900	1550-1650	192
1345	845-900	1550-1650	. . .
3140	815-870	1500-1600	187
4037	815-855	1500-1575	183
4042	815-855	1500-1575	192
4047	790-845	1450-1550	201
4063	790-845	1450-1550	223
4130	790-845	1450-1550	174
4135	790-845	1450-1550	. . .
4137	790-845	1450-1550	192
4140	790-845	1450-1550	197
4145	790-845	1450-1550	207
4147	790-845	1450-1550	. . .
4150	790-845	1450-1550	212
4161	790-84	1450-155	. . .

AISI/SAE steel	**Annealing temperature**		**Hardness (max), HB**
	°C	**°F**	
4337	790-84	1450-155	. . .
4340	790-84	1450-155	223
50B40	815-870	1500-1600	187
50B44	815-870	1500-1600	197
5046	815-870	1500-1600	192
50B46	815-870	1500-1600	192
50B50	815-870	1500-1600	201
50B60	815-870	1500-1600	217
5130	790-845	1450-1550	170
5132	790-845	1450-1550	170
5135	815-870	1500-1600	174
5140	815-870	1500-1600	187
5145	815-870	1500-1600	197
5147	815-870	1500-1600	197
5150	815-870	1500-1600	201
5155	815-870	1500-1600	217
5160	815-870	1500-1600	223
51B60	815-870	1500-1600	223
50100	730-790	1350-1450	197

AISI/SAE steel	**Annealing temperature**		**Hardness (max), HB**
	°C	**°F**	
51100	730-790	1350-1450	197
52100	730-790	1350-1450	207
6150	845-900	1550-1650	201
81B45	845-900	1550-1650	192
8627	815-870	1500-1600	174
8630	790-845	1450-1550	179
8637	815-870	1500-1600	192
8640	815-870	1500-1600	197
8642	815-870	1500-1600	201
8645	815-870	1500-1600	207
86B45	815-870	1500-1600	207
8650	815-870	1500-1600	212
8655	815-870	1500-1600	223
8660	815-870	1500-1600	229
8740	815-870	1500-1600	202
8742	815-870	1500-1600	. . .
9260	815-870	1500-1600	229
94B30	790-845	1450-1550	174
94B40	790-845	1450-1550	192

AISI/SAE steel	Annealing temperature		Hardness (max), HB
	°C	°F	
9840	790-845	1450-1550	207

Heating cycles that employ austenitizing temperatures in the upper ends of the ranges given in Table 3 should result in pearlitic structures. Predominantly spheroidized structures should be obtained when lower temperatures are used.

When an alloy steel is annealed to obtain a specific microstructure, greater precision is required in specifying temperatures and cooling conditions for annealing. Table 4 presents, for a variety of standard alloy steels, typical schedules for such annealing operations.

Table 4 Recommended temperatures and time cycles for annealing of alloy steels

Steel	Austenitizing temperature		Conventional cooling[a]							Isothermal method[b]			Hardness (approx), HB
			Temperature				Cooling rate		Time, h				
			°C		°F					Cool to		Hold, h	
	°C	°F	From	To	From	To	°C/h	°F/h		°C	°F		
To obtain a predominantly pearlitic structure[c]													
1340	830	1525	735	610	1350	1130	10	20	11	620	1150	4.5	183
2340	800	1475	655	555	1210	1030	8.5	15	12	595	1100	6	201
2345	800	1475	655	550	1210	1020	8.5	15	12.7	595	1100	6	201
3120[d]	885	1625	. . .	. . .	. . .	. . .	. . .	. . .	. . .	650	1200	4	179
3140	830	1525	735	650	1350	1200	10	20	7.5	660	1225	6	187
3150	830	1525	705	645	1300	1190	10	20	5.5	660	1225	6	201
3310[e]	870	1600	. . .	. . .	. . .	. . .	. . .	. . .	. . .	595	1100	14	187
4042	830	1525	745	640	1370	1180	10	20	9.5	660	1225	4.5	197
4047	830	1525	735	630	1350	1170	10	20	9	660	1225	5	207

Steel	Austenitizing temperature		Conventional cooling[a]							Isothermal method[b]			Hardness (approx), HB
			Temperature				Cooling rate		Time, h				
			°C		°F					Cool to		Hold, h	
	°C	°F	From	To	From	To	°C/h	°F/h		°C	°F		
4062	830	1525	695	630	1280	1170	8.5	15	7.3	660	1225	6	223
4130	855	1575	765	665	1410	1230	20	35	5	675	1250	4	174
4140	845	1550	755	665	1390	1230	15	25	6.4	675	1250	5	197
4150	830	1525	745	670	1370	1240	8.5	15	8.6	675	1250	6	212
4320[d]	885	1625	. . .	. . .	. . .	. . .	. . .	. . .	. . .	660	1225	6	197
4340	830	1525	705	565	1300	1050	8.5	15	16.5	650	1200	8	223
4620[d]	885	1625	. . .	. . .	. . .	. . .	. . .	. . .	. . .	650	1200	6	187
4640	830	1525	715	600	1320	1110	7.6	14	15	620	1150	8	197
4820[d]	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	605	1125	4	192
5045	830	1525	755	665	1390	1230	10	20	8	660	1225	4.5	192
5120[d]	885	1625	. . .	. . .	. . .	. . .	. . .	. . .	. . .	690	1275	4	179
5132	845	1550	755	670	1390	1240	10	20	7.5	675	1250	6	183
5140	830	1525	740	670	1360	1240	10	20	6	675	1250	6	187
5150	830	1525	705	650	1300	1200	10	20	5	675	1250	6	201
52100[f]	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
6150	830	1525	760	675	1400	1250	8.5	15	10	675	1250	6	201
8620[d]	885	1625	. . .	. . .	. . .	. . .	. . .	. . .	. . .	660	1225	4	187

Steel	Austenitizing temperature		Conventional cooling[a]							Isothermal method[b]			Hardness (approx), HB
			Temperature				Cooling rate		Time, h				
			°C		°F					Cool to		Hold, h	
	°C	°F	From	To	From	To	°C/h	°F/h		°C	°F		
8630	845	1550	735	640	1350	1180	10	20	8.5	660	1225	6	192
8640	830	1525	725	640	1340	1180	10	20	8	660	1225	6	197
8650	830	1525	710	650	1310	1200	8.5	15	7.2	650	1200	8	212
8660	830	1525	700	655	1290	1210	8.5	15	8	650	1200	8	229
8720[d]	885	1625	. . .	. . .	. . .	. . .	. . .	. . .	. . .	660	1225	4	187
8740	830	1525	725	645	1340	1190	10	20	7.5	660	1225	7	201
8750	830	1525	720	630	1330	1170	8.5	15	10.7	660	1225	7	217
9260	860	1575	760	705	1400	1300	8.5	15	6.7	660	1225	6	229
9310[e]	870	1600	. . .	. . .	. . .	. . .	. . .	. . .	. . .	595	1100	14	187
9840	830	1525	695	640	1280	1180	8.5	15	6.6	650	1200	6	207
9850	830	1525	700	645	1290	1190	8.5	15	6.7	650	1200	8	223
To obtain a predominantly ferritic and spheroidized carbide structure													
1320[d]	805	1480	. . .	. . .	. . .	. . .	. . .	. . .	. . .	650	1200	8	170
1340	750	1380	735	610	1350	1130	5	10	22	640	1180	8	174
2340	715	1320	655	555	1210	1030	5	10	18	605	1125	10	192
2345	715	1320	655	550	1210	1020	5	10	19	605	1125	10	192
3120[d]	790	1450	. . .	. . .	. . .	. . .	. . .	. . .	. . .	650	1200	8	163

Steel	Austenitizing temperature		Conventional cooling(a)							Isothermal method(b)			Hardness (approx), HB
			Temperature				Cooling rate		Time, h				
			°C		°F					Cool to		Hold, h	
	°C	°F	From	To	From	To	°C/h	°F/h		°C	°F		
3140	745	1370	735	650	1350	1200	5	10	15	660	1225	10	174
3150	750	1380	705	645	1300	1190	5	10	11	660	1225	10	187
9840	745	1370	695	640	1280	1180	5	10	11	650	1200	10	192
9850	745	1370	700	645	1290	1190	5	10	11	650	1200	12	207

(a) The steel is cooled in the furnace at the indicated rate through the temperature range shown.

(b) The steel is cooled rapidly to the temperature indicated and is held at that temperature for the time specified.

(c) In isothermal annealing to obtain pearlitic structure, steels may be austenitized at temperatures up to 70 °C (125 °F) higher than temperatures listed.

(d) Seldom annealed. Structures of better machinability are developed by normalizing or by transforming isothermally after rolling or forging.

(e) Annealing is impractical by the conventional process of continuous slow cooling. The lower transformation temperature is markedly depressed, and excessively long cooling cycles are required to obtain transformation to pearlite.

(f) Predominantly pearlitic structures are seldom desired in this steel.

In isothermal annealing to produce a pearlitic structure, particularly in forgings, an austenitizing temperature as much as 70 °C (125 °F) higher than that indicated in Table 4 may be selected in order to decrease the austenitizing time.

For most steels, as indicated in Table 4, annealing may be accomplished by heating to the austenitizing temperature and then either cooling in the furnace at a controlled rate or cooling rapidly to, and holding at, a lower temperature for isothermal transformation. Both procedures result in virtually the same hardness; however, considerably less time is required for isothermal transformation.

Uniformity of Temperature. One potential contribution to the failure of an annealing operation is a lack of knowledge of the temperature distribution within the load of steel in the furnace. Furnaces large enough to anneal 18 Mg (20 tons) of steel at a time are not uncommon. In some large forging shops, workpieces can weigh in excess of 270 Mg (300 tons). The larger the furnace, the more difficult it is to establish and maintain uniform temperature conditions throughout the load, and the more difficult it is to change the temperature of the steel during either heating or cooling.

Furnace thermocouples indicate the temperature of the space above, below, or beside the load, but this temperature may differ by 28 °C (50 °F) or more from the temperature of the steel itself, especially when the steel is in a pipe or box, or when bar or strip is packed in a dense charge in a quiescent atmosphere. When these conditions exist, the distribution of temperature throughout the load during heating and cooling should be established by placing thermocouples among the bars, forgings, coils, and so on. A good practice is to spot weld a thermocouple to the workpiece or to use embedded thermocouples (thermocouples placed in holes drilled into the workpiece). Regulation of the furnace during the annealing operation should be based on the temperatures indicated by these thermocouples, which are in actual contact with the steel, rather than on the temperatures indicated by the furnace thermocouples.

Spheroidizing

The majority of all spheroidizing activity is performed for improving the cold formability of steels. It is also performed to improve the machinability of hypereutectoid steels, as well as tool steels. A spheroidized microstructure is desirable for cold forming because it lowers the flow stress of the material. The flow stress is determined by the proportion and distribution of ferrite and carbides. The strength of the ferrite depends on its grain size and the rate of cooling. Whether the carbides are present as lamellae in pearlite or spheroids radically affects the formability of steel.

Steels may be spheroidized, that is, heated and cooled to produce a structure of globular carbides in a ferritic matrix. Figure 5 shows 1040 steel in the fully spheroidized condition. Spheroidization can take place by the following methods:

- Prolonged holding at a temperature just below Ae_1
- Heating and cooling alternately between temperatures that are just above Ac_1 and just below Ar_1
- Heating to a temperature just above Ac_1, and then either cooling very slowly in the furnace or holding at a temperature just below Ar_1
- Cooling at a suitable rate from the minimum temperature at which all carbide is dissolved to prevent reformation of a carbide network, and then reheating in accordance with the first or second methods above (applicable to hypereutectoid steel containing a carbide network)

It should be noted that it is difficult to establish consistent designations for critical temperatures. In discussions about heating with prolonged holding, the critical temperatures of interest should be the equilibrium temperatures Ae_1 and Ae_3. Terminology becomes more arbitrary in discussions of heating and cooling at unspecified rates and for unspecified holding times.

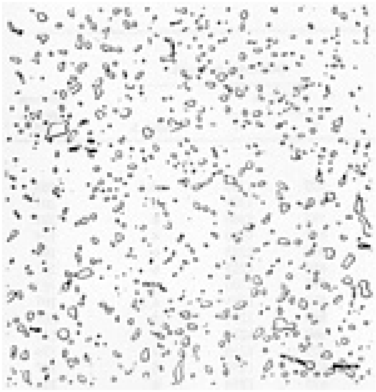

Fig. 5 Spheroidized microstructure of 1040 steel after 21 h at 700 °C (1290 °F). 4% picral etch. 1000×

Figure 6 shows the range of temperatures used for spheroidization of hypoeutectoid and hypereutectoid steels. The rates of spheroidizing provided by these methods depend somewhat on prior microstructure, being greatest for quenched structures in which the carbide phase is fine and dispersed. Prior cold work also increases the rate of the spheroidizing reaction in a subcritical spheroidizing treatment.

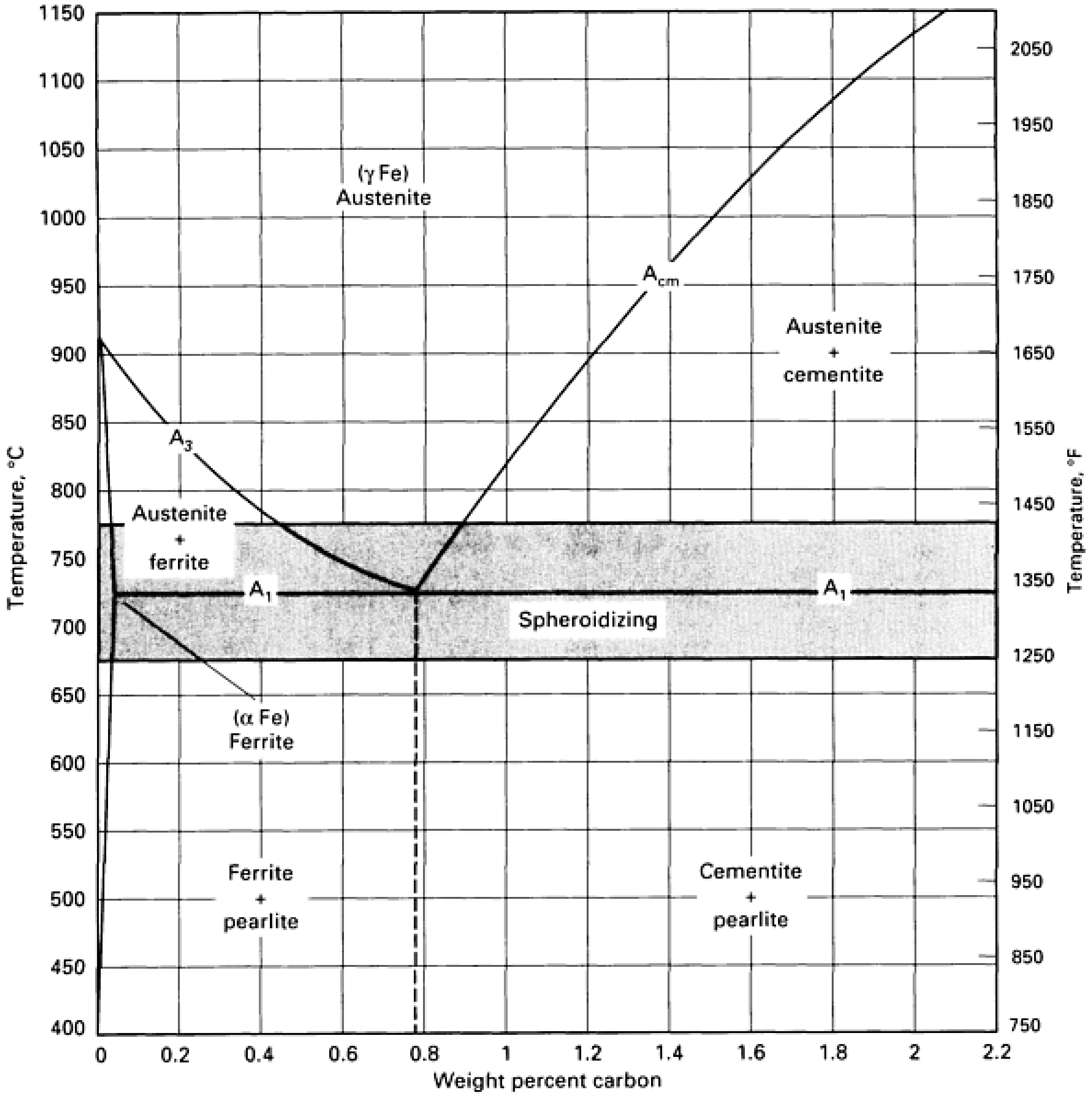

Fig. 6 The iron-carbon binary phase diagram showing region of temperatures for spheroidizing (Ref 5)

An example of the effect of prior microstructure on spheroidization is given in Fig. 7 for the same 1040 steel shown in Fig. 1 (further examples are found in Ref 7). The photomicrograph in Fig. 7(a) shows the extent of spheroidization of the 1040 steel with a prior martensitic microstructure after holding 21 h at 700 °C (1290 °F). Figure 7(b) shows the extent of spheroidization after the same time/temperature heating cycle with a prior ferrite-pearlite microstructure. Spheroidization has occurred in the 1040 steel with the prior martensitic microstructure. On the other hand, it has only just begun in the same steel with the prior fenite-pearlite microstructure. Figure 8 shows that after 200 h at 700 °C (1290 °F) the spheroidization process is almost completed in the prior ferrite-pearlite steel; however, traces of the pearlitic areas can still be seen.

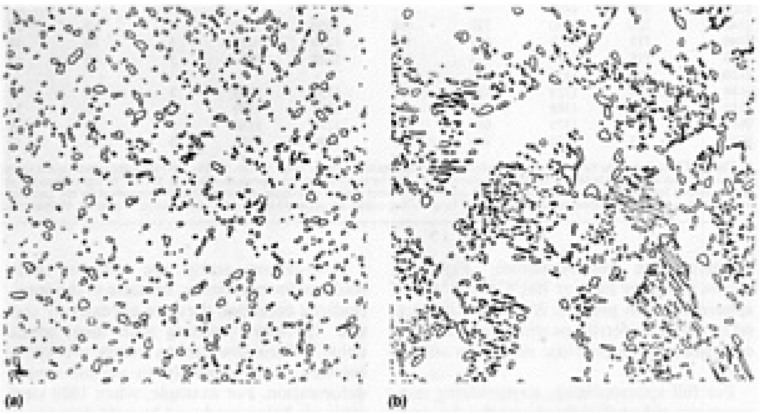

Fig. 7 Effect of prior microstructure on spheroidizing a 1040 steel at 700 °C (1290 °F) for 21 h. (a) Starting from a martensitic microstructure (as-quenched). (b) Starting from a ferrite-pearlite microstructure (fully annealed). Etched in 4% picral plus 2% nital. 1000×

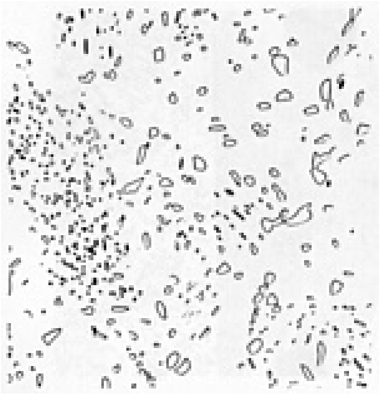

Fig. 8 The extent of spheroidization at 700 °C (1290 °F) for 200 h for the 1040 steel starting from a ferrite-pearlite microstructure etched in 4% picral. 1000×

For full spheroidizing, austenitizing temperatures either slightly above the Ac_1 temperature or about midway between Ac_1 and Ac_3 are used. If a temperature slightly above Ac_1 is to be used, good loading characteristics and accurate temperature controls are required for proper results; otherwise, it is conceivable that Ac_1 may not be reached and that austenitization may not occur.

Low-carbon steels are seldom spheroidized for machining, because in the spheroidized condition they are excessively soft and "gummy," cutting with long, tough chips. When low-carbon steels are spheroidized, it is generally to permit severe deformation. For example, when 1020 steel tubing is being produced by cold drawing in two or three passes, a spheroidized structure will be obtained if the material is annealed for $\frac{1}{2}$ to 1 h at 690 °C (1275 °F) after each pass. The final product will have a hardness of about 163 HB Tubing in this condition will be able to withstand severe deformation during subsequent cold forming.

As with many other types of heat treatment, hardness after spheroidizing depends on carbon and alloy content. Increasing the carbon or alloy content, or both, results in an increase in the as-spheroidized hardness, which generally ranges from 163 to 212 HB (Table 4).

References cited in this section

5. G. Krauss, *Steels: Heat Treatment and Processing Principles,* ASM International, 1989

7. L.E. Samuels, *Optical Microscopy of Carbon Steels,* American Society for Metals, 1980

Process Annealing

As the hardness of steel increases during cold working, ductility decreases and additional cold reduction becomes so difficult that the material must be annealed to restore its ductility. Such annealing between processing steps is referred to as in-process or simply process annealing. It may consist of any appropriate treatment. In most instances, however, a subcritical treatment is adequate and least costly, and the term "process annealing" without further qualification usually refers to an in-process subcritical anneal. Figure 9 shows the range of temperatures typically used for process annealing. It is often necessary to specify process annealing for parts that are cold formed by stamping, heading, or extrusion. Hot-worked high-carbon and alloy steels also are process annealed to prevent them from cracking and to soften them for shearing, turning, or straightening.

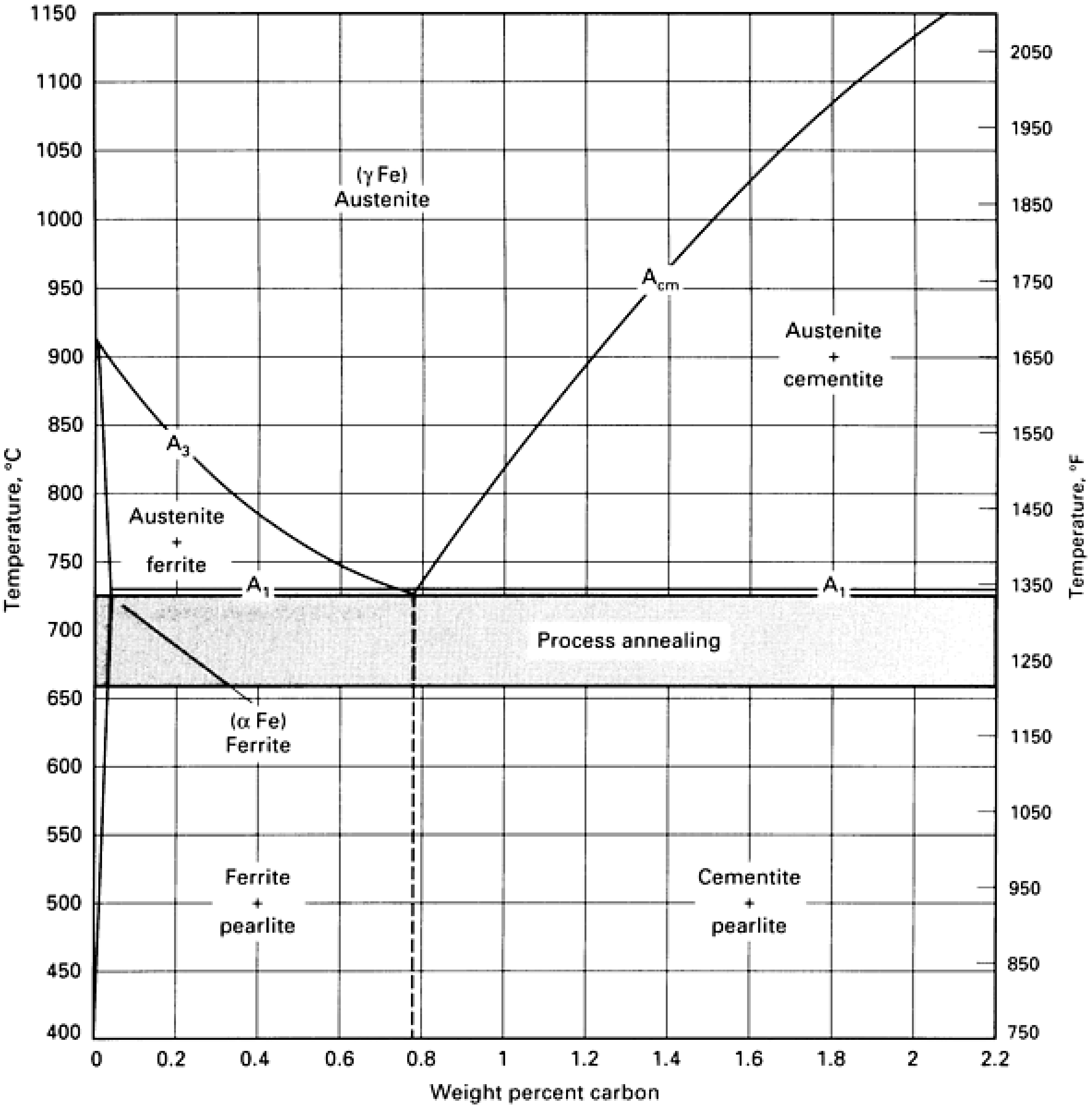

Fig. 9 The iron-carbon binary phase diagram showing region of temperature for process annealing (Ref 5)

Process annealing usually consists of heating to a temperature below Ae_1, soaking for an appropriate time and then cooling, usually in air. In most instances, heating to a temperature between 10 and 20 °C (20 and 40 °F) below Ae_1 produces the best combination of microstructure hardness, and mechanical properties. Temperature controls are necessary only to prevent heating the material above Ae_1 and thus defeating the purpose of annealing.

When process annealing is performed merely to soften a material for such operations as cold sawing and cold shearing, temperatures well below Ae_1 normally are used and close controls are unnecessary.

In the wire industry, process annealing is used as an intermediate treatment between the drawing of wire to a size slightly larger than the desired finished size and the drawing of a light reduction to the finished size. Wire thus made is known as annealed in process wire. Process annealing is used also in the production of wire sufficiently soft for severe upsetting and to permit drawing the smaller sizes of low-carbon and medium-carbon steel wire that cannot be drawn to the desired small size directly from the hot-rolled rod. Process annealing is more satisfactory than spheroidize annealing for a material that, because of its composition or size (or both), cannot be drawn to finished size because it either lacks ductility or does not meet physical requirements. Also, material that is cold sheared during processing is process annealed to raise the ductility of the sheared surface to a level suitable for further processing.

Reference cited in this section

5. G. Krauss, *Steels: Heat Treatment and Processing Principles,* ASM International, 1989

Annealed Structures for Machining

Different combinations of microstructure and hardness, considered together, are significant in terms of machinability. For instance, Fig. 10 shows that a partially spheroidized 5160 steel shaft was machined (by turning) with much less tool wear and better surface finish than the same steel in the annealed condition with a pearlitic microstructure and a higher hardness. Based on many observations, optimum microstructure for machining steels of various carbon contents are usually as follows:

Carbon, %	Optimum microstructure
0.06-0.20	As-rolled (most economical)
0.20-0.30	Under 75 mm (3 in.) diameter, normalized; 75 mm diameter and over, as-rolled
0.30-0.40	Annealed, to produce coarse pearlite, minimum ferrite
0.40-0.60	Coarse lamellar pearlite to coarse spheroidized carbides
0.60-1.00	100% spheroidized carbides, coarse to fine

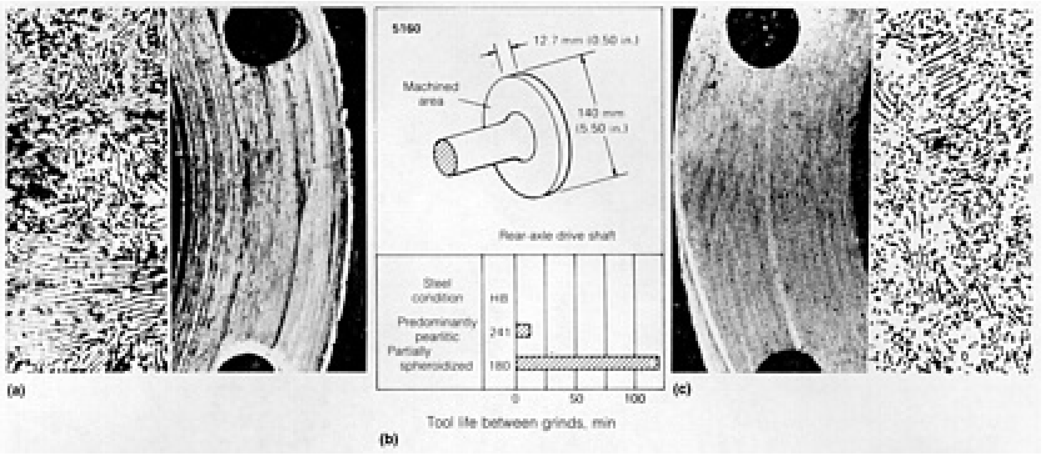

Fig. 10 The effect of partial spheroidization on surface finish and tool life in subsequent machining of 5160 steel. (a) Annealed (pearlitic) microstructure (hardness: 241 HB), and surface finish of flange after machining of eight pieces. (b) Tool life between grinds, min. (c) Partially spheroidized microstructure (hardness: 180 HB) and surface finish of flange after machining of 123 pieces

The type of machining operation is also a factor. For example, certain gears were made from 5160 steel tubing by the dual operation of machining in automatic screw machines and broaching of cross slots. The screw-machine operations were easiest with thoroughly spheroidized material, but a pearlitic structure was more suitable for broaching. A semispheroidized structure proved to be a satisfactory compromise.

Semispheroidized structures can be achieved by austenitizing at lower temperatures, and sometimes at higher cooling rates, than those used for achieving pearlitic structures. The semispheroidized structure of the 5160 steel tubing mentioned above was obtained by heating to 790 °C (1450 °F) and cooling at 28 °C/h (50 °F/h) to 650 °C (1200 °F). For this steel, austenitizing at a temperature of about 775 °C (1425 °F) results in more spheroidization and less pearlite.

Medium-carbon steels are much more difficult to fully spheroidize than are high-carbon steels such as 1095 and 52100. In the absence of excess carbides to nucleate and promote the spheroidizing reaction, it is more difficult to achieve complete freedom from pearlite in practical heat-treating cycles.

At lower carbon levels, structures consisting of coarse pearlite in a ferrite matrix often are found to be the most machinable. In some alloy steels, this type of structure can best be achieved by heating to temperatures well above Ac_3 to establish a coarse austenite grain size, then holding below Ar_1 to allow coarse, lamellar pearlite to form. This process sometimes is referred to as cycle annealing or lamellar annealing. For example, forged 4620 steel gears were heated rapidly in a five-zone furnace to 980 °C (1800 °F), cooled to 625 to 640 °C (1160 to 1180 °F) in a water-cooled zone, and held at that temperature for 120 to 150 min. The resulting structure--coarse, lamellar pearlite in a ferrite matrix--had a hardness of 140 to 146 HB (Ref 8).

Reference cited in this section

8. W. Snyder, Annealing and Carburizing Close Tolerance Driving Gears, *Met. Prog.,* Oct 1965, p 121

Types of Furnaces

Furnaces for annealing are of two basic types: batch furnaces and continuous furnaces. Within either of these two types, furnaces can be further classified according to configuration, type of fuel used, method of heat application, and means by which the load is moved through, or supported in, the furnace. Other factors that must be considered in furnace selection are cost, type of annealing cycle, required atmosphere, and physical nature of parts to be annealed. In many cases, however, the annealing cycle used is dictated by the available equipment.

Batch-type furnaces are necessary for large parts such as heavy forgings and often are preferred for small lots of a given part or grade of steel and for the more complex alloy grades requiring long cycles. Specific types of batch furnaces

include car-bottom, box, bell, and pit furnaces. Annealing in bell furnaces can produce the greatest degree of spheroidization (up to 100%). However, the spheroidizing cycles in bell furnaces are long and last from 24 to 48 h depending on the grade of material being annealed and the size of the load.

Continuous furnaces such as roller-hearth, rotary-hearth, and pusher types are ideal for isothermal annealing of large quantities of parts of the same grade of steel. These furnaces can be designed with various individual zones, allowing the work to be consecutively brought to temperature, held at temperature, and cooled at the desired rate. Continuous furnaces are not able to give complete spheroidization and should not be used for products that require severe cold forming. For more detailed discussion of the types of furnaces available for annealing, see Ref 9 and the article "Types of Heat-Treating Furnaces" in this Volume.

Reference cited in this section

9. *The Making, Shaping and Treating of Steel,* 10th ed., H.E. McGannon, Ed., Association of Iron and Steel Engineers, 1985

Furnace Atmospheres

Electric furnaces used with air atmospheres, and gas furnaces used with atmospheres consisting of the products of combustion, cannot be regulated for complete elimination of oxidation of the steel being treated. Only atmospheres independent of the fuel are generally considered satisfactory for clean or bright annealing. Excessive oxidation during annealing usually is prevented by the use of controlled atmospheres in conjunction with a suitable furnace that is designed to exclude air and combustion gases from the heating chamber. The gases and gas mixtures used for controlled atmospheres depend on the metal being treated, the treatment temperature, and the surface requirements of the parts being annealed. The need to eliminate decarburization as well as oxidation is often a significant factor in the selection of annealing atmospheres.

The gas most widely used as a protective atmosphere for annealing is exothermic gas. This gas is inexpensive, the raw materials for making it are readily available, and the results obtained with it are generally excellent. Hydrocarbon gases such as natural gas, propane, butane, and coke-oven gas are commonly burned in an exothermic-gas producer, creating a self-supporting, heat-producing combustion reaction. A commonly used exothermic gas mixture contains 15% H_2, 10% CO, 5% CO_2, 1% CH_4, and 69% N_2. This gas is used for bright annealing of cold-rolled low-carbon steel strip. It will decarburize medium-carbon and high-carbon steels, however, because of the carbon dioxide and water vapor it contains.

Exothermic gas sometimes is refrigerated to reduce its moisture content, particularly in geographic areas where the temperature of the water used for cooling is high. When decarburization of workpiece surfaces must be prevented, water vapor and carbon dioxide must be completely removed from the gas. Purified exothermic gas, with its carbon dioxide and water vapor removed, has many applications in heat treatment of steel without decarburization.

Purified rich exothermic gas, formed by partial combustion, is used for short-cycle annealing and process annealing of medium- and high-carbon steels of the straight-carbon and alloy types. For long-cycle batch annealing, however, this gas is unsuitable because its high carbon monoxide content results in soot deposits on the work and because of the possibility of surface etching as a result of the relatively long time for which the work is in the critical low-temperature range where gas reactions can occur. In short-cycle annealing these effects are minimal, and the high-CO gas is then desirable because of its high carbon potential. The fairly lean purified gas formed by more complete combustion is used for long-cycle annealing of medium- and high-carbon steels of the straight-carbon and alloy types, and for batch and continuous annealing of low-carbon steel strip for tin plating.

Allowable decarburization on spheroidize annealed blanks or coiled rod can be quite restrictive. As long as the furnace has excellent sealing characteristics, low dewpoint exothermic gas can protect the steel from decarburization. Many commercial heat treaters compensate for the sealing problems of furnaces by using a blend of exothermic and endothermic gases. Depending on the carbon content of the stock that is being processed, the blend can be varied. A great deal of caution has to be exercised when such blends are used because endothermic gas forms an explosive mixture with air as the temperature drops below 760 °C (1400 °F).

Other atmospheres commonly used in annealing include endothermic-base, dissociated ammonia, and vacuum atmospheres. Nitrogen-base atmospheres became popular among heat treaters in the 1980s due in part to rising costs of utilities such as natural gas and water. The nitrogen is blended with small percentages of additives such as methane,

propane, propylene, and carbon monoxide. For more complete information, see the article "Furnace Atmospheres" in this Volume.

Annealing of Sheet and Strip

In terms of total tonnage of material processed, annealing of sheet and strip during production of steel-mill products represents the major use of annealing. Because such annealing is done to prepare the material for further processing (such as additional cold rolling or fabrication into parts), and because the temperatures employed are usually below the A_1 temperature, the more specific terms subcritical annealing and process annealing are appropriate, although common practice is to use the term annealing without qualification.

In annealing of sheet and strip, two techniques predominate: the batch process and the continuous process. In the batch process (also called box annealing), coils or cut lengths of sheet are placed on an annealing base and covered with containers that are sealed to hold the appropriate atmosphere. A furnace is then placed over the covered steel. A protective atmosphere is introduced within the inner covers to protect the steel from oxidation and is circulated through the coils by use of fans and convector plates. Heating is provided by the outer furnace and may be done either through the use of radiant tubes or by direct firing. The charge is heated to the required temperature and held for a period of time that will result in the desired properties. The outer furnace is then removed, and the coils are allowed to cool under the inner covers. When the temperature has been reduced to the point where oxidation of the steel will not occur, the inner covers are removed and the steel is forwarded for further processing.

In the continuous process, steel coils are uncoiled and drawn through a furnace where they are subjected to the annealing cycle under a protective atmosphere. After the sheet or strip has been cooled and removed from the furnace, further in-line processing (such as hot dip galvanizing) may be done, or the steel may be cut into sheets. In general, however, the steel is recoiled and then forwarded as in the batch process. For more detailed information, see the article "Continuous Annealing" that immediately follows in this Section.

In addition to the obvious differences in equipment, the batch process and the continuous process differ considerably in several other ways. Batch annealing may require up to a week because of the large mass of material being treated, whereas continuous annealing is accomplished in about five minutes. Differences are also evident in the temperatures employed, with the batch process generally being conducted at lower temperatures. Because in batch annealing it is difficult to ensure that the temperature is uniform throughout the charge (which may consist of several hundred tons of steel), the continuous process offers the potential of more uniform properties. The short annealing times of the continuous process, however, frequently result in hardness levels slightly higher than those of similar material annealed by the batch process.

Cold-Rolled Plain Carbon Sheet and Strip. The usual method of manufacturing cold-rolled sheet and strip is to produce a hot-rolled coil, pickle it to remove scale (oxide), and cold roll it to the desired final gage. Cold rolling may reduce the thickness of the hot-rolled material in excess of 90%, which increases the hardness and strength of the steel but severely decreases its ductility. If any large amount of subsequent cold working is to be done, the ductility of the steel must be restored.

Annealing of the cold-rolled steel normally is designed to produce a recrystallized ferrite microstructure from the highly elongated, stressed grains resulting from cold work. Figure 11 shows the effect of annealing on the microstructure of a low-carbon cold-rolled sheet steel. The cold-rolled microstructure is shown in Fig. 11(a) in contrast to the partially and fully recrystallized microstructure in Fig. 11(b) and 11(c). During heating of the steel, and in the first segment of the holding portion of the cycle, the first metallurgical process to occur is recovery. During this process, internal strains are relieved (although little change in the microstructure is evident), ductility is moderately increased, and strength is slightly decreased.

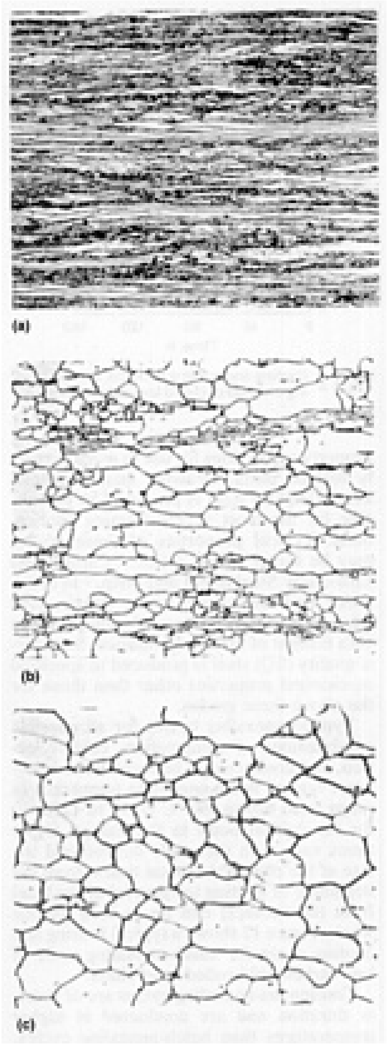

Fig. 11 A low-carbon sheet steel in the (a) as-cold-rolled unannealed condition, (b) partially recrystallized annealed condition, and (c) fully recrystallized annealed condition. Marshall's etch. 1000×

As annealing continues, the process of recrystallization occurs, and new, more equiaxed ferrite grains are formed from the elongated grains. During recrystallization, strength decreases rapidly, with a corresponding increase in ductility. Further time at temperature causes some of the newly formed grains to grow at the expense of other grains; this is termed grain growth and results in modest decreases in strength and small (but often significant) increases in ductility. Most plain carbon steels are given an annealing treatment that promotes full recrystallization, but care must be taken to avoid excessive grain growth, which can lead to surface defects (such as orange peel) in formed parts.

The rates at which the metallurgical processes noted above proceed are functions of both the chemical composition and the prior history of the steel being annealed. For example, small amounts of elements such as aluminum, titanium, niobium, vanadium, and molybdenum can decrease the rate at which the steel will recrystallize, making the annealing response sluggish and therefore necessitating either higher temperatures or longer annealing times to produce the same properties. Although the presence of these alloying elements is generally the result of deliberate additions intended to modify the properties of the sheet (as in the case of aluminum, titanium, niobium, and vanadium), some elements may be present as residual elements (molybdenum, for example) in quantities great enough to modify the response to annealing. Conversely, larger amounts of cold work (greater cold reductions) will accelerate the annealing response. Therefore, it is not possible to specify a single annealing cycle that will produce a particular set of mechanical properties in all steels; the chemical composition and the amount of cold work also must be taken into account.

Cold-rolled plain carbon steels are produced to a number of different quality descriptions. Commercial quality (CQ) steel is the most widely produced and is suitable for moderate forming. Drawing quality (DQ) steel is produced to tighter mechanical-property restrictions for use in more severely formed parts. Drawing quality special killed (DQSK) steel is

produced to be suitable for the most severe forming applications. Typical properties of these grades may be found in the article "Carbon and Low-Alloy Steel Sheet and Strip," in *Properties and Selection: Irons, Steels, and High-Performance Alloys,* Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.* Structural quality (SQ) steel is produced to specified mechanical properties other than those for the above three grades.

Typical annealing cycles for all possible combinations of composition, cold reduction, and grade cannot be listed here. However, typical batch-annealing temperatures range from 620 to 690 °C (1150 to 1270 °F) for the coldest point in the charge. Cycle times vary with the grade desired and the size of the charge, but total times (from the beginning of heating to removal of the steel from the furnace) can be as long as one week. Figure 12 shows a typical heating and cooling cycle for batch-annealing coils of low-carbon cold-rolled steel sheet.

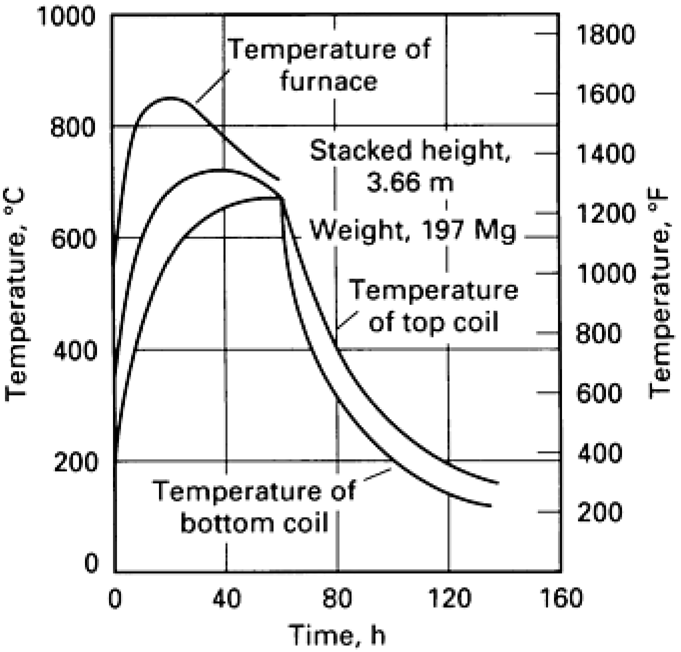

Fig. 12 Heating and cooling cycle for batch annealing of a load of coiled low-carbon steel sheet

Continuous-annealing cycles are of shorter duration and are conducted at higher temperatures than batch-annealing cycles. In some applications, the annealing temperature may exceed A_1. Typical cycles are 40 s at 700 °C (1290 °F) for cold-rolled commercial quality steel and 60 s at 800 °C (1470 °F) for drawing quality special killed sheet. Most continuous annealing of cold-rolled sheet includes an overaging treatment designed to precipitate carbon and nitrogen from solution in the ferrite and to reduce the likelihood of strain aging. Overaging for 3 to 5 min at 300 to 450 °C (570 to 840 °F) accomplishes the desired precipitation of carbon and nitrogen.

Batch annealing and continuous annealing differ slightly in the properties they produce. Typical average properties of batch-annealed and continuous-annealed commercial quality plain carbon steel are as follows:

Annealing process	**Yield strength**		**Elongation, %**
	MPa	**ksi**	
Batch	210	30.4	43.0

Continuous	228	33.0	41.7

High-strength cold-rolled sheet and strip are growing in importance due to their high load-bearing capacities. Strength of sheet and strip can be increased through modifications of chemical composition and/or selection of different annealing cycles, but these methods result in decreased ductility. Plain carbon steels, produced by conventional techniques, may be batch annealed or continuous annealed under conditions that result only in recovery or partial recrystallization. Typical batch-annealing cycles of this type employ soak temperatures of 425 to 480 °C (800 to 900 °F) and various soak times. High-strength low-alloy (HSLA) steels containing alloying elements such as niobium, vanadium, and titanium also may be produced as cold-rolled grades. The additional alloying produces a stronger hot-rolled steel, which is strengthened even more by cold rolling. Cold-rolled HSLA steels may be recovery annealed to produce higher-strength grades or recrystallization annealed to produce lower-strength grades. Successful production of cold-rolled HSLA steel requires selection of the appropriate combination of steel composition and hot-rolled strength, amount of cold reduction, and type of annealing cycle. For more information on HSLA steels, see the article "High-Strength Structural and High-Strength Low-Alloy Steels," in Volume 1 of *ASM Handbook,* formerly 10th Edition *Metals Handbook.*

Another series of high-strength sheet steels are the dual-phase steels. These steels are generally annealed for a short period (usually less than 5 min) in the intercritical range, followed by rapid cooling. The resulting microstructure is 10 to 20% martensite by volume in a matrix of ferrite. The continuous-annealing process is ideal for producing dual-phase sheet grades (more details are in the next article in this Section). Dual-phase steels are unique in that they deform by a continuous yielding behavior because the martensite is a continuous source of dislocations during plastic deformation (see the article "Dual-Phase Steels" in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook*). Most other low-carbon steels that display a yield point upon deformation need to be skin passed or temper rolled to provide a source of dislocations for continuous yielding behavior. Steels displaying a yield point are undesirable for many forming operations because of the formation of Lüders bands that blemish the surface.

Hot dip galvanized products are produced on lines that process either preannealed (batch annealed) or full hard coils. Lines for processing full hard coils incorporate an in-line annealing capability so that annealing and hot dip galvanizing can be accomplished in a single pass through the line. This in-line annealing, like continuous annealing of uncoated steel, generally results in slightly higher strength and slightly lower ductility than batch annealing. Maximum strip temperatures are below the A_1 temperature for commercial quality steel, but temperatures in excess of 845 °C (1550 °F) are required for DQSK grades. Galvanizing of preannealed steel results in properties similar to those of ungalvanized material.

The atmosphere in a continuous galvanizing line, in addition to protecting the sheet from oxidation, must remove any oxides present on the strip to promote metallurgical bonding between the steel and the zinc or zinc alloy.

Tin mill products are distinguished from their cold-rolled sheet mill counterparts chiefly by the fact that they are produced in lighter gages (0.13 to 0.38 mm, or 0.005 to 0.015 in.) and by the fact that some of them are coated with tin or chromium and chromium oxide for corrosion resistance. The sequence used for processing single-reduced tin mill products is similar to that for cold-rolled sheet, that is, pickling, cold reducing, annealing, and temper rolling of hot-rolled coils. Double-reduced products are cold rolled an additional 30 to 40% following annealing (this step replaces temper rolling). Whereas much of the tonnage produced in tin mills is batch annealed, a considerable amount is continuous annealed (facilities for continuous annealing currently are more prevalent in tin mills than in sheet mills).

Because tin mill products traditionally have been produced at facilities separate from sheet mills and because applications for these products are different from those for cold-rolled sheet, tin mill products have been assigned separate designations for indicating the mechanical properties developed during annealing. A list of these temper designations is given in Table 5.

Table 5 Temper designations for steel tin mill products

Designation	**Hardness aim, HR30T**
Batch (box) annealed products	

T-1	52 max
T-2	50-56
T-3	54-60
Continuously annealed products	
T-4 CA	58-64
T-5 CA (TU)	62-68
T-6 CA	67-73
Double-reduced products	
DR-8	73
DR-9	76
DR-9M	77
DR-10	80

Open-coil annealing, which is done in batch furnaces, involves loose rewinding of a cold-reduced coil to provide open spaces between successive laps. This allows the controlled atmosphere gases to be drawn between the laps, providing faster and more uniform heating and cooling than are obtained with tightly wound coils. In addition, by control of the hydrogen content and dew point of the atmosphere, decarburizing conditions can be established. The carbon content of the steel can thereby be reduced to low levels for such materials as enameling steel and electrical steel.

Loose rewinding of coils for open-coil annealing is done on a turntable having a vertical mandrel. As the coil is wound, a twisted wire spacer is inserted between the laps. This spacer remains in the coil during annealing and is removed after the coil has been removed from the furnace. The coil is then tightly rewound and is ready for temper rolling.

Annealing of Steel Forgings

Annealing of forgings is most often performed to facilitate some subsequent operation, usually machining or cold forming. The type of annealing required is determined by the kind and amount of machining or cold forming to be done as well as the type of material involved. For some processes it is essential that the microstructure be spheroidal, whereas for others spheroidal structures may not be necessary or even desirable.

Annealing of Forgings for Machinability. In many cases, a structure suitable for machining can be developed in low-carbon steel forgings by transferring the forgings directly from the forging operation to a furnace heated to a proper transformation temperature, holding them at this temperature for a time sufficiently long to permit all the austenite to transform, then cooling in air. In this process, the effective austenitizing temperature is the finishing temperature of forging, not the initial forging temperature. This process is capable of producing reasonably uniform structures in forgings of uniform sections. However, in forgings shaped such that some portions are cooler than others, this difference in

finishing temperature will cause the structures to be dissimilar. This process generally will not produce a spheroidal structure except in high-alloy steels containing large amounts of carbide-forming elements. If a lamellar structure is suitable for subsequent operations, however, this process can minimize the energy usage and lower costs by reducing processing and handling time.

In many instances where the product or subsequent process requires a more consistent hardness, forgings can be subcritical annealed by heating to a temperature between 10 and 20 °C (20 and 40 °F) below Ae_1, holding sufficiently long (determined by degree of softening required), and then cooling in air (or equivalent). Care should be taken to maintain the temperature below Ae_1 to prevent formation of austenite, which would require a much lower cooling rate.

In forgings produced from higher-carbon steels with or without significant amounts of alloying elements, a spheroidal structure generally is preferable for high-speed machining operations. Direct transfer of high-carbon steel forgings to a furnace for transformation sometimes can be used as the preliminary step of an annealing cycle and as a means of preventing the possibility of cracking in deep-hardening steel parts, but seldom will produce satisfactory properties alone. Most annealing of high-carbon steel forgings is done either in a batch furnace or in a continuous tray pusher furnace. Typical schedules for spheroidizing 52100 steel in a batch furnace are as follows:

- Austenitize by holding at least 2 h at 790 °C (1450 °F), furnace cool at 17 °C/h (30 °F/h) to 595 °C (1100 °F), then air cool
- Austenitize by holding at least 2 h at 790 °C (1450 °F), cool as rapidly as practical to 750 °C (1380 °F), cool at 6 °C/h (10 °F/h) to 675 °C (1250 °F), then air cool
- Austenitize by holding at least 2 h at 790 °C (1450 °F), cool as rapidly as practical to 690 °C (1275 °F), transform isothermally by holding at this temperature for 16 h, then air cool

In all instances, the load should be distributed to promote uniform heating and cooling. Use of circulating fans in the furnace chamber will greatly aid in producing a product that is uniform in both hardness and microstructure.

A typical continuous furnace for annealing steel forgings might consist of five or six zones. An example of a specific spheroidize annealing treatment in such a furnace is given in the next section.

Annealing of Forgings for Cold Forming and Re-Forming. If a steel forging or blank requires further cold forming, it may be necessary to soften it in order to enhance its plastic-flow characteristics. In general, this type of annealing is done only to the extent that the forming operation requires, that is, to satisfy dimensional, mechanical, and tool-life requirements, as well as to prevent cracking and splitting. Much intermediate annealing is done successfully, but cold forming processes are best performed on parts with totally spheroidized microstructures, especially for parts made of high-carbon steels.

In one plant, both 5160 and 52100 steels have been successfully spheroidized with a common cycle in a six-zone tray pusher furnace. In this cycle, the temperatures in the six zones are 750, 750, 705, 695, 695, and 680 °C (1380, 1380, 1300, 1280, 1280, and 1260 °F). Time in each zone is 150 min. This process yields 5160 steel forgings with hardnesses of 170 to 190 RB and 52100 steel parts with hardnesses of 175 to 195 RB, both suitable for cold or warm restrike operations.

In another cold-forming plant, 15B35 steel is processed in either a continuous roller hearth furnace or a bell furnace depending on the severity of the cold-forging operation. The continuous furnace is a two-zone furnace with zone temperatures at 750 °C (1380 °F) and 695 °C (1280 °F). Annealing time in each zone is between 90 to 120 min. The parts then enter a water-cooled cooling bed and exit the furnace at about 260 °C (500 °F). Only a partially spheroidized structure is obtainable in this furnace. If a nearly full-spheroidized structure is required, bell furnaces are used (see Fig. 13). A typical cycle for a 4500 kg (10,000 lb) load involves soaking at 760 °C (1400 °F) for 8 h followed by a slow cool to 675 °C (1250 °F) and a rapid cool afterwards.

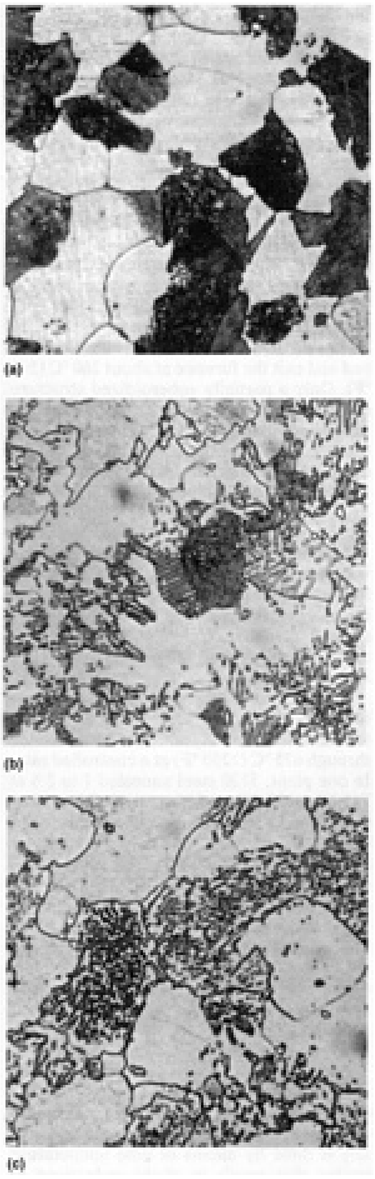

Fig. 13 Microstructures of 15B35 steel. (a) In the as-received hot-rolled condition, microstructure is blocky pearlite. Hardness is 87 to 88 HRB. (b) In the partially spheroidized condition following annealing in a continuous furnace. Hardness is 81 to 82 HRB. (c) In the nearly fully spheroidized condition following annealing in a bell furnace. Hardness is 77 to 78 HRB.

A commercial heat treater uses a further variation of the processing cycle in its bell furnaces. The cycle for a 14,000 kg (31,000 lb) load involves soaking at 765 °C (1410 °F) for 24 h, furnace cooling to 675 °C (1250 °F), and holding at that temperature for 16 h followed by a rapid cooling.

Low-carbon steels generally can be cold formed successfully after being heated to temperatures near A_1 and then being cooled through 675 °C (1250 °F) at a controlled rate. In one plant, 5120 steel annealed 1 to 2 h at 745 °C (1375 °F) and slow cooled has been cold formed successfully. Large quantities of 1008, 1513, 1524, 8620, and 8720 steels are being cold formed after annealing cycles consisting of 1 to 6 h at 720 °C (1325 °F) followed by slow cooling. The severity of the forming operation, as well as the grade of steel and history of the part, determines the extent of annealing required. Batch furnaces, continuous tray pusher furnaces, and continuous belt furnaces are being used successfully to perform these types of annealing operations on low-carbon steels.

Any part that contains significant stresses resulting from cold forming or restrike operations should be reviewed for some type of stress-relief process. Stress relieving usually is done by means of time-temperature cycles that result in slight reductions in hardness. These cycles often consist of 1 h at 425 to 675 °C (800 to 1250 °F).

Annealing to Obtain Pearlitic Microstructures. Forgings--especially plain and alloy high-carbon steel forgings--are isothermally annealed to produce a pearlitic microstructure that is preferred for a subsequent process. In steels that are to be induction hardened, for example, the carbide distribution of a fine pearlitic structure offers excellent preparation for optimum control in selective hardening while producing a reasonably machinable core structure. Isothermal annealing to obtain line pearlite can be performed in batch or continuous furnaces; however, temperature control and uniformity are more critical than in conventional slow cooling cycles because a particular microstructure and a particular hardness level usually are desired. In one plant, a continuous belt-type furnace is used for isothermal annealing of 1070 steel forgings. The forgings are uniformly heated for 30 min at 845 °C (1550 °F), cooled to 675 °C (1250 °F), and held for 20 min, then rapidly cooled. The microstructure produced is essentially fine lamellar pearlite with a hardness of 219 to 228 HB. The hardness and the structure can be modified by adjusting the transformation temperature.

Annealing of Bar, Rod, and Wire

Significant tonnages of bar, rod, and wire are subjected to thermal treatments that decrease hardness and prepare the material for subsequent cold working and/or machining. For low-carbon steels (up to 0.20% C), short-time subcritical annealing often is sufficient for preparing the material for further cold working. Steels with higher carbon and alloy contents require spheroidizing to impart maximum ductility.

Most carbon and alloy steel coiled products can be successfully spheroidized. In batch annealing, it is helpful to use higher-than-normal temperatures (for example, 650 °C, or 1200 °F) during initial heating for purging because the higher initial temperature promotes a lower temperature gradient in the charge during subsequent heating into the temperature range between A_1 and A_3. Use of a higher purge temperature also promotes agglomeration of the carbides in the steel, which makes them more resistant to dissolution in the austenite when the charge temperature is finally elevated. These undissolved carbides will be conducive to the formation of a spheroidal rather than a lamellar structure when transformation is complete.

A knowledge of the temperature distribution in the furnace and in the load can be a major factor in achieving a good, consistent response to spheroidization. Temperature distribution and control are much more critical in batch and vacuum furnaces, which may handle loads of up to 27 Mg (30 tons), than in continuous furnaces, in which loads of only 900 to 1800 kg (2000 to 4000 lb) may be transferred from zone to zone. Test thermocouples should be placed strategically at the top, middle, and bottom (inside and outside) of the charge during development of cycles. In spheroidizing, to minimize formation of pearlite on cooling, it is important to ensure that no part of the charge be allowed to approach A_3. Conversely, if temperatures only slightly above A_1 are used and temperature controls are inaccurate because of poor placement of thermocouples, it is probable that the A_1 temperature will not be attained and that no austenitization will occur.

Table 6 gives typical mechanical properties that can be obtained in hypoeutectoid plain carbon steels by spheroidizing. Recommended temperatures and times for lamellar and spheroidize annealing of hypoeutectoid alloy steels are presented in Table 4.

Table 6 Typical mechanical properties of spheroidized plain carbon steels

Steel	Tensile strength			
	Hot rolled		Spheroidized	
	MPa	ksi	MPa	ksi
1010	365	53	295	43
1018	450	65	365	53
1022	470	68	385	56

1030	585	85	415	60
1038	600	87	485	70
1045	675	98	515	75
1060	860	125	550	80
1065	910	132	600	87
1524	510	74	450	65
1541	710	103	540	78

Prior cold working increases the degree of spheroidization and provides even greater ductility. For example, 4037 steel in the as-rolled condition normally can be spheroidized to a tensile strength of about 515 MPa (75 ksi). If, however, the material is drawn 20% and then spheroidized (referred to as spheroidize annealed in-process), the resulting tensile strength will be around 470 MPa (68 ksi).

Although prior cold work can enhance response to annealing, caution must be observed in spheroidizing cold-worked plain carbon steels with 0.20% C or less. Unless a reduction of at least 20% is applied, severe grain coarsening may be observed after spheroidizing. Such grain coarsening is the result of a unique critical combination of strain and annealing temperature for the particular steel and may severely impair subsequent performance.

In the wire industry, a wide variety of in-process annealing operations have been evolved for rendering coiled material suitable for further processing that may require formability, drawability, machinability, or a combination of these characteristics. One large wire mill reports current use of 42 separate and distinct annealing cycles, the majority of which represent compromises between practical considerations and optimum properties. For example, annealing temperatures below those that might yield optimum softness sometimes must be used in order to preclude scaling of wire coils, which often can occur even in controlled-atmosphere furnaces. Even slight scaling may cause the coil wraps to stick together, which can impede coil payoff in subsequent operations.

Some of the terms used to describe various in-process annealing treatments are in common usage throughout the wire industry, whereas others have been developed within specific plants or mills. No attempt will be made here to list or define all the names that refer to specific treatments.

"Patenting" is a special form of annealing that is unique to the rod and wire industry. In this process, which usually is applied to medium- and higher-carbon grades of steel, rod or wire products are uncoiled, and the strands are delivered to an austenitizing station. The strands are then cooled rapidly from above A_3 in a molten medium-- usually lead at about 540 °C (1000 °F)--for a period of time sufficient to allow complete transformation to a fine pearlitic structure. Both salt baths and fluidized beds have also been used for this purpose. This treatment increases substantially the amount of subsequent wiredrawing reduction that the product can withstand and permits production of high-strength wire. Successive drawing and patenting steps may be employed if necessary, in order to obtain the desired size and strength level.

Austenitizing for patenting can be accomplished in oil, gas, or electric furnaces; in high-temperature lead or salt baths; or by induction or direct resistance heating. As an alternative to quenching in molten lead, continuous air cooling often is employed. Such air patenting is less expensive than lead patenting but results in coarser pearlite and often more proeutectoid ferrite, a microstructure that is less desirable from the standpoint of drawing high-strength wire.

Annealing of Plate

Plate products are occasionally annealed to facilitate forming or machining operations. Annealing of plate usually is done at subcritical temperatures, and long annealing times generally are avoided. Maintaining adequate flatness can be a significant problem in annealing of large plates.

Annealing of Tubular Products

Tubular products known as mechanical tubing are used in a variety of applications that can involve machining or forming. For these products, which are made from various grades of steel, annealing is a common treatment. In most annealing cycles, subcritical temperatures and short annealing times are used to reduce hardness to the desired level. High-carbon grades, such as 52100, generally are spheroidized to facilitate machining. Tubular products manufactured in pipe mills are rarely annealed. These products normally are used in the as-rolled, the normalized, or the quenched and tempered condition.

Continuous Annealing of Steel

R. Pradhan, Bethlehem Steel Corporation

Introduction

ANNEALING OF STEEL SHEET products, a process often (but not solely) used to produce a recrystallized ferrite microstructure after cold rolling, is performed on a commercial scale by either batch annealing or continuous annealing. In batch annealing, multiple coils of sheet are placed under a cover with a reducing atmosphere (Fig. 1a) and heated for a time period that may involve days (see Fig. 1b). In contrast, continuous annealing of sheet involves the rapid passage of uncoiled sheet through heating and cooling equipment (Fig. 1a).

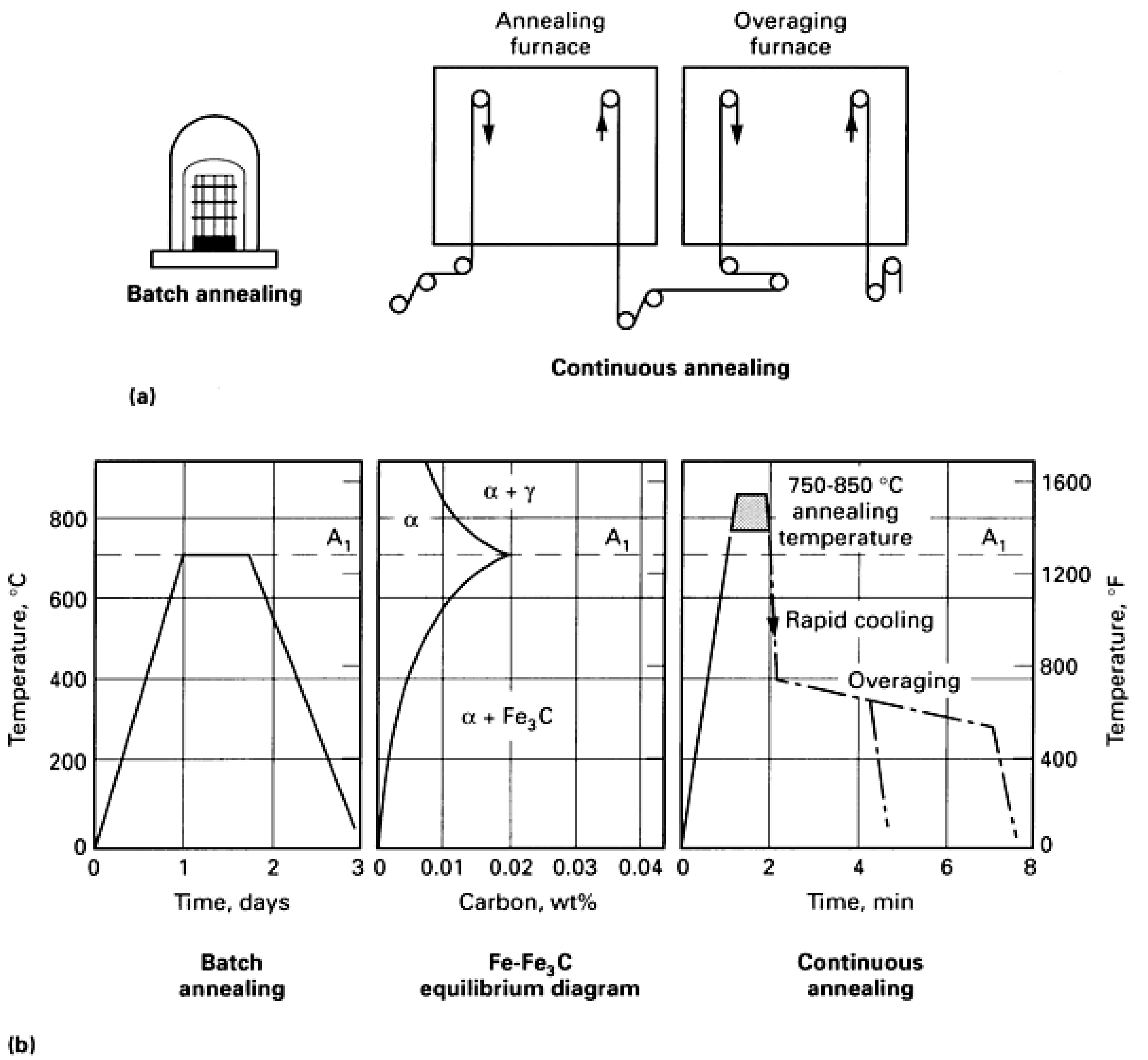

Fig. 1 Comparison of (a) processing methods and (b) thermal treatment profiles for batch annealing and continuous annealing. As in batch annealing, the continuous-anneal temperature can be as low as 675 °C (1250 °F) for the recrystallization of commercial-quality (CQ) sheet, but is generally in the range of 750 to 850 °C (1380 to 1560 °F) for critical formability products.

In addition to the obvious differences in equipment, batch and continuous annealing have important differences in heating and cooling profiles (Fig. 1b). The very large mass of steel heats and cools very slowly during batch annealing, and the process requires several days for completion. Annealed grain sizes are coarse, and the slow cooling rates ensure that all carbon dissolved during annealing precipitates upon cooling. Thus excellent ductility results, although some nonuniformity develops because the inside and outside parts of a coil experience different thermal histories.

During continuous annealing, uncoiled steel sheet is passed though a two-stage furnace for times on the order of a few minutes. The first stage heats the steel and accomplishes recrystallization, while the second stage heats at a lower temperature to overage the steel and remove carbon from the solution effectively. Without this step, the thin sheet would cool too rapidly and retain carbon in solution. This carbon would eventually cause strain or quench aging and reduce sheet formability. There are several processing approaches to overaging, some of which are discussed in this article.

For several decades, continuous-annealing lines have been widely used for the production of such sheet steel products as hot-dip galvanized steels, tinplate, nonoriented electrical steels, and stainless steels. The thermal profile on these lines generally involves short-time annealing followed by relatively slow cooling (~10 °C/s, or 20 °F/s) to ambient temperature with no inline overaging. Since the late 1970s, however, continuous-annealing technology, in conjunction with modern steelmaking and upstream processing facilities, has used rapid cooling and in-line overaging to enable the production of sheet steels for very demanding automotive and appliance applications. The metallurgical advantages of continuous

annealing over conventional batch annealing include improved product uniformity, surface cleanliness and shape, and the versatility to produce a wide range of steel grades.

Process Description

The modern continuous-annealing lines combine several processes. At the entry end, the uncoiled sheet is chemically and/or electrolytically cleaned and rapidly heated to an annealing temperature between 675 and 850 °C (1250 and 1550 °F). The cold-rolled sheet is "soaked" for an annealing time on the order of about 1 min and is then subjected to cooling and overaging (tempering) schedules such as those shown in Fig. 2. These stages in the heat treatment are discussed below. In most cases, a continuous-annealing line also includes a stage for tension leveling or temper rolling.

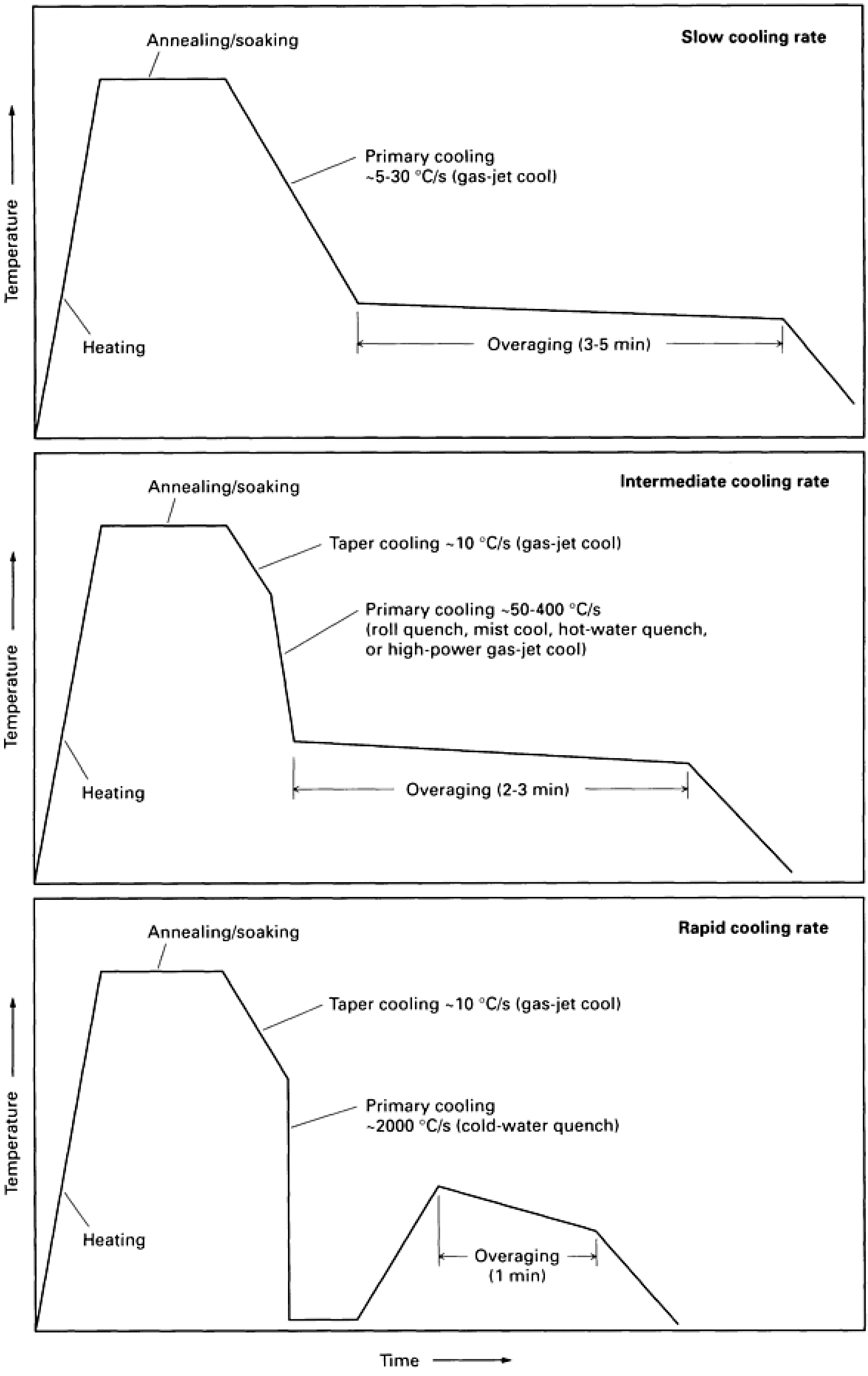
Annealing/soaking
Slow cooling rate
Primary cooling
~5-30 °C/s (gas-jet cool)
Temperature
Heating
Overaging (3-5 min)
Annealing/soaking
Intermediate cooling rate
Taper cooling ~10 °C/s (gas-jet cool)
Primary cooling ~50-400 °C/s
(roll quench, mist cool, hot-water quench,
or high-power gas-jet cool)
Temperature
Heating
Overaging (2-3 min)
Annealing/soaking
Rapid cooling rate
Taper cooling ~10 °C/s (gas-jet cool)
Primary cooling
~2000 °C/s (cold-water quench)
Temperature
Heating
Overaging
(1 min)
Time

Fig. 2 Typical continuous-annealing thermal profiles. Anneal/soak temperature, approximately 750 to 850 °C (1380 to 1560 °F); overage temperature, approximately 350 to 400 °C (660 to 750 °F)

The heating and soaking/annealing stage provides recrystallization of the cold-rolled structure and achieves some degree of grain growth. The soaking temperature, which can range from 675 to 850 °C (1250 to 1560 °F), is generally above the A_1 temperature. The low end of the annealing temperature range (675 °C, or 1250 °F) is used for commercial-quality (CQ) products, whereas the high end is used for drawing-quality (DQ) and deep-drawing-quality special-killed (DQSK or DDQ) products. In some dual-phase steels, the soaking temperature is chosen to generate the proper amount of austenite phase, depending on the desired strength of the product.

The slow-cooling (or taper-cooling) stage, immediately following the annealing treatment, involves a gas-jet cooling (~10 °C/s, or 20 °F/s) to below the A_1 temperature. The slow cooling serves to promote partial precipitation of the solute carbon (that is, the dissolved carbon) from the ferrite phase and, in systems having rapid primary cooling, to prevent the formation of martensite in non-dual-phase steels.

The primary cooling stage involves rapid cooling at rates of 10 to 1000 °C/s (20 to 2000 °F/s), depending on the cooling medium used. The primary cooling medium and associated cooling rate used (Fig. 3) have several engineering consequences. For fast cooling rates (gas-water spraying, hot- or cold-water quenching, roll quenching), sophisticated proprietary techniques are employed to provide uniform cooling without which severe buckling and poor flatness/shape would occur. On the other hand, gas-jet cooling lines require very few controls other than steering or tracking over rolls and in-line tension (Ref 1). For those cooling systems involving contact with water, in-line pickling and rinsing are required to remove the thin oxide layer. No such provisions are needed in those lines having nonoxidizing gas-jet cooling.

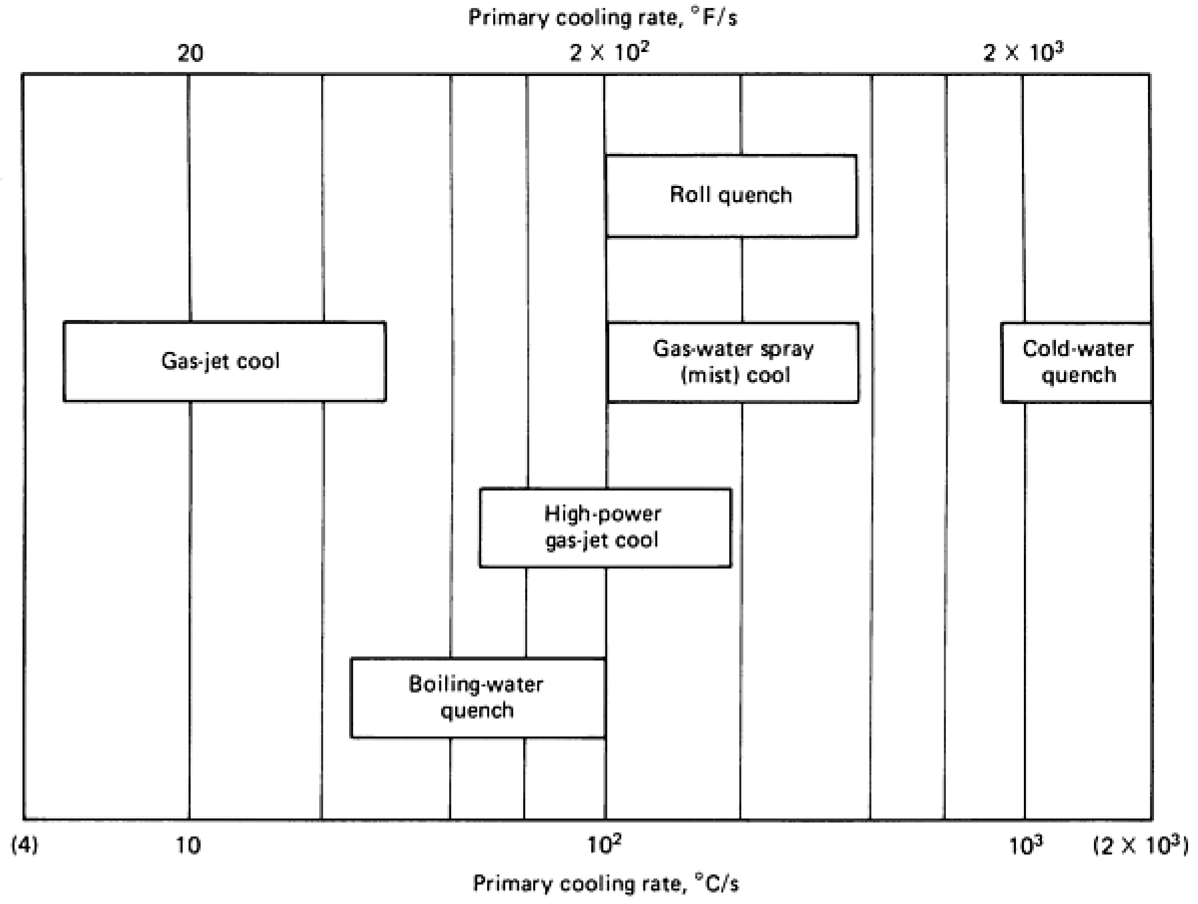

Fig. 3 Primary cooling systems and associated cooling rates

The choice of the primary cooling medium has metallurgical consequences as well (Ref 2, 3, 4). For plain carbon steels, especially where exposed outer-body applications are involved, adequate resistance to ambient strain-aging is a critical requirement in order to prevent stretcher-strain formation in the stamped part. In these cases, a solute-carbon concentration of less than about 10 ppm is needed in the final product. A higher primary cooling rate leads to a larger carbon supersaturation in the ferrite, which increases the driving force for carbon precipitation during subsequent overaging. Accordingly, the overaging time is reduced: 3 to 5 min with the slow gas-jet cooling, compared to 1 min with water quenching. On the other hand, a higher cooling rate increases the density of fine carbides in the ferrite, thereby slightly impairing formability (total elongation and *n*-value), as can be seen in Fig. 4. The optimum balance of properties is realized at a primary cooling rate of about 100 °C/s (180 °F/s) for carbon steel (Fig. 5).

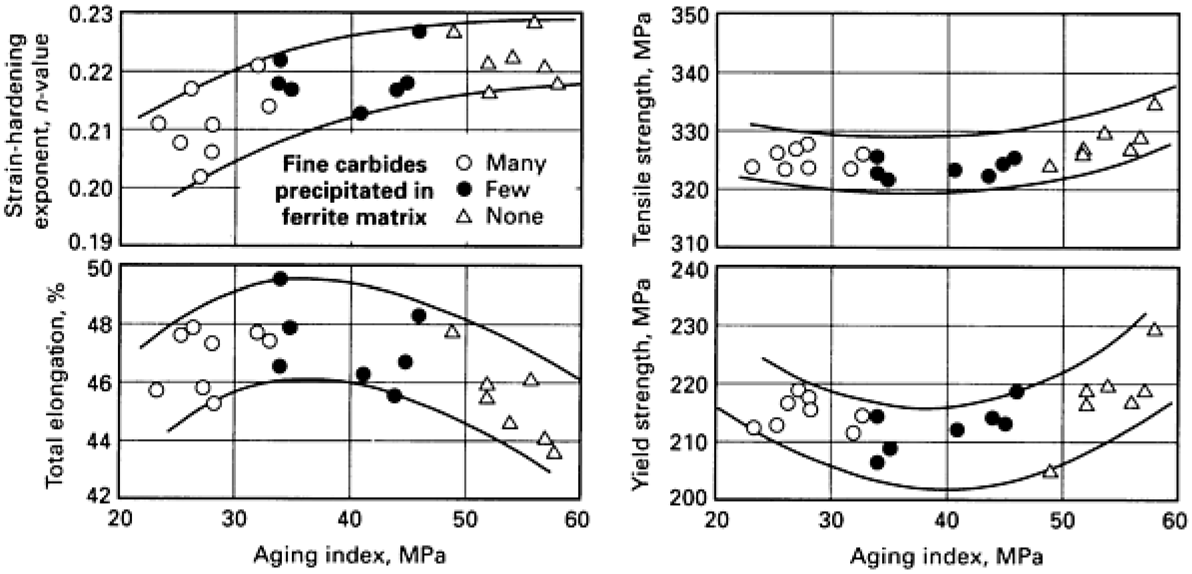

Fig. 4 Relationship between the fine carbide morphology and the aging index and tensile properties of a plain carbon steel. Source: Ref 4

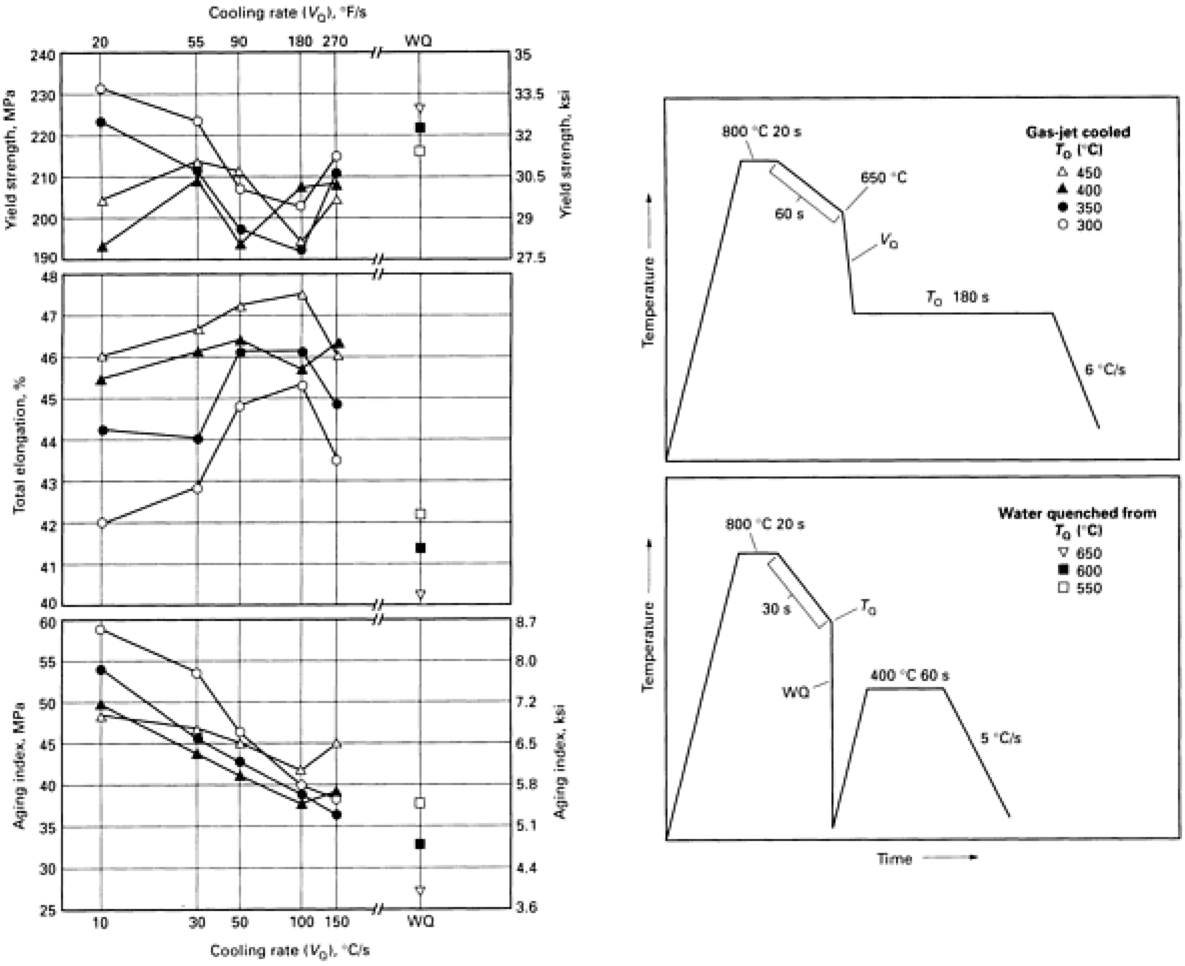

Fig. 5 Effect of the primary cooling rate and overaging temperature on the mechanical properties of a 0.035% C steel. WQ, water quench. Source: Ref 2

In addition to the primary cooling rate, the starting temperature of primary cooling is an important parameter, especially for the higher cooling rates, in optimizing the combination of ductility and aging resistance: A lower starting temperature favors improved ductility at the expense of aging resistance. A lower starting temperature is favorable in the case of faster cooling rates; for example, the optimum starting temperature is 560 °C (1040 °F) for water quenching, compared to 600 °C (1110 °F) for the slower roll quenching (Ref 4).

For the processing of high-strength dual-phase grades, the higher primary cooling rate associated with the water-quenching system has a distinct advantage in that the level of alloying (generally, manganese) needed for hardenability is considerably lower.

Gas-Jet and Water-Spray Cooling. At Nippon Steel Corporation, early continuous-anneal process line (CAPL) technology involved gas-jet cooling (Ref 5) in which a protective nitrogen-hydrogen gas mixture was passed through jets to impinge the steel. Cooling rates of about 5 to 30 °C/s (10 to 55 °F/s) could thus be achieved. A recent development in high-injection-rate technology has enabled higher cooling rates of 100 to 200 °C/s (180 to 360 °F/s) with high gas-jet cool (H-GJC) techniques. Nippon Steel has also designed a cooling system (Acc cooling, or AcC) that involves spraying the steel with a mixed flow of nitrogen and atomized water (Ref 6). Here the cooling rate can be varied between 100 to 400 °C/s (180 to 720 °F/s) by altering the water flow. The gas-water spray system is employed in automotive lines, while the gas-jet cooling system is used in tinplate lines. By using a high-power gas-jet cooling system, Kawasaki Steel Corporation (Ref 7, 8) has been able to attain cooling rates of 50 to 70 °C/s (90 to 125 °F/s) for 0.8 mm (0.315 in.) thick sheet. The multipurpose system (KM-CAL) is employed in the processing of both automotive and tinplate products (Ref 9).

Quenching. The continuous-anneal technology (CAL) developed at NKK Corporation involves a quenching system (Ref 10) consisting of submerged waterjets and is capable of rapid cooling rates of over 1000 °C/s (1800 °F/s). A disadvantage

of the coldwater quenching system, in contrast to the slower cooling systems, is that it is impossible to arrest the primary cooling at the overaging temperature. Reheating to the overaging temperature increases energy costs. Le Centre de Recherches Metallurgiques (Belgium) has developed a process of quenching the moving sheet into boiling water to achieve cooling rates of 25 to 100 °C/s (45 to 180 °F/s) (Ref 11).

Roll-cooling or roll-quenching technology, also developed by NKK (Ref 12) involves cooling the steel by bringing it into direct contact with metallic rolls having a water-cooled interior. The cooling rate ranges between 100 and 400 °C/s (180 to 720 °F/s) depending on sheet thickness. Some continuous-annealing lines have dual-cooling (that is, water- and roll-quenching) capabilities.

The overaging stage reduces the concentration of solute carbon to less than 10 ppm in the ferrite of ferritic-pearlitic steels in order to improve ductility and the resistance to aging. The overaging temperature is typically 400 °C (750 °F) with the time at temperature being governed by the starting temperature of primary cooling and the cooling rate. To further improve the efficiency of the overaging treatment, some lines have a tapered overaging thermal profile. For example, in the water-quenching continuous-anneal line, the steel is first heated to 400 °C (750 °F) and then cooled to a final temperature of 350 °C (660 °F) within 1 to 1.5 min (Ref 3). For the ferrite-plus-martensite (dual-phase) steels, the overaging treatment additionally serves to temper the martensite phase in order to improve ductility. In hot-dip coating lines that incorporate both annealing and coating, the overaging section is generally excluded because coating (at ~480 °C, or 900 °F) after overaging would result in redissolution of the carbides, while overaging after the coating treatment poses the potential problem of zinc pickup on the furnace rolls.

Final cooling from the overaging temperature to the ambient temperature is preferably about 2 °C/s (4 °F/s) for the best properties. In order to restrict the line length (to reduce capital costs), however, a cooling rate up to 10 °C/s (20 °F/s) is tolerated, and in some lines, the steel is quenched from below about 150 °C (300 °F).

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Processing of Specific Types of Steels

With the trend toward more and more continuous processing, batch annealing is gradually being replaced by continuous annealing. The prime advantage of continuous annealing is the considerable increase in product uniformity along the length of the given coil. This is of increasing importance as tolerances and allowable property variabilities are reduced as a result of the increasing automation of forming processes.

Steels for Automotive Applications

Continuous annealing provides the capability to produce a wide variety of automotive cold-rolled sheet grades, all with greater property uniformity and surface cleanliness than conventional batch-annealed steels. Most of these steel grades are

variants of existing batch-annealed products, but some (for example, dual-phase grades) can only be produced by continuous annealing. Also, with continuous annealing, high-strength steels can be produced using lower levels of alloying than is possible with batch annealing.

Commercial-Quality (CQ), Drawing-Quality (DQ), and Deep-Drawing-Quality (DDQ/DQSK). The continuous-annealing lines used in the tin-mill and hot-dip galvanizing facilities of the 1960s and 1970s were comprised of short-time soaking and slow cooling to ambient with no in-line overaging. The CQ product processed on such lines was higher in yield strength (about 250 MPa, or 36 ksi) than conventional automotive batch-annealed grades and had low drawability (average $\bar{r}$ = ~1.0) and poor antiaging properties (see Fig. 6 caption for definition of $\bar{r}$).

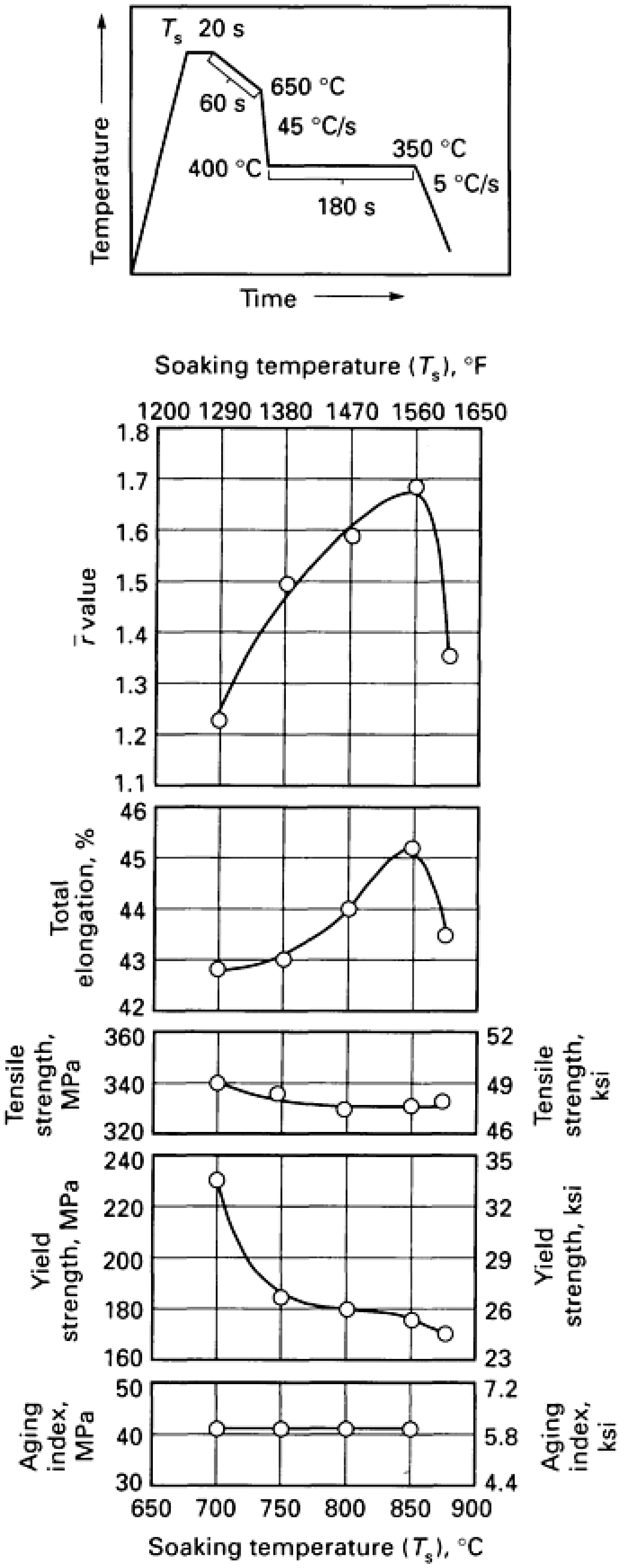


Fig. 6 Effect of soaking temperature on the properties of a 0.035% C steel. The quantity $\bar{r}$ represents the mean of the drawability values taken from measurements in the longitudinal (L), transverse (T), and two 45° (A + B) orientations. $\bar{r} = \frac{1}{4}$ (L + T + 45A° + 45B°). Source:

Ref 2

In a typical modern continuous-annealing line, the antiaging behavior is primarily improved by the adoption of rapid cooling after soaking and overaging, as described earlier. In addition, the heating capacity of the soaking furnace is increased to realize steel temperatures up to about 850 °C (1560 °F). The effect of the soaking temperature on mechanical properties is shown in Fig. 6. Increasing the soak temperature, up to the A_3 temperature, serves to improve formability (total elongation, average $\bar{r}$-value) and lower the yield strength by means of grain growth.

Additional control over steel chemistry and hot-mill processing is required. The influence of carbon content on mechanical properties is shown in Fig. 7. In order to economically achieve the optimum combination of properties, (that is, low strength, high total elongation, *n*- and $\bar{r}$-values, and low strain-aging index), the ideal carbon content is between 0.015 and 0.02%. Reducing the manganese content improves the $\bar{r}$-value. Lowering the nitrogen content to less than about 30 ppm also helps achieve optimum properties by reducing the volume fraction of aluminum nitride (AIN) particles, which inhibit grain growth. A high-temperature hot-mill coiling practice (>700 °C, or 1300 °F) is used (Ref 3) in order to:

- Ensure complete AIN precipitation and hence prevent any nitrogen strain-aging in the product
- Coarsen the AIN particles to promote grain growth during annealing
- Obtain coarse cementite in the hot band with the purpose of realizing strong {111} texture and high $\bar{r}$-value in the final product (Ref 13)

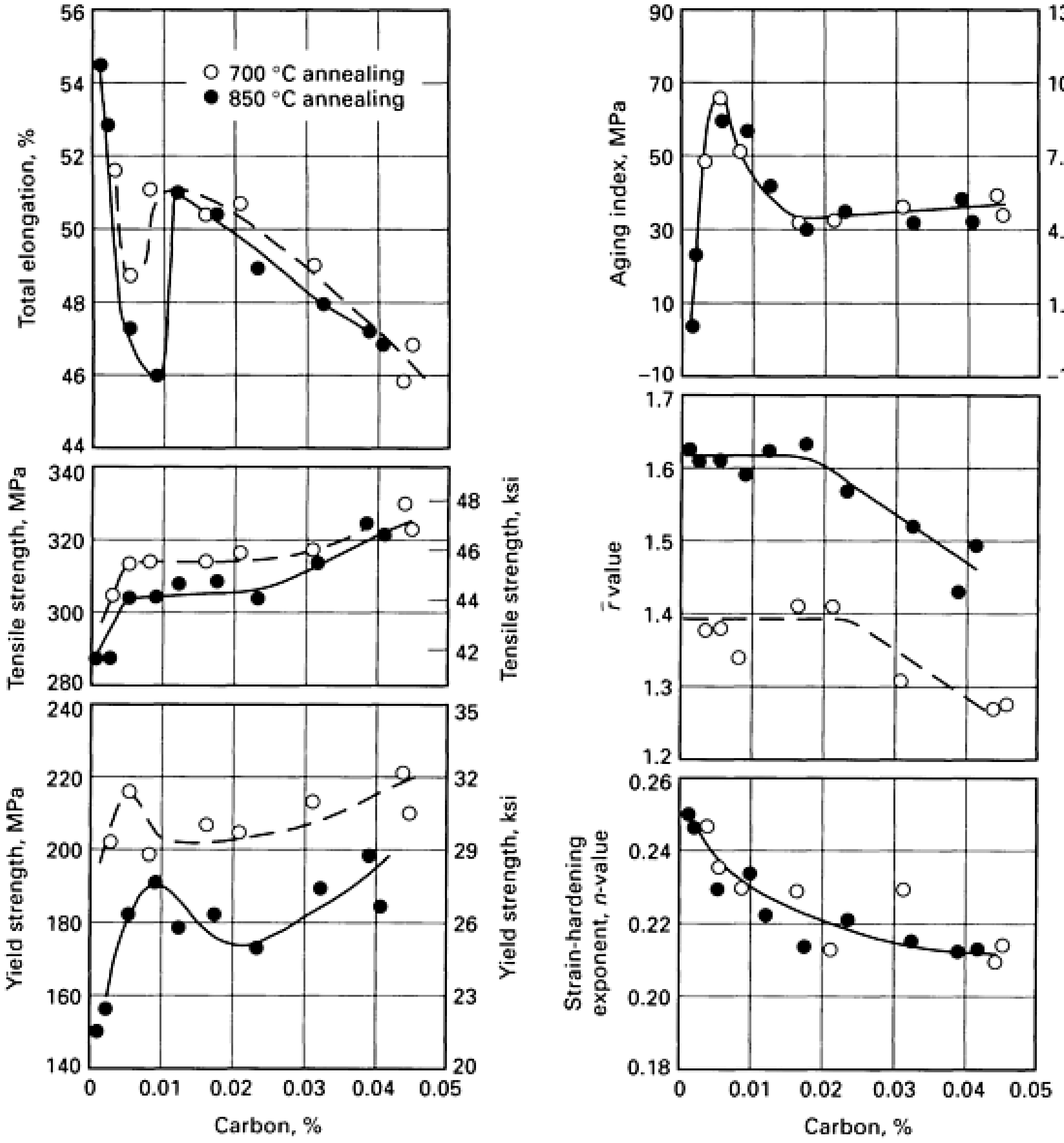


Fig. 7 Influence of carbon content on the mechanical properties of continuously annealed steel sheets. See Fig. 6 for definition of $\bar{r}$ Source: Ref 4

One disadvantage of the high-temperature coiling practice is that faster cooling conditions at the head and tail of the hotrolled coil length lead to insufficient coarsening (compared to the rest of the coil) of the AIN particles and the carbides, resulting in the degradation and nonuniformity of product properties at the coil ends after continuous annealing. This nonuniformity can be rectified by reducing the carbon and nitrogen contents to very low levels, lowering the hot-mill slab soaking temperature to suppress AIN dissolution, or raising the temperature in the head and tail sections by means of differential cooling on the hot-mill runout table (Ref 3).

The deleterious effect of AIN particles in inhibiting grain growth during annealing can be circumvented by the addition of boron (Ref 14). The addition of boron, up to the B:N stoichiometric level, results in a lowering of strength (Fig. 8) without the necessity of resorting to high hot-mill coiling temperatures. However, product with boron added has a low $\bar{r}$-value (Ref 15).

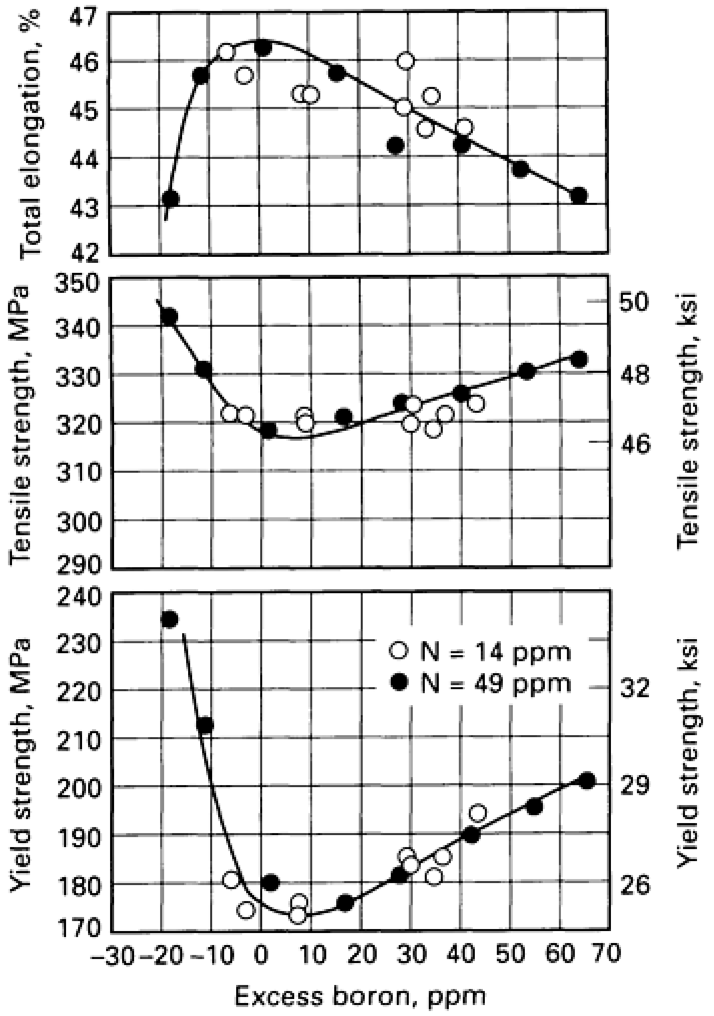


Fig. 8 Effect of boron addition on the tensile properties of a continuously annealed 0.035% C steel. Excess boron = B - 11/14 N. Source: Ref 14

Depending on the chemistry and processing controls used (as described above), the mechanical properties can fall within specific ranges:

- Yield strength, 170 to 250 MPa (25 to 36 ksi)
- Total elongation, 35 to 45%
- $\bar{r}$-value, 1.0 to 1.7

These ranges encompass both DQ and DDQ/DQSK requirements. One exception, however, is that the continuously annealed steels are not totally resistant to carbon strainaging. This is of concern when the temper-rolled product must undergo coil-coating surface treatments that involve curing at elevated temperatures (200 to 300 °C, or 400 to 600 °F), prior to forming. A return of the yield-point elongation can result in stretcher-strain defects during forming. A similar problem is encountered with hot-dip coated steel processed on an annealing and coating line that generally does not have in-line overaging (necessitating postannealing in a batch furnace). In these cases, interstitial-free steels can be used to advantage.

Interstitial-Free Steels. In IF steels, the elimination of interstitials (carbon and nitrogen) is accomplished by adding sufficient amounts of carbide/nitride-forming elements (generally titanium and/or niobium) to tie up carbon and nitrogen completely, the levels of which can be reduced to less than 50 ppm by modern steelmaking/casting practices, including vacuum degassing.

The choice of the microalloying additions (titanium, niobium, or titanium plus niobium) and the hot-mill coiling practice influence the recrystallization temperature (that is, the minimum temperature required on the annealing line to ensure 100% recrystallization) and product properties (Fig. 9). A higher coiling temperature lowers the recrystallization temperature and, in conjunction with heavy cold reduction (~80%), results in superior forming properties. A high annealing temperature is preferred for increased grain growth and high $\bar{r}$-values (Fig. 10). The cooling rate after annealing is not critical, and no overaging treatment is required. Because of this, the IF steels are ideally suited for the production of highly formable, continuously annealed, cold-rolled, hot-dip coated steels.

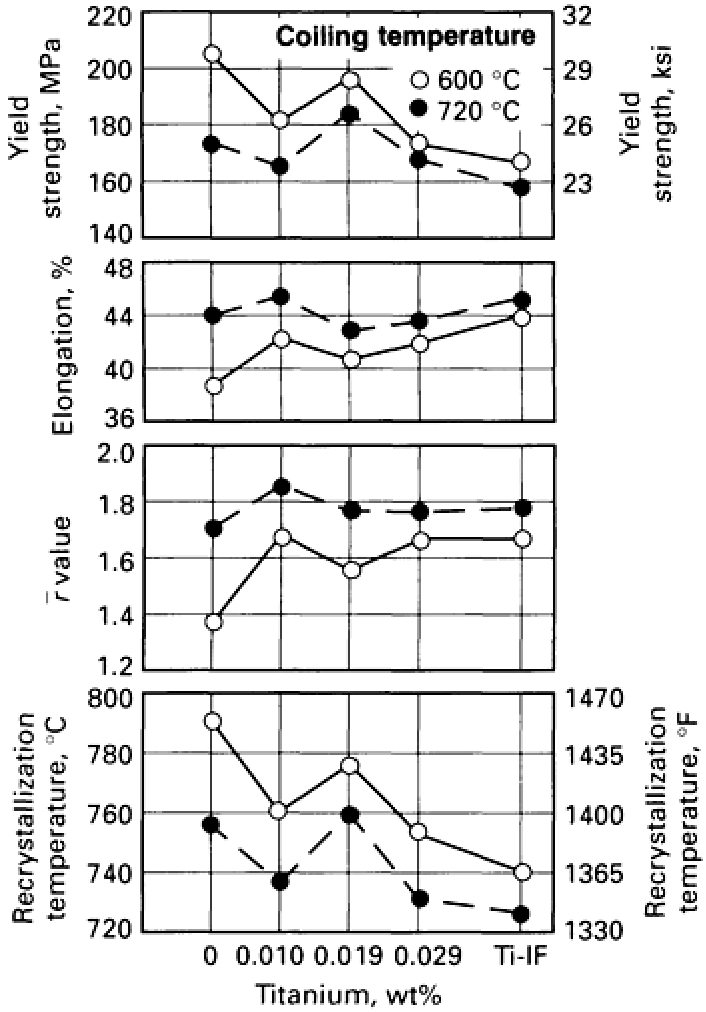
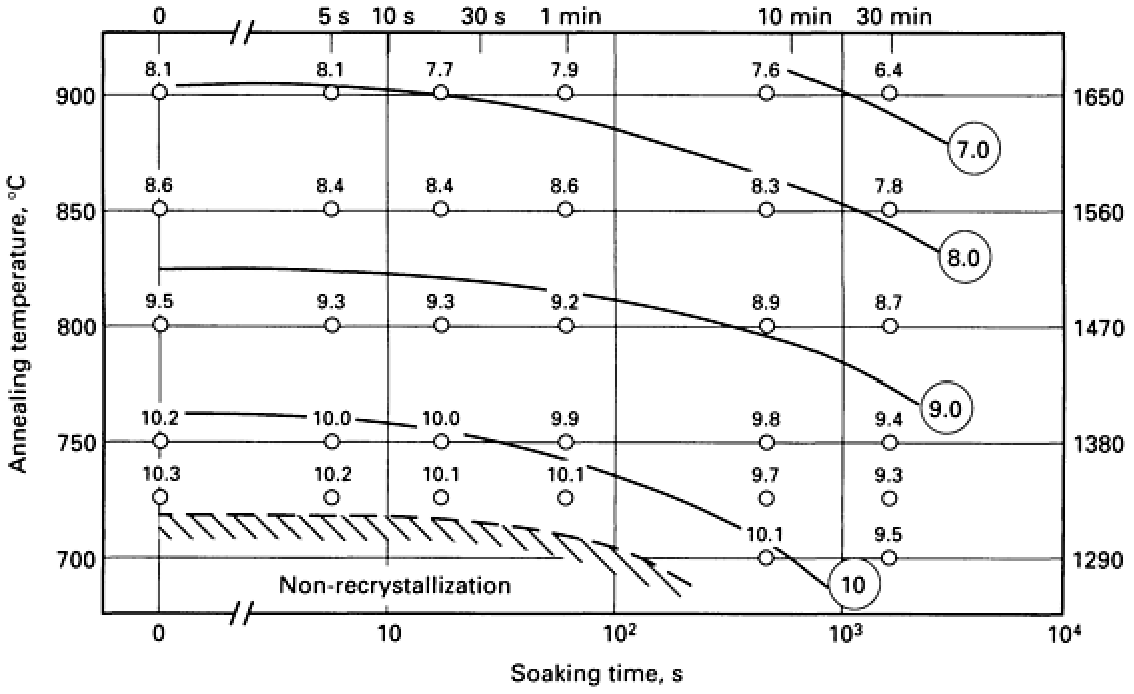
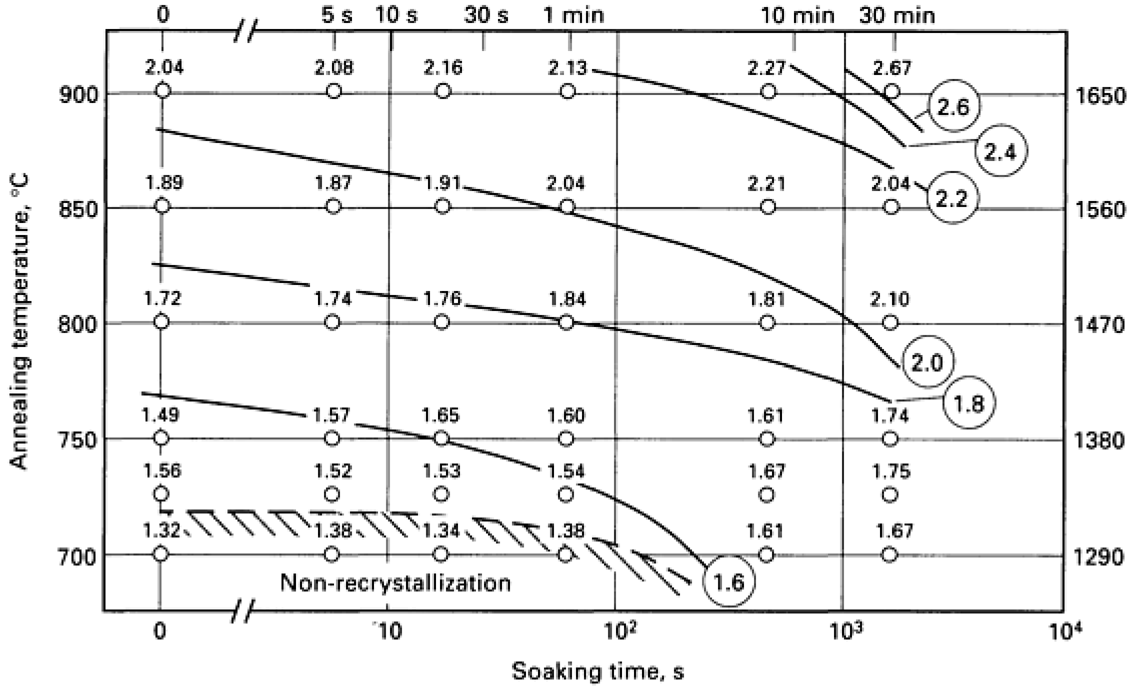


Fig. 9 Dependence of recrystallization temperature and mechanical properties on titanium content and hot-mill coiling temperature for interstitial-free steel (36 ppm C, 35 ppm N, 0.023% Nb, 0.05% Al). Source: Ref 16



(a)



(b)

Fig. 10 Dependence of (a) grain size and (b) $\bar{r}$-value on annealing temperature/time for titanium-stabilized IF steel. In (a), numbers are ASTM grain sizes. In (b), numbers are $\bar{r}$-values. Source: Ref 17

Depending on the processing conditions, the mechanical properties of IF steels fall in the ranges:

- Yield strength, 130 to 170 MPa (19 to 25 ksi)
- Total elongation, 40 to 47%
- $\bar{r}$-value, 1.6 to 2.2

- *n*-value, 0.25 to 0.28

Higher yield strengths up to 300 MPa (34 ksi) are achieved by solid-solution strengthening with phosphorus, manganese, or silicon (Ref 16).

Bake-hardening steels are characterized by their ability to exhibit an increase in yield strength due to carbon strain aging during paint-baking operations at moderate temperatures (125 to 180 °C, or 260 to 355 °F). Bake hardening has little effect on tensile strength.

Plain Carbon Steels. In the continuous annealing of plain carbon steels, the final solute carbon is restricted to less than about 10 ppm by the fine-tuning of the primary cooling rate and the overaging temperature/time (Ref 2, 4) to ensure adequate freedom from ambient strain-aging. This level of solute carbon, however, is sufficient to realize a bake-hardening (175 °C, or 350 °F, for 20 min) yield strength increment of up to 50 MPa (7 ksi) (Ref 18).

In dual-phase steels, the martensite phase ($\leq$20 to 30 vol%) suppresses ambient strain-aging (Ref 19). Accordingly, a higher solute carbon concentration and a consequent larger bake-hardening yield strength increment ($\leq$90 MPa, or 13 ksi) are feasible.

In IF steels, a bake-hardening strength increment can be generated if several conditions are satisfied (Ref 20):

- Nb or Nb-plus-Ti chemistry with a niobium-to-carbon atomic ratio less than or equal to 1
- High annealing temperatures (~850 °C, or 1560 °F) in the continuous-annealing line to permit partial dissolution of the NbC precipitates
- Rapid cooling of $\leq$20 °C/s (35 °F/s) after annealing
- No overaging, in order to prevent the reprecipitation of carbon

In addition, if processed on a hot-dip galvanizing line, rapid cooling between the coating pot temperature and about 200 °C (400 °F) is necessary to circumvent precipitation of the solute carbon as Fe_3C. A bake-hardening yield strength increment of 20 to 40 MPa (3 to 6 ksi) has been reported (Ref 16).

Solution-Strengthened and Microalloyed HSLA Steels (Ref 21, 22, 23, 24). In solution-strengthened steels, alloying additions of manganese, phosphorus, and/or silicon are made to increase strength by substitutional solid-solution strengthening: approximately 3 MPa (0.4 ksi) per 0.1% Mn, 7 MPa (1 ksi) per 0.01% P, and 8.5 MPa (1.2 ksi) per 0.1% Si. These elements are equally effective whether the steel is batch or continuously annealed. With continuous annealing, lower alloying additions are needed to achieve a desired strength level, however, because of the finer ferrite grain size. The finer grain size is a result of, first, the very fast heating rate (compared to batch annealing), which leads to more nucleation, and, in turn, a fine grain size, and second, the short soak time (<1 min), which prevents the growth of the fine recrystallized-ferrite grains. The continuous-annealing thermal profile used to produce solid-solution-strengthened steels consists primarily of a recrystallization annealing followed by overaging, as in the case of DQ and/or DDQ steels.

In microalloyed high-strength low-alloy (HSLA) steels, which contain microadditions of niobium, titanium, or vanadium (niobium is generally preferred), higher strength levels are achieved by precipitation strengthening and grain refinement. In a continuous-annealing process, the microalloy carbonitride particles can provide effective precipitation strengthening because the short annealing time prevents the occurrence of any appreciable particle coarsening. In contrast, the coarsening of the precipitate particles that occurs during batch annealing results in a considerable decrease in the precipitation strengthening, although the particles do retard grain growth to some extent. As a consequence, for the same composition, a higher yield strength is achievable with continuous annealing (Fig. 11).

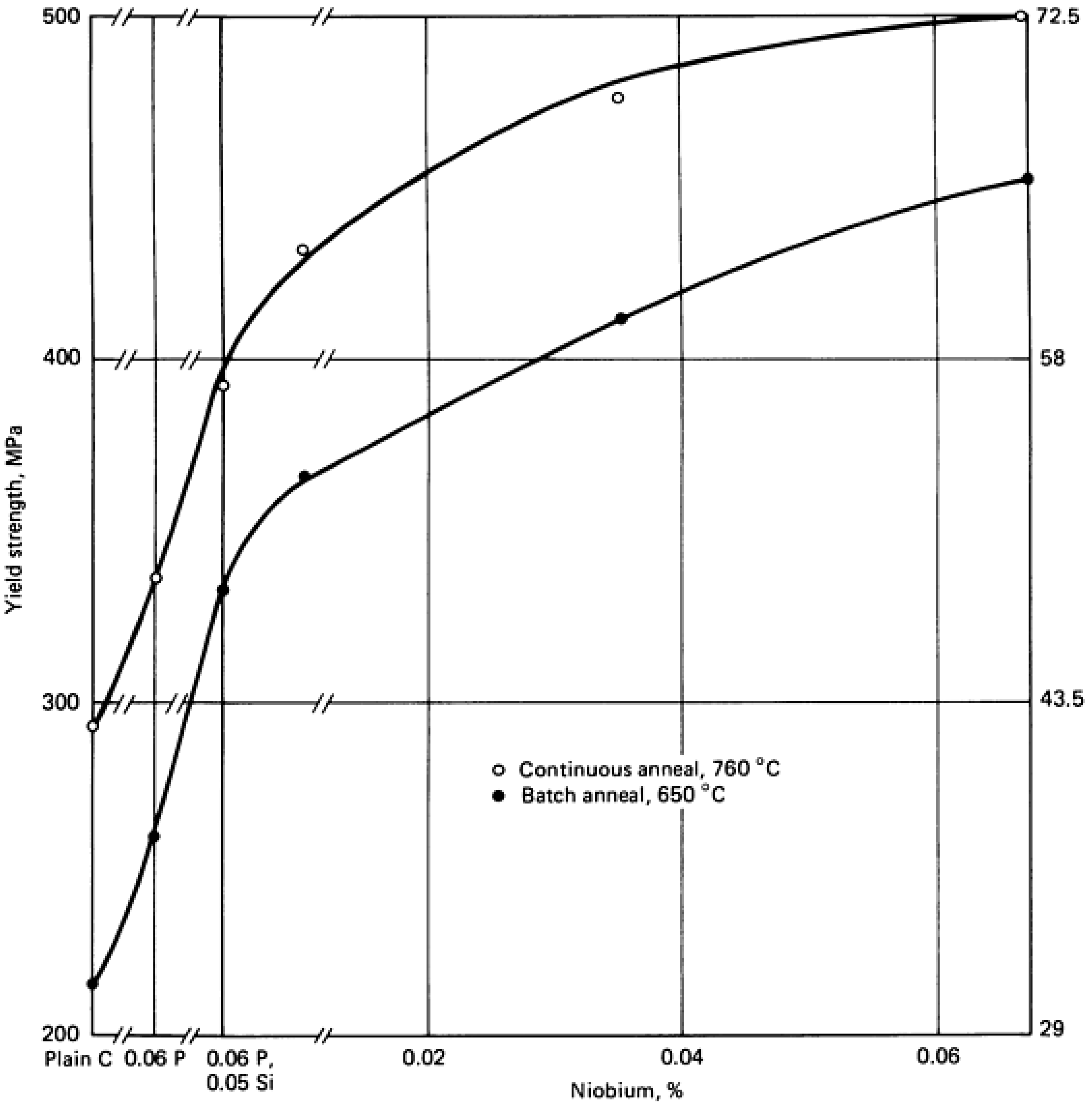


Fig. 11 Comparison of strength levels achievable by means of continuous and batch annealing of solution-strengthened and HSLA steels. Source: Ref 21

The HSLA steels are sensitive to the hot-mill coiling temperature, and a low-temperature coiling practice is preferred to maximize precipitation strengthening. The thermal profile on a continuous-annealing line for microalloyed HSLA steels is similar to that for the solution-strengthened steels. However, the HSLA steels require higher annealing temperatures in order to ensure complete recrystallization because the carbonitride particles of niobium, titanium, and vanadium retard recrystallization (Fig. 12).

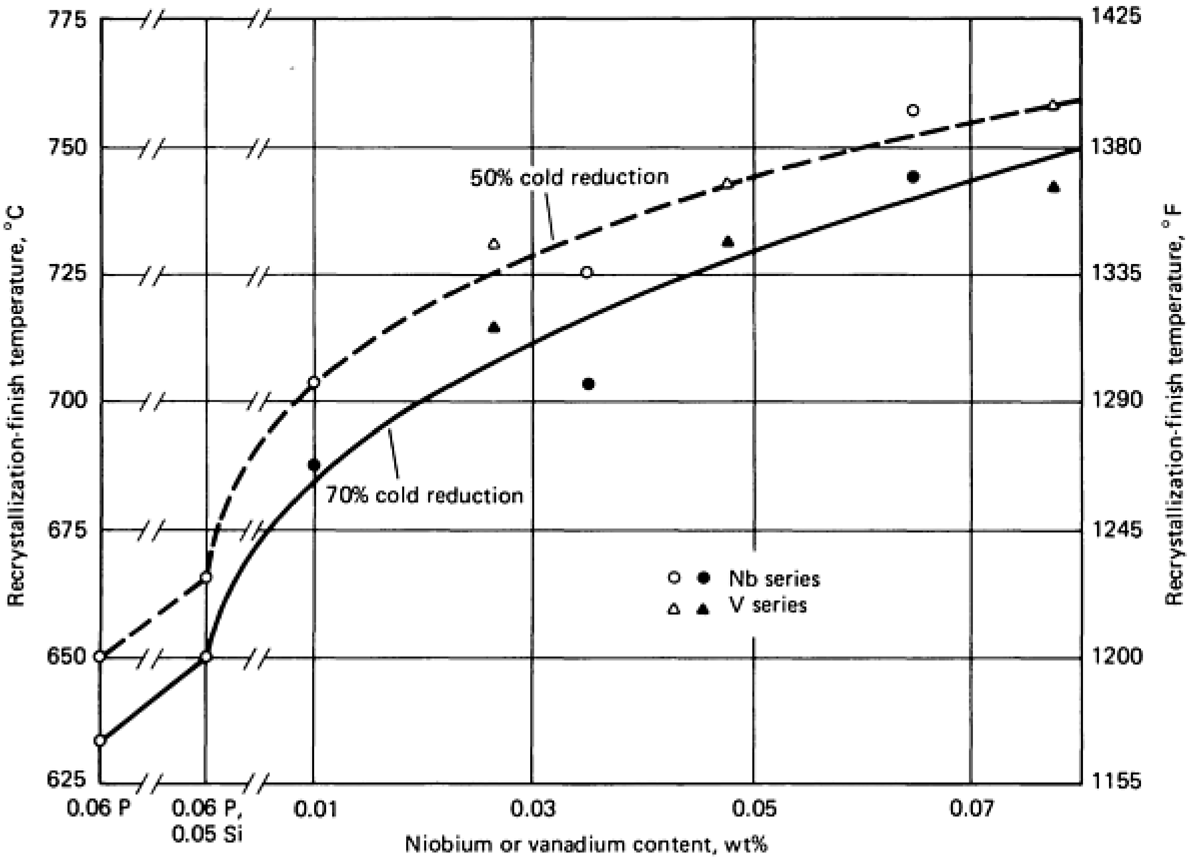


Fig. 12 Variation of recrystallization-finish temperature with alloy content in solution-strengthened and HSLA steels. Source: Ref 22

Yield strength levels ranging from about 280 to 550 MPa (40 to 80 ksi) are possible and practical with solution-strengthened and microalloyed HSLA steels. Yield ratio, that is, the ratio of yield strength to tensile strength, is about 0.8. Like the plain carbon steels, these steels exhibit bake-hardening characteristics.

Recovery-annealed steels, also known as stress-relief annealed steels, can be produced by a low-temperature annealing treatment (Fig. 13) of about 565 °C (1050 °F). High strength levels are achievable by preventing recrystallization (substructure strengthening), while some improvement in ductility can be realized because of the recovery of the cold-worked structure. The substructure strengthening is of the order of 340 MPa (50 ksi), and further increases in strength can be achieved with additions of phosphorus or silicon and also niobium, in a manner similar to that used with the fully recrystallized steels (Ref 24). Yield strengths of commercially available steels range from 600 to 800 MPa (90 to 120 ksi), with a yield ratio of about 0.95.

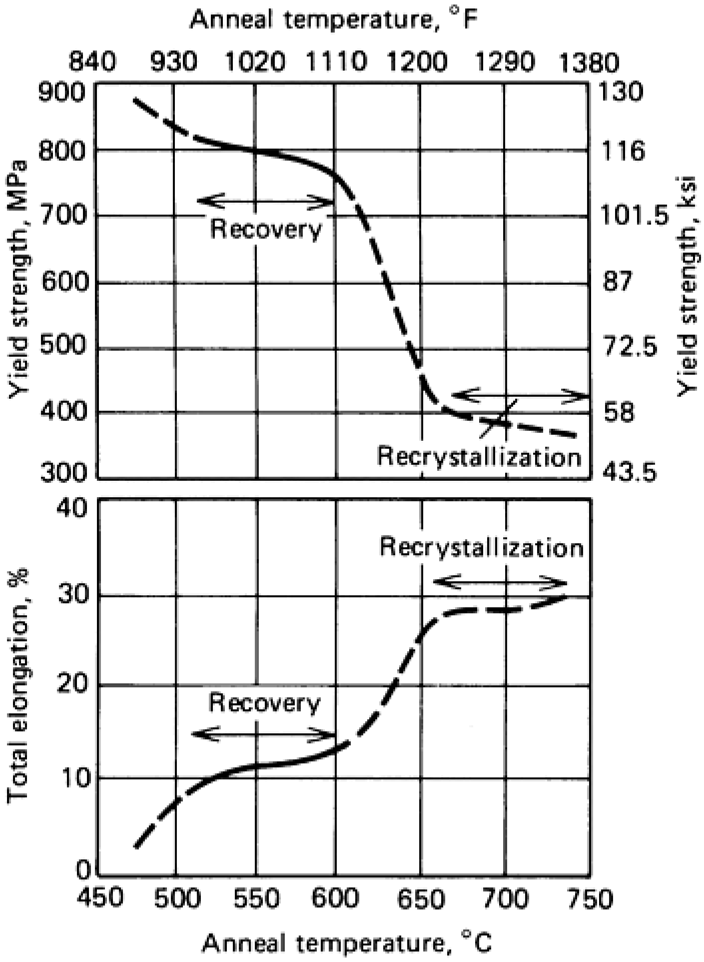


Fig. 13 Tensile properties as a function of anneal (soak) temperature for a 0.06% P, 0.50% Si steel; 70% cold reduction. Source: Ref 23

Dual-Phase Steels. Annealing of dual-phase steels involves soaking in the intercritical or two-phase (ferrite-plus-austenite) region, followed by the transformation of some of the austenite into martensite. The martensite is responsible for the higher strength levels, especially tensile strength, of these steels (Ref 25, 26). To promote the austenite-to-martensite transformation, a critical level of hardenability is needed, depending on the cooling rate. Lower hardenability, from a reduced amount of manganese (and/or molybdenum, chromium) in the steel, can be tolerated with a higher cooling rate (Fig. 14). As described below, there are several types of dual-phase steels, determined by the thermal profile on the annealing line following the intercritical anneal.

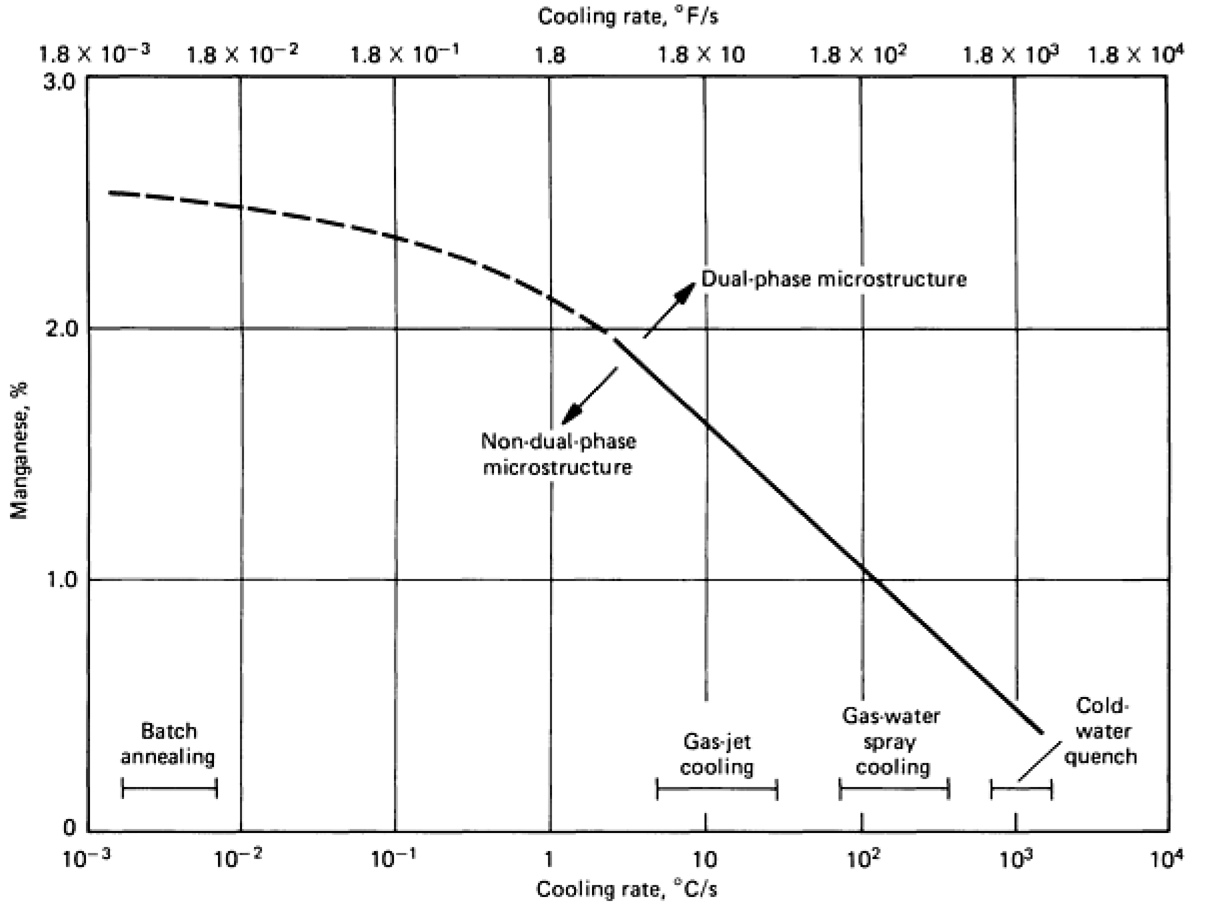
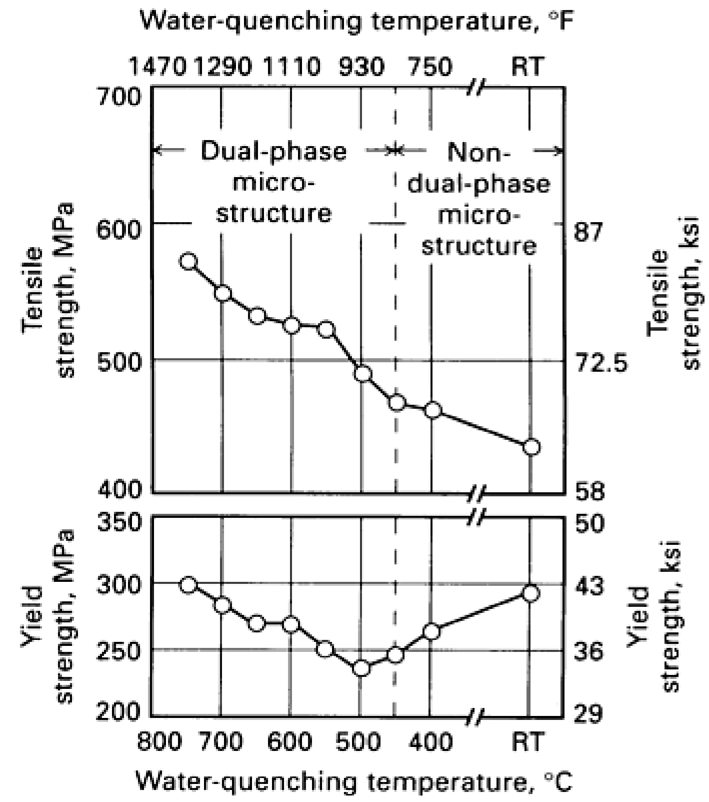


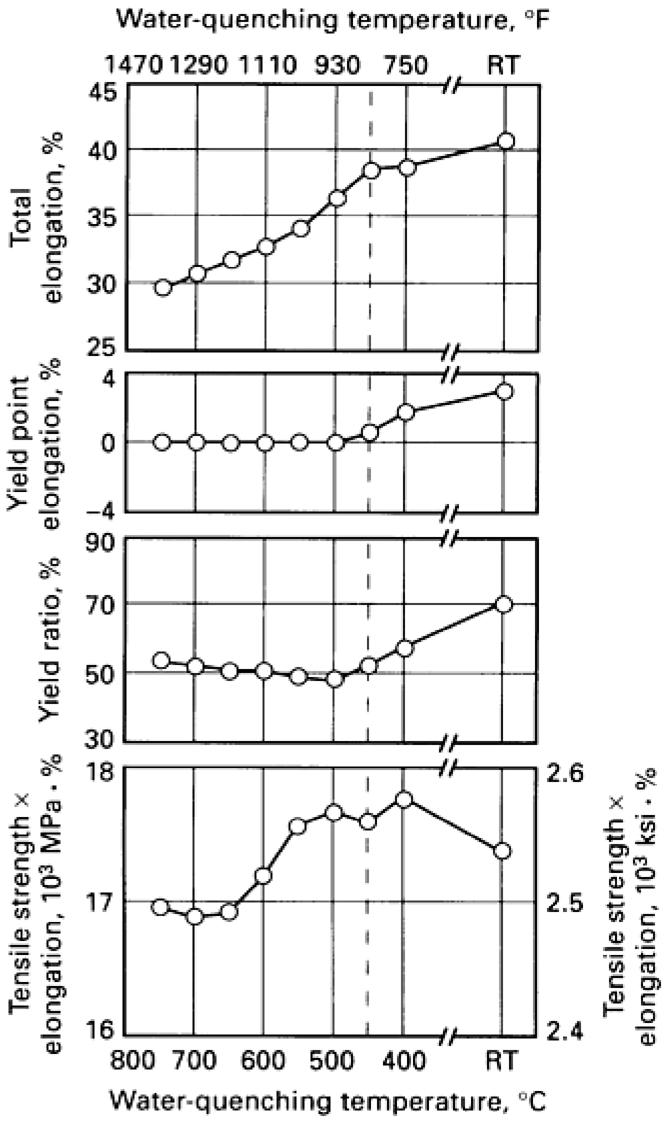
Fig. 14 Effect of cooling rate from the intercritical temperature on the manganese required to form dual-phase microstructures. Source: Ref 1

Quenching from the Intercritical Temperature. The most economical dual-phase steels can be produced by water quenching low-hardenability (0.3 to <1% Mn) steels directly from the intercritical-annealing temperature (>740 °C, or 1365 °F). The overaging treatment tempers the martensite phase and lowers the solute carbon content in the ferrite. Overaging is conducted at 400 °C (750 °F) if ductility is to be maximized or at 260 °C (500 °F) if bake hardenability is to be maximized (Ref 25, 26, 27). The overaging treatment can result in the return of the yield-point elongation, necessitating subsequent temper rolling. Different tensile strength levels (400 to 1200 MPa, or 60 to 170 ksi) are realized by altering the volume fraction of the martensite phase through changes in the carbon content, manganese content, and quenching temperature (Ref 25, 26). Dual-phase steels of this type are characterized by a yield ratio of about 0.7 and, while the $\bar{r}$-value is generally low, it can be improved somewhat by resorting to high hot-mill coiling temperatures, in conjunction with high soak temperatures on the annealing line (Ref 3).

Dual-Phase Steels with Increased Hardenability. Dual-phase steels (tensile strengths of 400 to 1000 MPa, or 60 to 140 ksi) having a low yield ratio (about 0.5), along with a superior tensile strength-ductility combination and strain-hardening behavior (high *n*-value) can be produced by lowering the quenching temperature to about 450 °C (840 °F) (Fig. 15). Because lowering the quench temperature requires gas-jet cooling (~20 °C/s, or 35 °F/s) between the soak and quench stages, the hardenability must be increased by the addition of manganese (Fig. 16). Although the manganese level is generally about 1.6%, partial substitution with molybdenum (for example, 1.3% Mn plus 0.3% Mo) offers some advantages (Ref 29). These types of dual-phase steels can be processed even on a gas-jet cooling line, with similar alloying levels. Overaging is generally restricted to less than about 150 °C (300 °F) and, because the steels are continuous yielding in the as-annealed condition, no temper rolling is required.



Water-quenching temperature, °F
1470 1290 1110 930 750 RT
Dual-phase micro-structure
Non-dual-phase micro-structure
Tensile strength, MPa
Tensile strength, ksi
700
600
500
400
87
72.5
58
350
300
250
200
50
43
36
29
Yield strength, MPa
Yield strength, ksi
800 700 600 500 400 RT
Water-quenching temperature, °C



Water-quenching temperature, °F
1470 1290 1110 930 750 RT
Total elongation, %
45
40
35
30
25
Yield point elongation, %
4
0
−4
Yield ratio, %
90
70
50
30
Tensile strength × elongation, 10³ MPa · %
Tensile strength × elongation, 10³ ksi · %
18
17
16
2.6
2.5
2.4
800 700 600 500 400 RT
Water-quenching temperature, °C

Fig. 15 Mechanical properties of a 1.5% Mn steel versus quenching temperature. RT, room temperature. Source: Ref 28

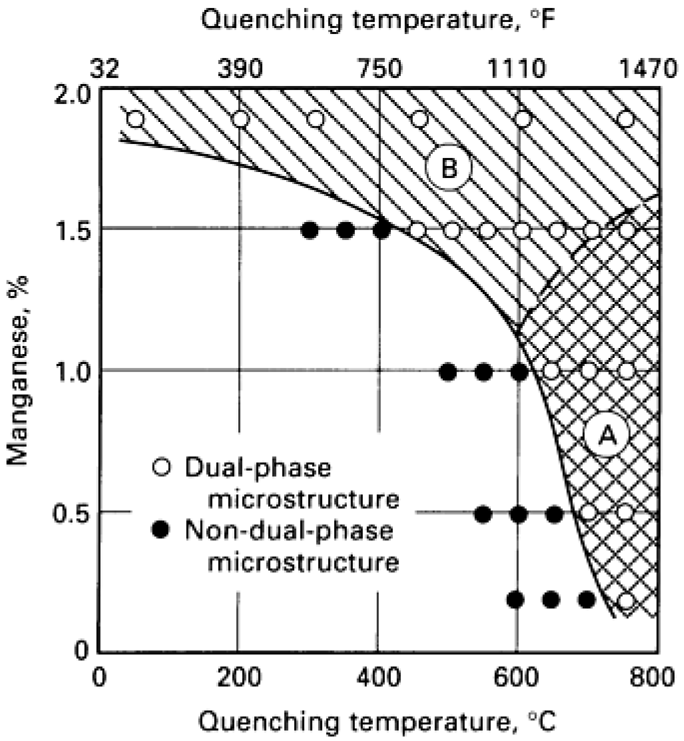


Fig. 16 Relation between quench temperature and the manganese content required to obtain a dual-phase microstructure. A, overaging (tempering) required; B, no tempering required. Source: Ref 3

Fully Martensitic Steel. A related category of steels comprises the fully martensitic steels produced by annealing and water quenching from above the A_3 critical temperature. Ultrahigh tensile strength levels, ranging from 900 to 1500 MPa (130 to 210 ksi), are realized using relatively lean compositions (0.08 to 0.25% C, 0.45% Mn). To ensure a martensitic structure, some boron (10 ppm) is generally added. These steels have very limited ductility. Bendability can be improved by low-temperature (<260 °C, or 500 °F) overaging.

Both the yield and tensile strengths of martensitic steels are primarily determined by the carbon content. The 0.2% yield strength of low-carbon martensite increases with increasing carbon, as shown by (Ref 30):

$$\sigma_{0.2}(\text{MPa}) = 413 + 17.2 \times 10^5 \sqrt{wt\%C} \qquad \textbf{(Eq 1)}$$

Advantages of Continuous Annealing. Paint performance, particularly as it relates to adhesion and corrosion resistance, is dependent on sheet surface cleanliness. The presence of in-line electrolytic cleaning/scrubbing in modern annealing lines, followed by annealing at high temperatures, provides a cleaner surface than is attained for batch-annealed sheet, which is not usually cleaned electrolytically. Continuous-annealed and batch-annealed sheets are compared with regard to surface carbon contamination in Fig. 17.

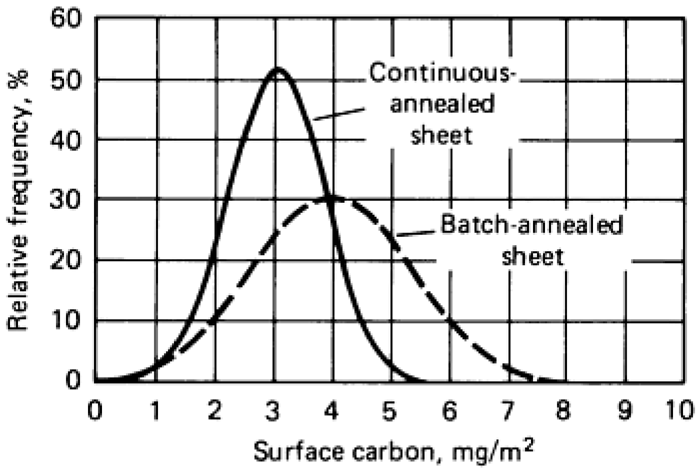


Fig. 17 Comparison of surface carbon contamination on batch- and continuous-annealed sheets. Source: Ref 31

Because a single strand of sheet is annealed on the continuous lines, the control of temperature is better than for batch annealing, and more uniform properties are obtained along the coil length. This is especially true of high-strength steel grades in which the strengthening components--precipitation (HSLA steels), substructure (recovery-annealed steels), and martensite (dual-phase steels)--are dependent on the annealing temperature. For example, in the case of a 420 MPa (60 ksi) yield strength HSLA grade, standard deviations of yield strength are reported to be 10 MPa (1.5 ksi) with continuous annealing, compared to 22 MPa (3 ksi) with batch annealing (Ref 23). For a 700 MPa (100 ksi) yield strength recovery-annealed grade, the standard deviations are 12 MPa (1.7 ksi) with continuous annealing and 31 MPa (4.5 ksi) with batch annealing.

Steels for Tinplate Applications

The conventional tinplate continuous-annealing lines involve soaking at 650 to 700 °C (1200 to 1300 °F), followed by slow gas-jet cooling (~10 °C/s, or 20 °F/s) to the ambient. The T4 (Rockwell Hardness, HR 30T = 61 ± 3) and T5 (HR 30T = 65 ± 3) tempers are being produced on these lines using plain carbon aluminum-killed chemistries.

The production of T2 (HR 30T = 53 ± 3) and T3 (HR 30T = 57 ± 3) tempers by continuous annealing have necessitated several chemistry restrictions and process modifications (Ref 32, 33, 34, 35). The optimum carbon level is 0.02 to 0.07%, with total nitrogen restricted to less than 0.003%. Hotmill coiling is restricted to below 630 °C (1165 °F) to prevent deterioration of corrosion resistance due to the presence of coarse carbides (Ref 32). The effects of pertinent continuous-annealing parameters on black-plate hardness (0.035% C, 0.003% N steel) are shown in Fig. 18. Rapid cooling (40 to 70 °C/s, or 70 to 125 °F/s) from 700 °C (1300 °F), followed by overaging at 400 to 450 °C (750 to 840 °F) for 60 s, is necessary to reduce the carbon concentration solute and, consequently, the hardness. The rapid cooling is achieved by means of high-speed gas-jet cooling systems (Ref 9, 34).

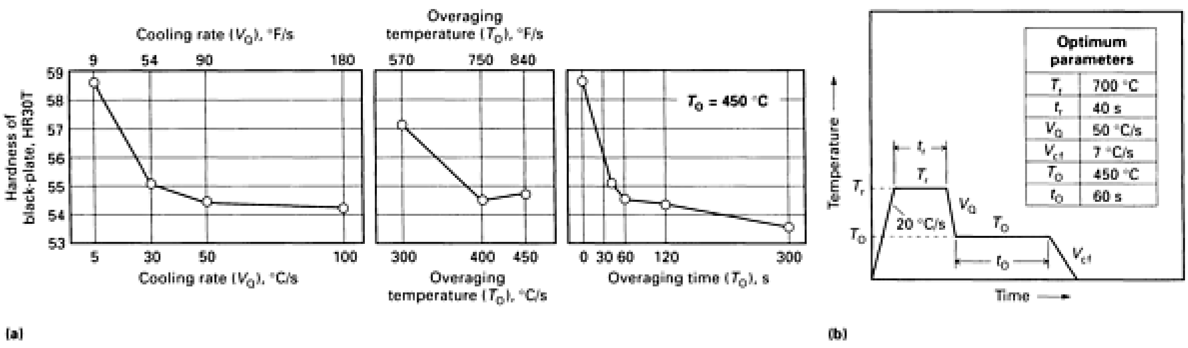


Fig. 18 (a) Effect of annealing-cycle parameters on black-plate hardness of a 0.035% C steel. (b) Heat cycle parameters and optimum

conditions determined from plots shown in (a). Source: Ref 33

Improved hardness distribution in the continuous-annealed T3 product is shown in Fig. 19 (Ref 33). Other advantages over batch-annealed product include improved corrosion resistance as a result of enhanced surface cleanliness and the prevention of surface defects caused by the surface enrichment of carbon and manganese.

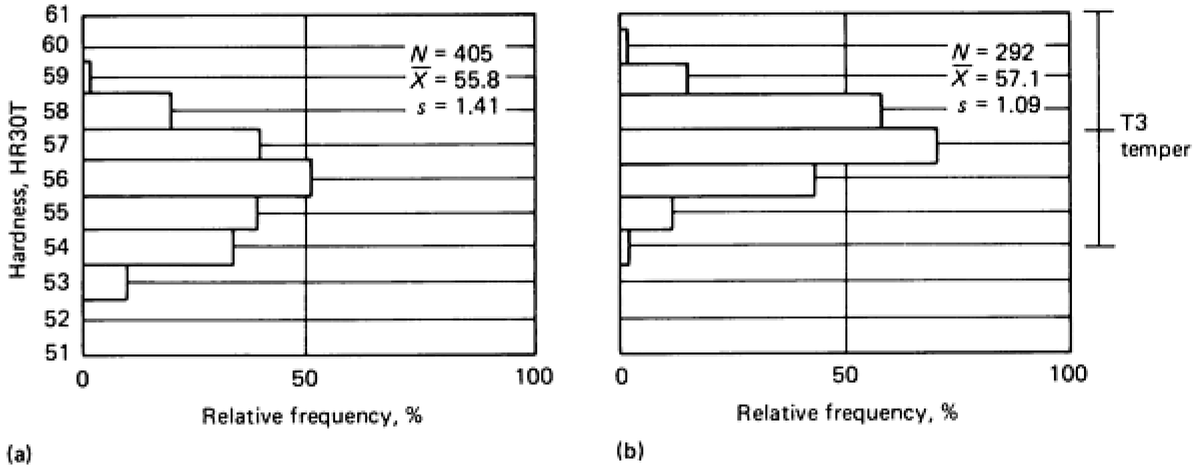


Fig. 19 Comparison of the hardness distribution of T3 tinplate produced by (a) batch annealing and (b) continuous annealing. *N*, number of specimens; *X*, mean; *S*, standard deviation. Source: Ref 33

Steels for Enameling Applications

Specific requirements for steels to be used in porcelain-enameled appliance parts, other than good formability, surface cleanliness, and flatness; include freedom from carbon boil and absence of fish scaling (Ref 1, 36, 37). Carbon boiling is associated with the presence of coarse carbides near the sheet surface that react with the enamel frit and produce carbon monoxide/dioxide bubbles and pits in the enamel surface. The formation of such carbides is unlikely with continuous annealing.

While a low carbon level of 0.015 to 0.02% is desirable from a formability stand-point (Fig. 7), a higher carbon level is preferred in enameling steels to provide resistance to fish scaling, which is the expulsion of enamel fragments caused by the diffusion of hydrogen from the steel. Alternate means of improving the fish scaling resistance include the introduction of BN particles by the addition of boron (30 to 60 ppm) or of TiN/TiS particles by the use of an IF-type chemistry. The second alternative also provides excellent formability.

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Quenching of Steel

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Introduction

QUENCHING refers to the process of rapidly cooling metal parts from the austenitizing or solution treating temperature, typically from within the range of 815 to 870 °C (1500 to 1600 °F) for steel. Stainless and high-alloy steels may be quenched to minimize the presence of grain boundary carbides or to improve the ferrite distribution but most steels including carbon, low-alloy, and tool steels, are quenched to produce controlled amounts of martensite in the microstructure. Successful hardening usually means achieving the required microstructure, hardness, strength, or toughness while minimizing residual stress, distortion, and the possibility of cracking.

The selection of a quenchant medium depends on the hardenability of the particular alloy, the section thickness and shape involved, and the cooling rates needed to achieve the desired microstructure. The most common quenchant media are either liquids or gases. The liquid quenchants commonly used include:

- Oil that may contain a variety of additives
- Water
- Aqueous polymer solutions
- Water that may contain salt or caustic additives

The most common gaseous quenchants are inert gases including helium, argon, and nitrogen. These quenchants are sometimes used after austenitizing in a vacuum.

The ability of a quenchant to harden steel depends on the cooling characteristics of the quenching medium. Quenching effectiveness is dependent on the steel composition, type of quenchant, or the quenchant use conditions. The design of the quenching system and the thoroughness with which the system is maintained also contribute to the success of the process.

Fundamentals of Quenching and Quenchant Evaluation

Fundamentally, the objective of the quenching process is to cool steel from the austenitizing temperature sufficiently quickly to form the desired microstructural phases, sometimes bainite but more often martensite. The basic quenchant function is to control the rate of heat transfer from the surface of the part being quenched.

Quenching Process

The rate of heat extraction by a quenching medium and the way it is used substantially affects quenchant performance. Variations in quenching practices have resulted in the assignment of specific names to some quenching techniques:

- Direct quenching
- Time quenching
- Selective quenching
- Spray quenching
- Fog quenching
- Interrupted quenching

Direct quenching refers to quenching directly from the austenitizing temperature and is by far the most widely used practice. The term direct quenching is used to differentiate this type of cycle from more indirect practices which might involve carburizing, slow cooling, reheating, followed by quenching.

Time quenching is used when the cooling rate of the part being quenched needs to be abruptly changed during the cooling cycle. The change in cooling rate may consist of either an increase or a decrease in the cooling rate depending on which is needed to attain desired results. The usual practice is to lower the temperature of the part by quenching in a medium with high heat removal characteristics (for example, water) until the part has cooled below the nose of the time-temperature-transformation (TTT) curve, and then to transfer the part to a second medium (for example, oil), so that it cools more slowly through the martensite formation range. In some applications, the second medium may be air or an inert gas. Time quenching is most often used to minimize distortion, cracking, and dimensional changes.

Selective quenching is used when it is desirable for certain areas of a part to be relatively unaffected by the quenching medium. This can be accomplished by insulating an area to be more slowly cooled so the quenchant contacts only those areas of the part that are to be rapidly cooled.

Spray quenching involves directing high-pressure streams of quenching liquid onto areas of the workpiece where higher cooling rates are desired. The cooling rate is faster because the quenchant droplets formed by the high-intensity spray impact the part surface and remove heat very effectively. However, low-pressure spraying, in effect a flood-type flow, is preferred with certain polymer quenchants.

Fog quenching utilizes a fine fog or mist of liquid droplets in a gas carrier as the cooling agent. Although similar to spray quenching, fog quenching produces lower cooling rates because of the relatively low liquid content of the stream.

Interrupted quenching refers to the rapid cooling of the metal from the austenitizing temperature to a point above the M_s where it is held for a specified period of time, followed by cooling in air. There are three types of interrupted quenching: austempering, marquenching (martempering), and isothermal quenching. The temperature at which the quenching is interrupted, the length of time the steel is held at temperature, and the rate of cooling can vary depending on the type of steel and workpiece thickness. Comparisons of direct and interrupted quench cycles are shown in Fig. 1.

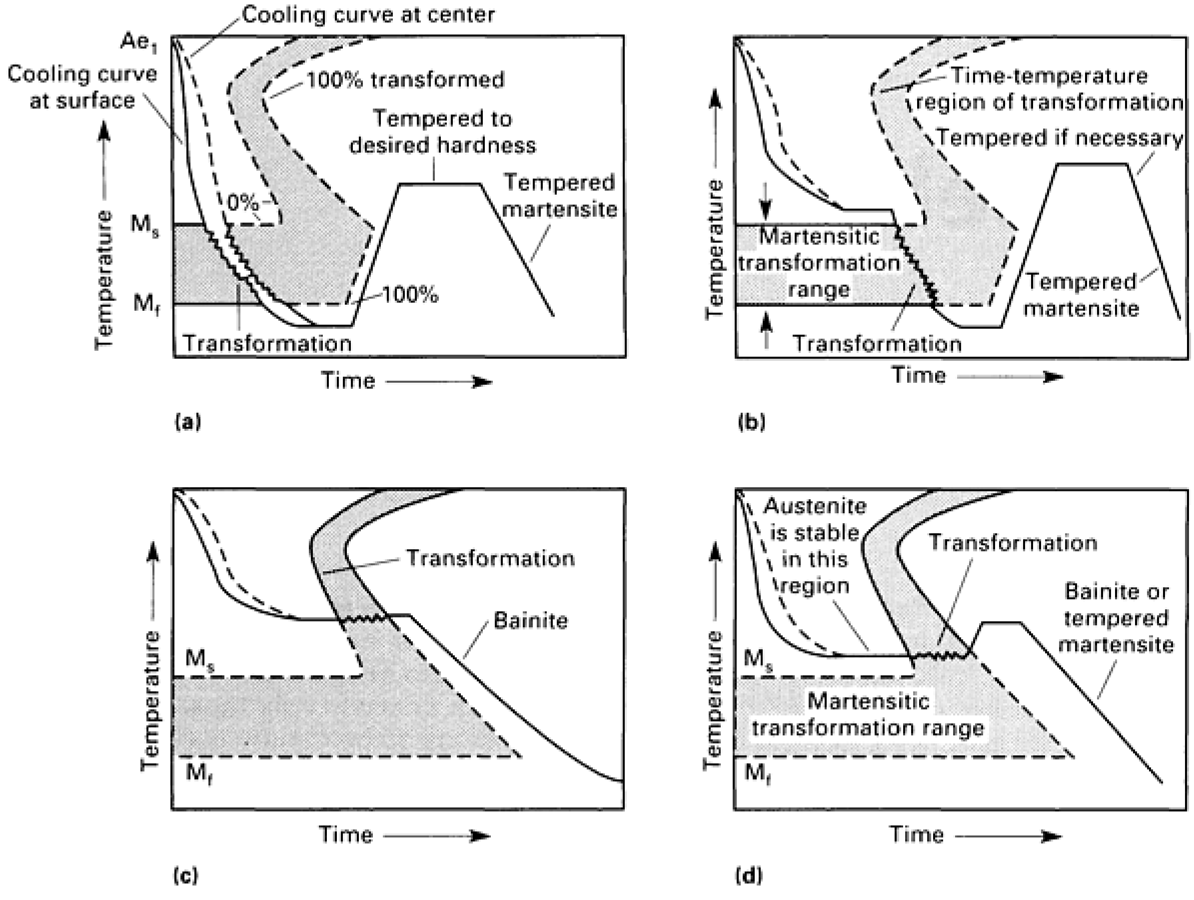

Fig. 1 Comparison of cooling rates and temperature gradients as workpieces pass into and through martensite transformation range for a conventional quenching and tempering process and for interrupted quenching processes. (a) Conventional quenching and tempering processes that use oil, water, or polymer quenchants. (b)

Marquenching, which uses either salt or hot oil as a quenchant. (c) Austempering, which uses a salt as a quenchant. (d) Isothermal quenching, which uses either salt or hot oil as a quenchant. Source: Ref 1

Austempering consists of rapidly cooling the metal part from the austenitizing temperature to about 230 to 400 °C (450 to 750 °F) (depending on the transformation characteristics of the particular steel involved), holding at a constant temperature to allow isothermal transformation, followed by air cooling.

Austempering is applicable to most medium-carbon steels and alloy steels. Low-alloy steels are usually restricted to 9.5 mm ($\frac{3}{8}$ in.) or thinner sections, while more hardenable steels can be austempered in sections up to 50 mm (2 in.) thick.

Molten salt baths are usually the most practical for austempering applications. Oils have been developed that suffice in some cases, but molten salts possess better heat-transfer properties and eliminate the fire hazard.

Marquenching. The marquenching (martempering) process is similar to austempering in that the workpiece is quenched rapidly from the austenitizing range into an agitated bath held near the M_s temperature. It differs from austempering in that the workpiece remains at temperature only long enough for the temperature to be equalized throughout the workpiece. When the temperature has attained equilibrium but before transformation begins, the workpiece is removed from the salt bath and air cooled to room temperature. Oils are used successfully for marquenching, but molten salt is usually preferred because of its better heat-transfer properties.

Cooling from the marquenching bath to room temperature is usually conducted in still air. Deeper hardening steels are susceptible to cracking while martensite forms if the cooling rate is too rapid. Alloy carburizing steels, which have a soft core, are insensitive to cracking during martensite formation, and the rate of cooling from the M_s temperature is not critical.

Marquenching does not remove the necessity for subsequent tempering. The structure of the metal is essentially the same as that formed during direct quenching.

Isothermal quenching is also similar to austempering in that the steel is rapidly quenched through the ferrite and pearlite formation range to a temperature just above M_s. However, isothermal quenching differs from austempering in that two quench baths are employed. After the first quench, and before transformation has time to begin, the workpiece is transferred to a second bath at a somewhat higher temperature where it is isothermally transferred, followed by cooling in air.

Reference cited in this section

1. *Tool and Manufacturing Engineers Handbook,* Vol 3, 4th ed., Society of Manufacturing Engineers, 1985, p 10-25. Originally in *Practical Metallurgy for Engineers,* 5th ed., E.F. Houghton & Co., 1952

Cooling Curves and Processing Effects on Curve Shape

The examination of quenching performance by cooling curve analysis is becoming increasingly popular and perhaps the most informative method of characterizing a quenchant medium. Cooling curves are obtained by quenching a test piece containing one or more thermocouples into a test sample of the quenching fluid, in a laboratory quenching bath, or in the production bath itself. The test piece (probe) may be constructed from the alloy of interest, from an austenitic stainless steel, or a nickel-base alloy such as Inconel. The use of austenitic steel and nickel alloy specimens reduces or eliminates the need for a protective atmosphere while the test pieces are being solution treated. Silver has also been used as the probe material.

The test probes are heated to an elevated temperature and then quenched into the medium of interest. A high-speed recorder is used to record temperature changes with respect to time. The resulting time-temperature curves reflect the heat removal characteristics of the quenching fluid and the mass and surface area of the test probe.

The resulting cooling curves provide information about the cooling rates achieved in the part. Most metallurgical transformation data is presented in terms of the cooling rate needed to achieve a specific microstructure and these rates

can often be related to the cooling rates obtained from quenchant cooling curve analysis. In a given grade of steel, low cooling rates usually produce ferritic microstructures while progressively higher rates produce pearlite, bainite, and finally, martensite. Cooling rates produced by quenchants may be related to specific microstructures, as will be subsequently discussed.

There are generally considered to be three stages of heat removal, referred to as A, B, and C stages, associated with quenching in liquids. A temperature-time cooling curve illustrating the three stages is shown in Fig. 2. This curve was obtained with a 38 mm (1.5 in.) stainless steel probe solution treated at 845 °C (1550 °F) and quenched in unagitated water. The probe had a thermocouple located at the geometric center. A cooling rate curve, which is obtained by taking the first derivative of the time-temperature curve, is also shown.

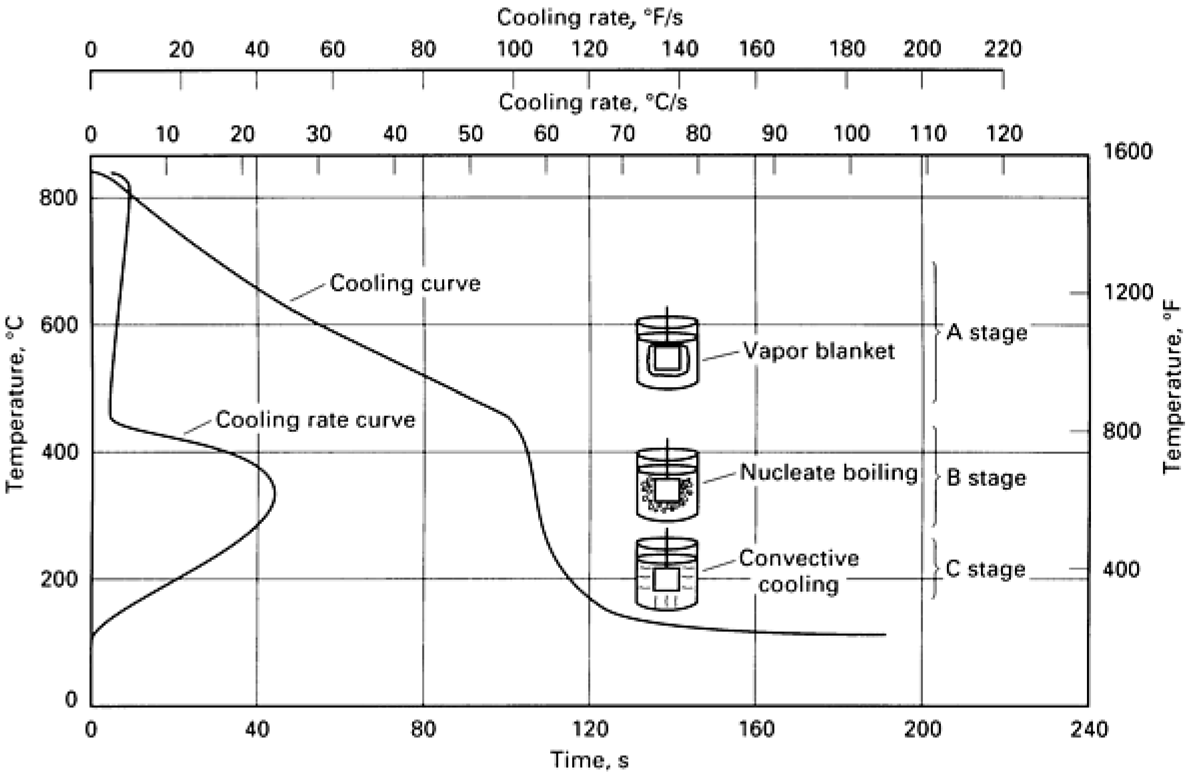

Fig. 2 Cooling curve and cooling rate curve at the center of a 25 mm (1.0 in.) diameter probe quenched with 95 °C (200 °F) water flowing at 15 m/min (50 ft/min)

Stage-A Heat Removal. The first stage of cooling, referred to as the A-stage, is characterized by a quenchant vapor blanket around the part. Stage A, also called the vapor blanket cooling stage, is characterized by the Leidenfrost phenomenon, namely, the formation of a uniform vapor blanket around the test piece. The vapor blanket develops and is maintained while the supply of heat from the interior of the part to the surface exceeds the amount of heat needed to evaporate the quenchant and maintain the vapor phase.

Relatively slow cooling occurs during this period because the vapor envelope acts as an insulator, and cooling occurs principally by radiation through the vapor film. The temperature above which a total vapor blanket is maintained is called the characteristic temperature of the liquid. The characteristic temperature is also known as the Leidenfrost temperature. Beck has shown that the Leidenfrost temperature of a quenchant medium is independent of the initial temperature of the metal being quenched, as illustrated in Fig. 3.

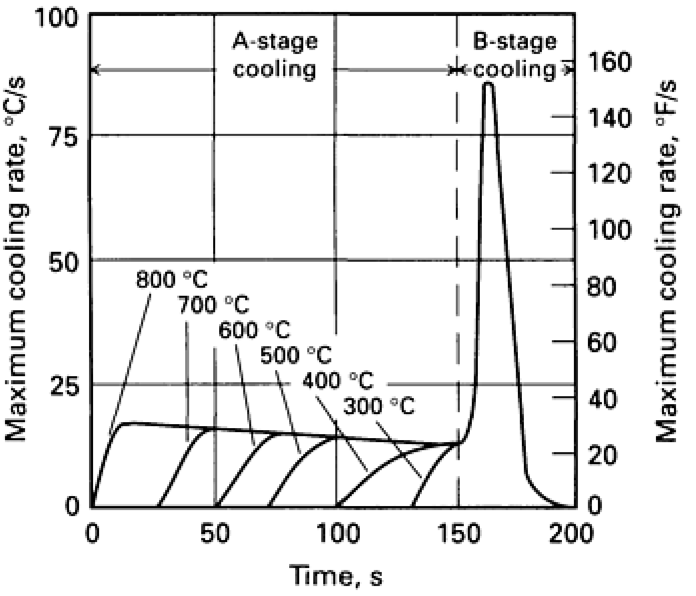

Fig. 3 Cooling rate in a 24 mm ($\frac{15}{16}$ in.) diam by 72 mm ($\frac{27}{32}$ in.) long Inconel 600 probe quenched from temperatures between 300 and 800 °C (570 to 1470 °F) into 100 °C (212 °F) water. Source: Ref 2)

The A-stage of cooling is not usually present in parts quenched in aqueous solutions containing more than about 5 wt% of an ionic material such as potassium chloride, lithium chloride, sodium hydroxide, or sulfuric acid. Cooling curves for these solutions start immediately with stage B. The presence of the salts at the hot metal quenchant interface initiates nucleate boiling almost immediately.

A-stage cooling is not observed when quenching in nonvolatile quenchant media such as molten salt baths. Conversely, heat transfer in gas quenchants such as air and inert gases occurs exclusively by a vapor blanket mechanism.

Stage-B Heat Removal. The highest cooling rates occur in stage B or the nucleate boiling stage. During this period, the vapor envelope collapses, and high heat extraction rates are achieved that are associated with nucleate boiling of the quenchant on the metal surface. Heat is rapidly removed from the surface as liquid quenchant contacts the metal surface and is vaporized.

Stage-C Heat Removal. Stage C is called the liquid cooling stage. Stage C begins when the temperature of the metal surface is reduced below the boiling point of the quenching liquid. Below this temperature, boiling stops and cooling takes place by conduction and convection into the quenchant. C-stage cooling rates are dependent on the viscosity of the quenchant. All other factors being equal, cooling rates decrease with increasing viscosity.

Figure 4 illustrates the three stages of cooling: vapor blanket (A-stage), nucleate boiling (B-stage), and convective (C-stage). These cooling stages are typically obtained when an austenitized steel rod is quenched into an aqueous polyalkylene glycol (PAG) polymer solution. Similar studies have also been performed with other quenchants including water, oil, and other aqueous polymer quenchants (Ref 3, 4, 5).

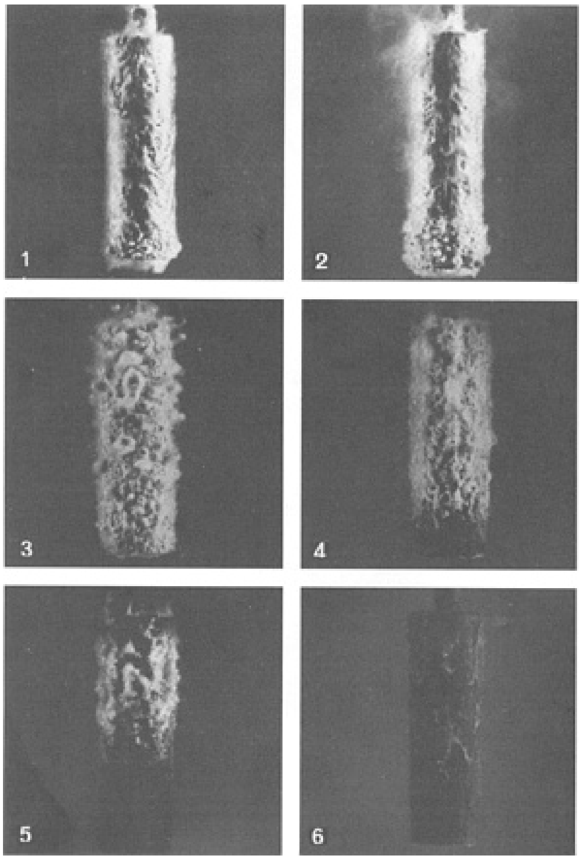

Fig. 4 Photo sequence of a hot steel rod being quenched in a 25% polyalkylene glycol (PAG) polymer in water solution. (1) When the rod is immersed, a polymer film forms on its surface. (2) After 15 s, polymer activates and begins to boil. (3) After 25 s, boiling occurs over the entire rod as the cooling rate increases. (4) After 35 s, boiling collapses and the convection stage begins. (5) After 60 s, the polymer starts to redissolve. (6) After 75 s, polymer film has completely redissolved and the heat removal is achieved entirely by convection.

Agitation refers to liquid quenchant movement relative to the part. Agitation is usually obtained by stirring the liquid, but in some cases it is obtained by moving the part in the liquid. Agitation has an extremely important influence on the heat transfer. Agitation causes mechanical disruption of the vapor blanket in Stage A and a faster transition to B-stage cooling. Increasing agitation usually produces a shorter A-stage cooling time and faster cooling rates in all three regions.

Conversely, higher quench bath temperatures typically produce longer A-stage cooling times and slower cooling rates in the B- and C-stage regions. However, modestly higher temperatures in oil quench baths can improve the heat removal characteristics by reducing oil viscosity. An improvement in quench oil wetting characteristics may be obtained with increasing bath temperature, which results in higher cooling rates. Therefore, the cooling performance of many quench oils is often independent of modest variations in bath temperature.

Nonuniform quenching may result if agitation is not used because of localized hot spots resulting from uneven heat removal from the metal surface. This may lead to spotty hardness, increased surface cracking, distortion, and higher residual stresses.

Factors Affecting Heat Transfer Rate. The rate of heat transfer from a part being quenched may be affected by oxidation of the surface. This can either increase or decrease the heat transfer rate, depending on the thickness of the oxide developed.

The effect of irregular configuration on heat flow from a gear to the quenching area is illustrated in Fig. 5. High temperatures persist near the surface at the roots of the teeth where large vapor bubbles are trapped. If the gear were induction or flame heated, and thus had a uniformly thin heated layer conforming to the contour, quenching would progress more rapidly and uniformly because heat also would flow simultaneously to the cold metal underlying the heated exterior and the quenchant.

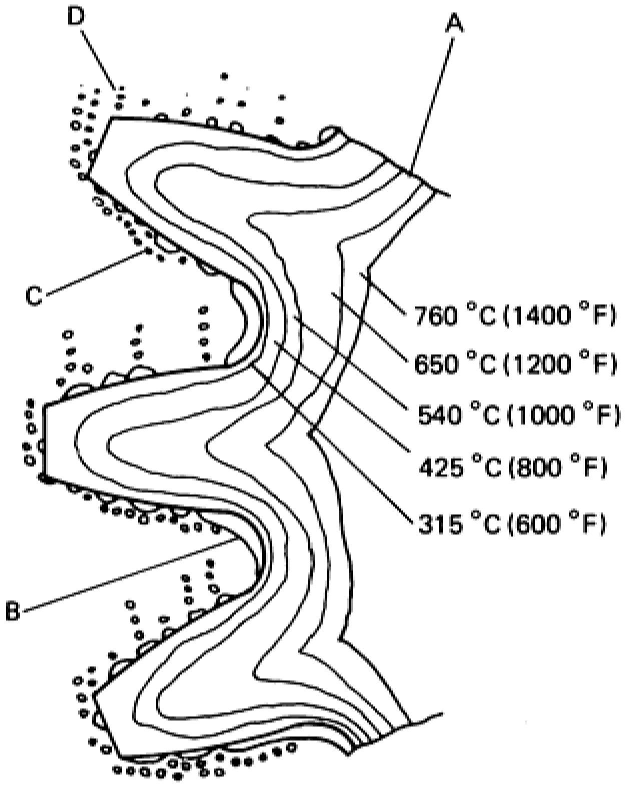

Fig. 5 Temperature gradients and other factors affecting the edgewise quenching of a gear in a quiescent volatile liquid. A, flow of heat from hot core of gear. Temperature and flow rate vary with time; B, vapor blanket stage still exists due to large source of heat and poor agitation; C, trapped vapor bubbles condensing slowly; D, vapor bubbles escaping and condensing

The actual cooling rates and temperature ranges associated with the three stages of cooling vary with the type of quenchant and the mass and surface area of the part being quenched. The highest cooling rates are generally obtained with brine solutions, followed by water, synthetic polymer quenchants, oils, salt baths, fluidized beds, and gases. There are, of course, substantial variations in the attainable cooling rates within particular classes of quenchants depending on the temperature, extent of agitation, viscosity, molecular weight, wetting characteristics, polymer or oil additive concentration, gas pressure, and gas velocity.

The cooling rates are also functions of the thickness and geometry of the part, and characteristics of the quenching facility including the extent of agitation, racking procedure, extent of surface oxidation, and the effective heat transfer coefficient between the part and the quenchant.

The same heat transfer mechanisms involved in cooling test pieces and instrumented probes are involved in quenching parts during a heat-treating operation. Although a particular cooling curve is strictly related only to the size and material of the test piece, thermocouple location in the test piece, and conditions of the quenching liquid under which a test was performed, cooling curves developed under one set of conditions may be translated to other conditions by applying appropriate heat transfer formulas.

Cooling Curve Analysis

An analysis of cooling curves is particularly useful when studying quenchants because they illustrate the mechanisms involved in the quenching process over a wide temperature range. Cooling curves can also be analyzed to provide quantitative heat transfer data as a function of temperature.

Today, it is generally recognized that the cooling rate curve, which is the first derivative of the temperature-time data with respect to time, is probably more informative than the time-temperature curve. Cooling rate curves can be readily

calculated when data are collected using digital recorders or personal computers equipped with an analog-to-digital (A/D) converter.

The heat removal characteristics of a quenchant medium are commonly studied using a standard test piece (probe) which may be a bar, a plate, or a sphere. The most common probe configuration is a cylindrical bar with a length of at least four times the diameter to minimize end cooling effects. A thermocouple is usually located at the geometric center of the probe. For some studies, it may be informative to construct a probe with a second thermocouple located at, or near, the probe surface. This will allow quantification of the temperature change across the test piece during the quenching process.

Two of the more common parameters obtained from cooling curves are the maximum cooling rate ($\dot{T}_{max}$ or CR_{max}) and the cooling rate at about 300 °C (CR_{300}). Usually it is desirable for the CR_{max} to occur at higher temperatures, in the region of the ferrite and pearlite transformation region if maximum hardness is desired, because this minimizes ferrite and pearlite formation. Cooling rates in the region where martensite starts to form from austenite, M_s, should be minimized to reduce the potential for cracking and distortion. The cooling rate at 300 °C (CR_{300}) is often used since this is near the M_s temperature for many carbon and low-alloy steels. Although CR_{max} and CR_{300} temperatures (and other representative values) provide useful descriptions of the quenching process, more comprehensive quantification is often desirable.

Tensi has suggested a set of cooling rate criteria which provides a reasonably complete quantification of the quenching process (see Fig. 6). The values suggested by Tensi include:

- Time (t_u), temperature (T_u), and cooling rate ($\dot{T}_{DHmin}$) where the transition from A-stage to B-stage cooling occurs
- Maximum cooling rate (CR_{max}) and the temperature (T_{max}) where this occurs
- Rate of cooling at defined temperatures where C-stage cooling occurs such as 300 °C (CR_{300}) or 200 °C (CR_{200})

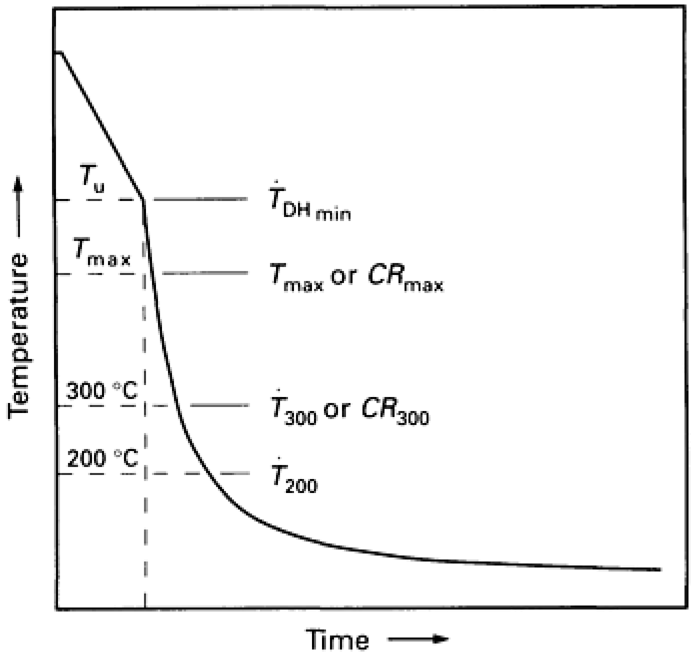

Fig. 6 Critical cooling curve parameters. Source. Ref 6

One of the limitations in the various methods of cooling curve analysis procedures published to date is that very little metallurgical property correlations have been performed. Tensi has addressed this issue by demonstrating that the wettability of a quenchant on a metal workpiece (rewetting time) may be correlated with hardness. A procedure has been developed for obtaining rewetting times by recording cooling curves obtained simultaneously from a probe with multiple

thermocouples (see Fig. 7). These values have been used to develop correlation plots between hardness (HRC) and rewetting time with various steels including an AISI 1045 steel, as illustrated in Fig. 8.

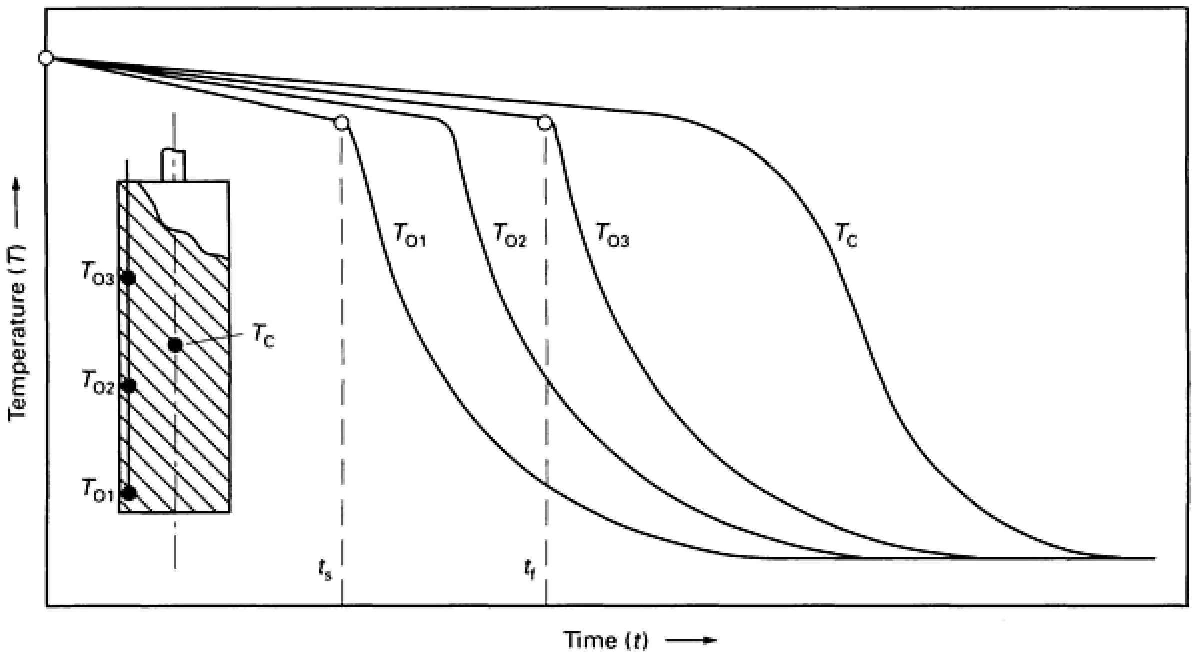

Fig. 7 Wetting kinetics data obtained by using a multiple thermocouple probe. T_c, center thermocouple placement; TO_1, TO_2, and TO_3, outside thermocouple placement

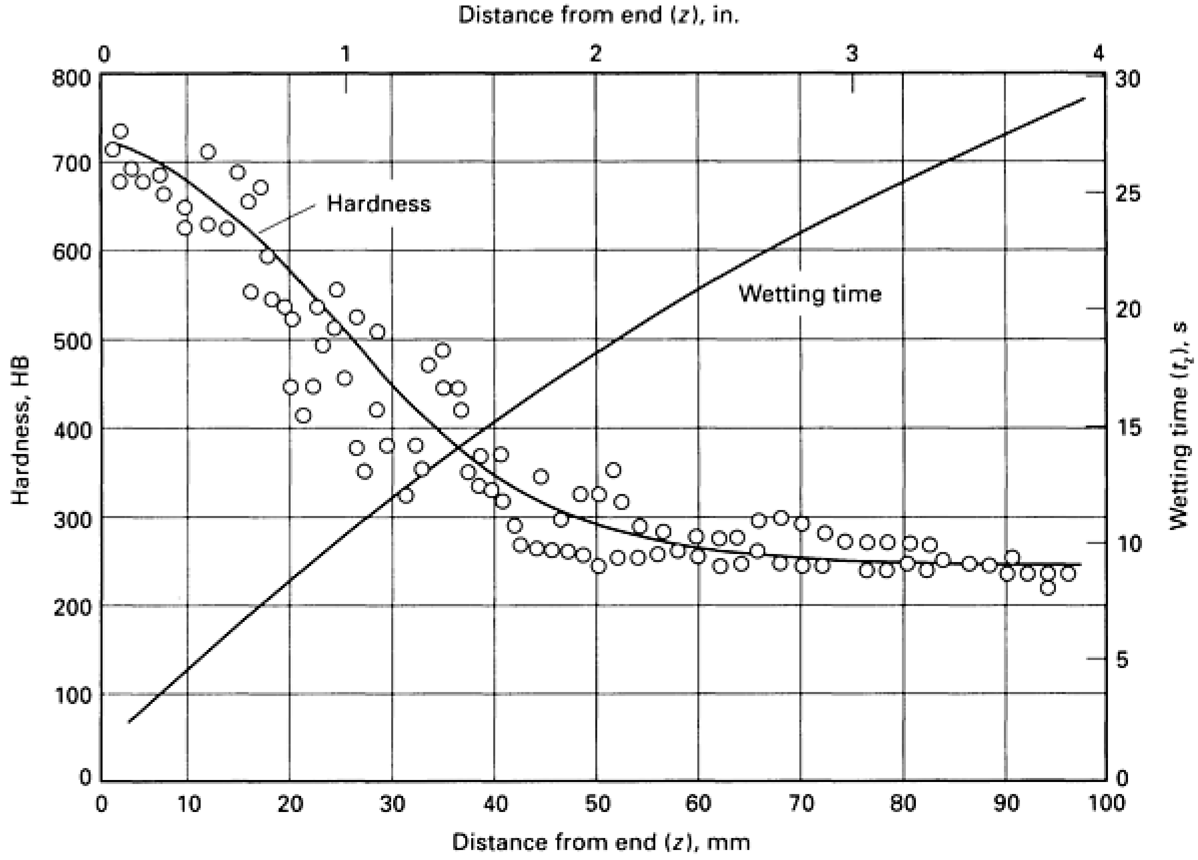

Fig. 8 Wetting time and surface hardness of quenched 1045 steel as a function of the distance from the end of

the specimen. Source: Ref 11

Another method of estimating asquenched hardness of steel from cooling curves is by quench factor analysis (Ref 12). Quench factor analysis permits the direct correlation of the shape of a cooling curve with the appropriate property curve that is developed for the steel of interest. This approach will be described in more detail in the section "Quench Factor Analysis."

Heat Transfer during Quenching. Heat removal from parts during quenching can be mathematically described in terms of the effective interface heat transfer coefficient. A quenchant must impart a sufficiently high interface heat transfer coefficient to produce a cooling rate that will minimize transformation of austenite to ferrite or pearlite and yield the desired amount of martensite or bainite.

The interface heat transfer coefficient is defined as:

$$h = \frac{q}{A\ (T_1 - T_2)} \qquad \textbf{(Eq 1)}$$

where h is the interface heat transfer coefficient; q is the heat flow from the part to the quenchant; A is the part area; T_1 is the part surface temperature; and T_2 is the bath temperature.

A similar ratio, more widely used in steel quenching, is the Grossmann number (H) defined by the following equation:

$$H = \frac{h}{2k} \qquad \textbf{(Eq 2)}$$

where k is the conductivity of the metal.

Thus, the interface heat transfer coefficient is equal to the Grossmann number multiplied by twice the thermal conductivity of the metal.

The interface heat transfer coefficient under conditions of interest can be determined by recording a cooling curve using a thermocouple located in the center of cylindrical test probes, determining the cooling rate over a particular temperature interval (such as 595 to 705 °C, or 1100 to 1300 °F) from the cooling curve, and using this value in a polynomial expression that relates the cooling rate to the interface heat transfer coefficient. This approach provides an effective interface heat transfer coefficient over a temperature range that brackets the nose of most TTT curves. If the effective heat transfer coefficient is divided by twice the thermal conductivity, the Grossmann *H*-factor can be obtained.

Table 1, published in 1947, provides Grossmann numbers for selected quenchants. This table has provided valuable guidance to heat treaters since its publication in spite of the fact that quenchant velocities were not well defined.

Table 1 Approximate Grossmann quenching severity factor of various media in the pearlite temperature range

Circulation or agitation	Grossmann quench severity factor, *H*			
	Brine[a]	Water[a]	Oil[a] and salt	Air[b]
None	2	0.9-1.0	0.25-0.30	0.02
Mild	2-2.2	1.0-1.1	0.30-0.35	. . .

Moderate	. . .	1.2-1.3	0.35-0.40	. . .
Good	. . .	1.4-1.5	0.4-0.5	. . .
Strong	. . .	1.6-2.0	0.5-0.8	. . .
Violent	5	4	0.8-1.1	. . .

Source: Ref 15

(a) Ref 3.

(b) Ref 14.

Often a heat treater requires a more precise estimate of the Grossmann quench severity factor (*H*-factor) of the quench bath than attainable from Table 1. For example, many of the recently introduced software packages for predicting as-quenched hardness require an input of an *H*-factor in order to predict as-quenched hardness, and so on. Therefore, a relatively simple method of estimating the *H*-factor would be particularly valuable.

An algorithm was recently published which permits the estimation of the *H*-factor directly from cooling curve data (Ref 16). The algorithm has the general form:

$$H = A(CR_{1300})^{C} \exp(BX^{D}) \qquad \textbf{(Eq 3)}$$

where CR_{1300} is the cooling rate at 705 °C (1300 °F) obtained with a type 304 stainless steel probe and *A*, *B*, *C*, and *D* are statistical curve fitting parameters given in Table 2. Models have been developed that permit the estimated *H*-factors obtained from 13, 25, 38, and 50 mm (0.5, 1.0, 1.5, and 2.0 in.) diameter cylindrical AISI type 304 stainless steel probes from the cooling rate, as illustrated in Fig. 9.

Table 2 Model parameters used to calculate the *H*-factor

Probe diameter		**Model parameters**			
mm	**in.**	***A***	***B***	***C***	***D***
12.7	0.5	0.002802	0.1857×10^{-7}	1.201	2.846
25.4	1.0	0.002348	0.2564×10^{-9}	1.508	4.448
38.1	1.5	0.002309	0.5742×10^{-9}	1.749	5.076
50.8	2.0	0.003706	0.3546×10^{-10}	1.847	6.631

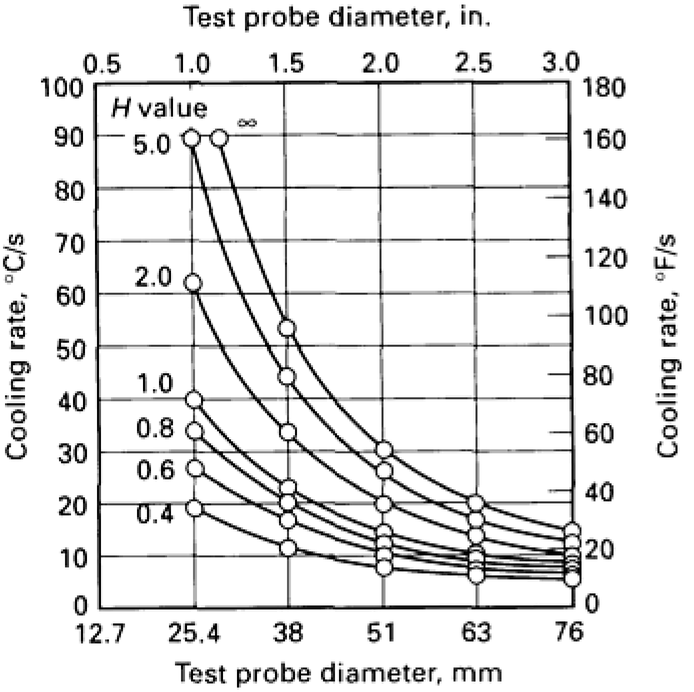

Fig. 9 Calculation of the Grossmann constant, *H,* from cooling rate data at a temperature of 705 °C (1300 °F)

The severity of a quenchant medium is dependent on its ability to mediate heat transfer at the hot metal interface during quenching. Quenchant data obtained by cooling curve analysis is presented in Table 3 for water, fast oil, conventional oil, martemper oil, a 25% solution of an aqueous polyvinyl pyrrolidone polymer quenchant, and air at selected temperatures and velocities . As previously discussed, substantial variations in cooling characteristics may occur depending on the exact formulation of the quenchant and quenchant use conditions. One of the most valuable features of this data is that it illustrates how the heat transfer coefficients vary depending on use conditions. The primary function of a quenchant after all, is to mediate heat transfer from the metal to the quenchant during the quenching process.

Table 3 Grossmann numbers and film coefficients for selected quenchants

Quenchant	Quenchant temperature		Quenchant velocity		Grossmann number, ($H = h/2k$)	Effective film coefficient	
	°C	°F	m/s	ft/min		$W/m^2 \cdot K$	$Btu/ft^2 \cdot h \cdot °F$
Water	32	90	0.00	0	1.1	5000	880
			0.25	50	2.1	9000	1600
			0.51	100	2.7	12000	2100
			0.76	150	2.8	12000	2100
	55	130	0.00	0	0.2	1000	180

			0.25	50	0.6	2500	440
			0.51	100	1.5	6500	1100
			0.76	150	2.4	10500	1850
Fast oil	60	140	0.00	0	0.5	2000	350
			0.25	50	1.0	4500	790
			0.51	100	1.1	5000	880
			0.76	150	1.5	6500	1200
25% polyvinyl pyrrolidone	43	110	0.00	0	0.8	3500	620
			0.25	50	1.3	6000	1100
			0.51	100	1.5	6500	1200
			0.76	150	1.8	7500	1300
Conventional oil	65	150	0.51	100	0.7	3000	530
Martempering oil	150	300	0.51	100	1.2	5000	880
Air	27	80	0.00	0	0.05	200	35
			2.54	500	0.06	250	44
			5.08	1000	0.08	350	62

Source: Ref 12

The data in Table 3 show that unagitated water at 32 °C (90 °F) has a Grossmann number of about 1 and an interface heat transfer coefficient of about 5000 W/m^2 · K. The effective interface heat transfer coefficient produced by 32 °C (90 °F) water increased to 9000 and 12,000 W/m^2 · K (1600 and 2100 Btu/ft^2 · °F) at velocities of 0.25 and 0.50 m/s (50 and 100 ft/min), respectively. High heat transfer coefficients produce more rapid cooling. Cold water, a relatively severe quenchant, may produce high thermal gradients from the surface to the center of parts and large temperature differences between thick and thin sections that can lead to an increase in distortion or cracking.

The effective interface heat transfer coefficient produced by water generally decreases with increasing water temperature. Unagitated water at 55 °C (130 °F) had an interface heat transfer coefficient of about 1000 W/m^2 · K (180 Btu/ft^2 · h · °F) A water velocity of 0.76 m/s (2.5 ft/s) increased the interface heat transfer coefficient of the 55 °C (130 °F) water to 10,500 W/m^2 · K (1850 Btu/ft^2 · h · °F)

The benefit of knowing or experimentally determining interface heat transfer coefficients produced by specific quenchants under known conditions is that these values can be used in finite element or finite difference heat transfer programs to calculate cooling curves in parts or sections of a part that have not actually been instrumented. These calculated cooling curves can then be used to estimate the as-quenched hardness in these locations.

Quench Intensity. Liščić and Filetin (Ref 17), Wünning (Ref 18), Tensi (Ref 19), and others have developed processes for evaluating quenchant severity (intensity) that is applicable for both the heat-treating plant and for laboratory quenching studies. Liščić's approach is based on a technique for determining the heat flux at the surface of a part during quenching by measuring the temperature gradient from the surface to the center of a 50 mm (2 in.) diameter by 200 mm (8 in.) long test probe. The best probe is illustrated in Fig. 10.

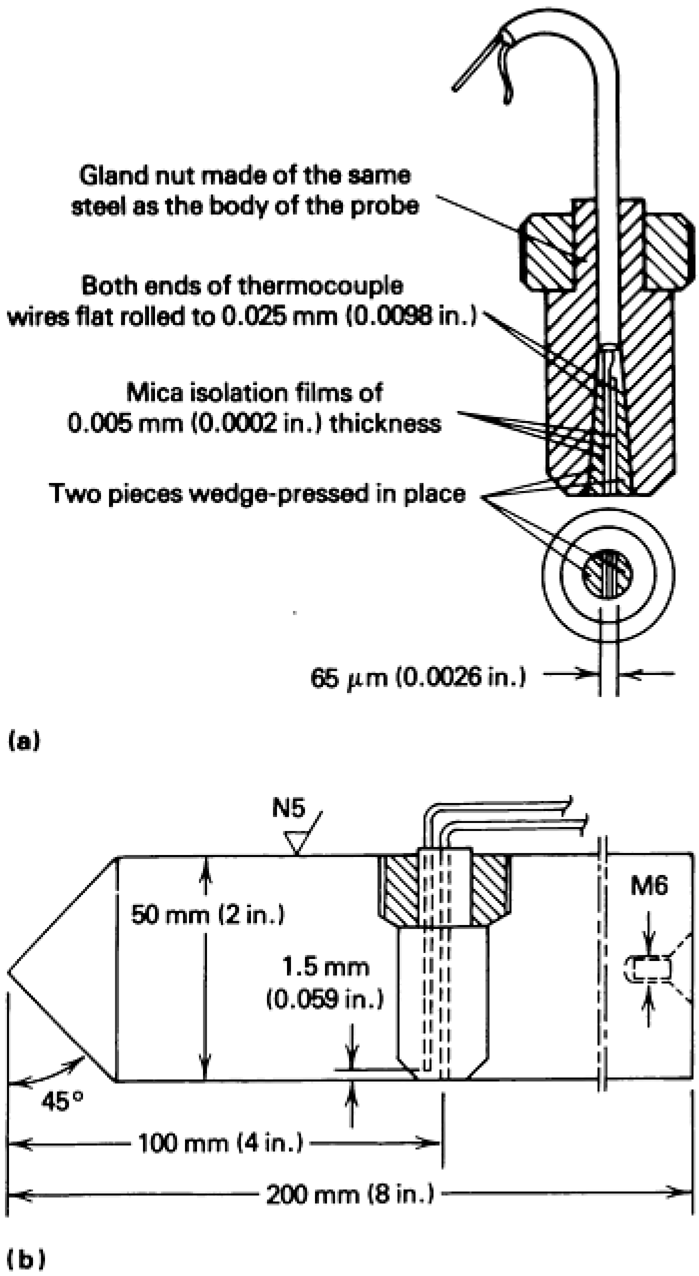

Fig. 10 Schematic of a Liščić-NANMAC probe that incorporates fast-response thermocouples to provide transient thermal measurements of metal surface temperatures. (a) Probe construction. (b) Probe installed in a test specimen

Calculation of cooling curves obtained using this probe is based upon the algorithm:

$$\phi = \lambda\left(\frac{\partial T}{\partial n}\right) \quad \textbf{(Eq 4)}$$

where *f* is the heat flux (W/m^2); λis the thermal conductivity of the probe material (W/m · K); and ∂ *T* is the temperature gradient across the probe perpendicular to the surface ∂ *n* (K/m). Typical cooling curve and heat flux output for water and mineral oil at 20 °C (70 °F) are shown in Fig. 11(a) and 11(b), respectively.

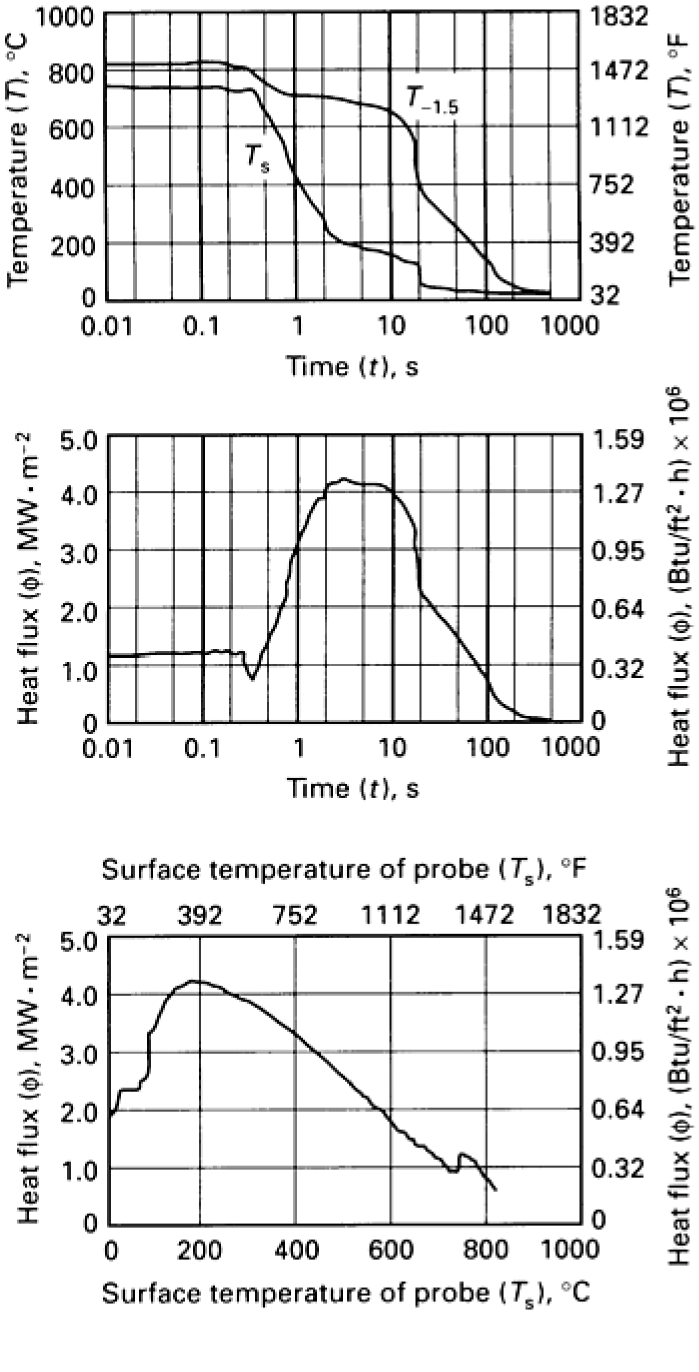

Fig. 11(a) Heat transfer characteristics of unagitated tap water at 20 °C (70 °F). Top: Recorded cooling curves for the very surface of the probe, T_s, and for the point 1.5 mm (0.059 in.) below the surface $T_{-1.5}$, during quenching in plain water at 20 °C (70 °F) without agitation. Middle: Relevant heat flux versus surface temperature curve. Bottom: Heat flux versus surface temperature curve

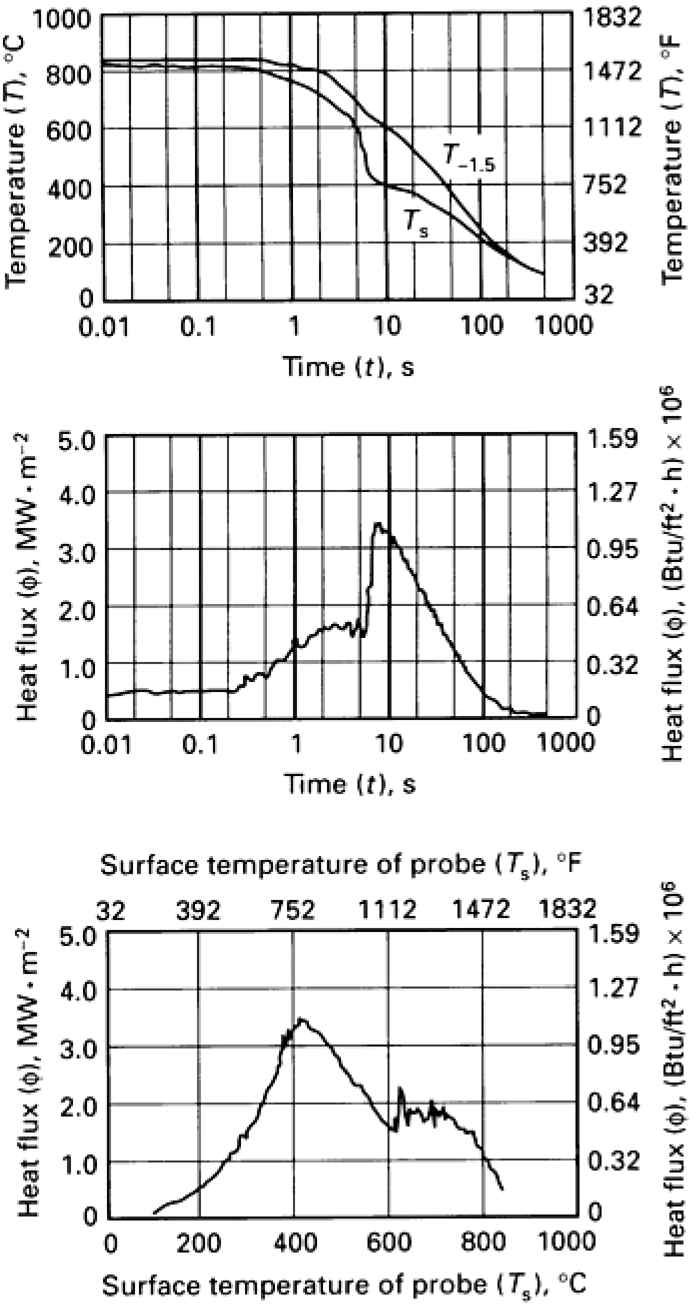

Fig. 11(b) Heat transfer characteristics of unagitated mineral oil at 20 °C (70 °F) Top: Recorded cooling curves for the very surface of the probe, T_s, and for the point 1.5 mm (0.059 in.) below the surface $T_{-1.5}$, during quenching in mineral oil at 20 °C (70 °F) without agitation. Middle: Relevant heat flux versus surface temperature curve. Bottom: Heat flux versus surface temperature curve

In addition to heat flux data obtained from the instrumented probe, a second specimen with the same dimensions as the probe (50 mm, or 2 in., diameter by 200 mm, or 8 in., long) and a Jominy specimen of the same steel is quenched in the same quenchant media using the same quenching conditions. This test specimen is sectioned to determine the cross-sectional hardness by making measurements at the surface, center, $\frac{1}{4}R$, $\frac{1}{2}R$, and $\frac{3}{4}R$ positions (where R is the radius). These data are used for building a database for various quenching conditions and for determining equivalent Jominy distances. The step-by-step process of data analysis proposed by LiŠČiĆ is:

- *Step 1:* Record the quenching intensity measurement of each of the quenching conditions selected as a function of T_s; the surface temperature of the probe (°C); *t,* the time (s); and f, the heat flux of the

probe (MW/m^2)

- *Step 2:* Specify the steel grade and quenching conditions
- *Step 3:* Harden a test specimen by quenching it under the conditions identified in Step 2
- *Step 4:* Make the cross-sectional hardness survey as described above and illustrated in Fig. 12
- *Step 5:* From the Jominy curve for the steel alloy of interest, measure the equivalent Jominy distances; E_s, $E_{3/4R}$, $E_{1/2R}$, $E_{1/4R}$, and E_C that yield the same hardness as determined at the positions specified for cross-sectional hardness survey
- *Step 6:* Calculate the quenching intensity (I) at each of the above characteristic points from the relationship:

$$E_i = A \cdot (D \cdot \exp B_1)/(H \cdot \exp B_2) \quad \textbf{(Eq 5)}$$

where E_i is the corresponding equidistant point on the Jominy curve; A, B_1, and B_2 are regression coefficients; D is the bar diameter; and H is the Grossmann quench intensity factor.

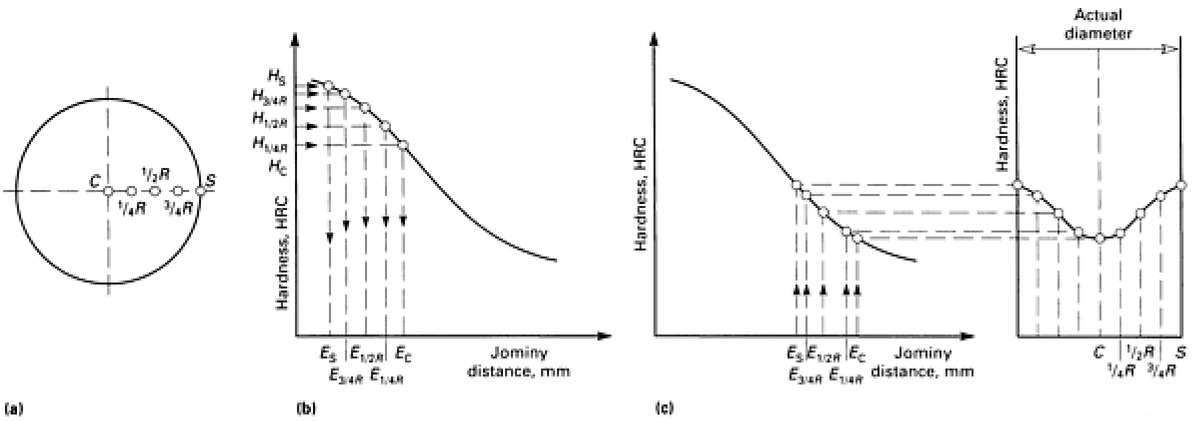

Fig. 12 Procedure for predicting hardness distribution in a steel bar using a Jominy hardenability curve. (a) Cross section of a 50 mm (2 in.) diameter end quench test specimen. (b) Determination of Grossmann quench intensity factor. (c) Determination of equivalent Jominy distance and actual bar diameter

The following relationships have been developed by regression analysis:

$$E_S = D \exp 0.718/(5.11 \cdot H \exp 1.28) \quad \textbf{(Eq 6)}$$

$$E_{3/4R} = D \exp 1.05/(8.62 \cdot H \exp 0.668) \quad \textbf{(Eq 7)}$$

$$E_{1/2R} = D \exp 1.16/(9.45 \cdot H \exp 0.51) \quad \textbf{(Eq 8)}$$

$$E_{1/4R} = D \exp 1.14/(7.7 \cdot H \exp 0.44) \quad \textbf{(Eq 9)}$$

$$E_C = D \exp 1.18/(8.29 \cdot H \exp 0.44) \quad \textbf{(Eq 10)}$$

These equations are valid for: 20 mm $< D < 90$ mm, $0.2 < I < 2.0$, and 1 mm $< E < 40$ mm. From these calculations and the corresponding Jominy curve, hardness distributions in other parts can be calculated (Ref 17).

While this procedure is quite involved, it does integrate all of the classical techniques for quenchant characterization and also permits the surface and the bulk temperature of the part to be measured.

Cooling Curve Applications

Water is an excellent and inexpensive quenchant, but its heat removal characteristics are variable depending on the bath temperature and the relative velocity between the water and the parts being quenched. Water also can be a rather severe quenchant, so oils or aqueous polymer solutions often are used to moderate the heat removal rates.

Bath Temperature Effects. The effect of water bath temperature on cooling curves and cooling rate curves produced when 38 mm (1.5 in.) diameter bars were quenched in water at 27, 32, 60, and 71 °C (80, 90, 140, and 160 °C) flowing at a velocity of 0.25 m/s (50 ft/min) are shown in Fig. 13. All instrumented probes were austenitized at 845 °C (1550 °F) and quenched into water flowing at a velocity of 0.25 m/s (50 ft/min). Some characteristics of these conditions are presented in Table 4. Water at 60 °C (140 °F) produced a cooling rate at 705 °C (1300 °F) of 9.4 °C/s (16.8 °F/s) With a lower water bath temperature of 27 °C (80 °F), the cooling rate at 705 °C (1300 °F) (which is commonly used as an indicator of the ability of quenchants to extract heat) was 32.8 °C/s (58.6 °F/s), about 3.5 times higher than water at 60 °C (140 °F).

Table 4 Effects of quenchant temperature on cooling rates and predicted hardness in 38.1 mm (1.5 in.) diameter 4130 low-alloy steel bars quenched in water (velocity at 0.25 m/s, or 50 ft/min) from 845 °C (1550 °F)

Bath temperature		Cooling rate at						Film coefficient	
		705 °C (1300 °F)		345 °C (650 °F)		205 °C (400 °F)			
°C	°F	°C/s	°F/s	°C/s	°F/s	°C/s	°F/s	$W/m^2 \cdot K$	$Btu/ft^2 \cdot h \cdot °F$
27	80	32.6	58.6	14.6	26.2	7.3	13.2	9382.9	1652.5
32	90	32.3	58.1	14.6	26.3	7.2	13.0	9024.6	1589.4
38	100	31.0	55.8	14.3	25.8	7.0	12.5	7645.4	1346.5
49	120	24.3	43.7	14.4	25.9	6.8	12.2	3504	617.1
60	140	9.3	16.8	14.3	25.7	6.3	11.3	754.0	132.8
71	160	5.6	10.1	13.7	24.6	5.9	10.6	417	73.5
82	180	4.7	8.5	13.5	24.2	5.4	9.7	341	60.1
93	200	3.5	6.3	13.2	23.7	5.1	9.1	241	42.5

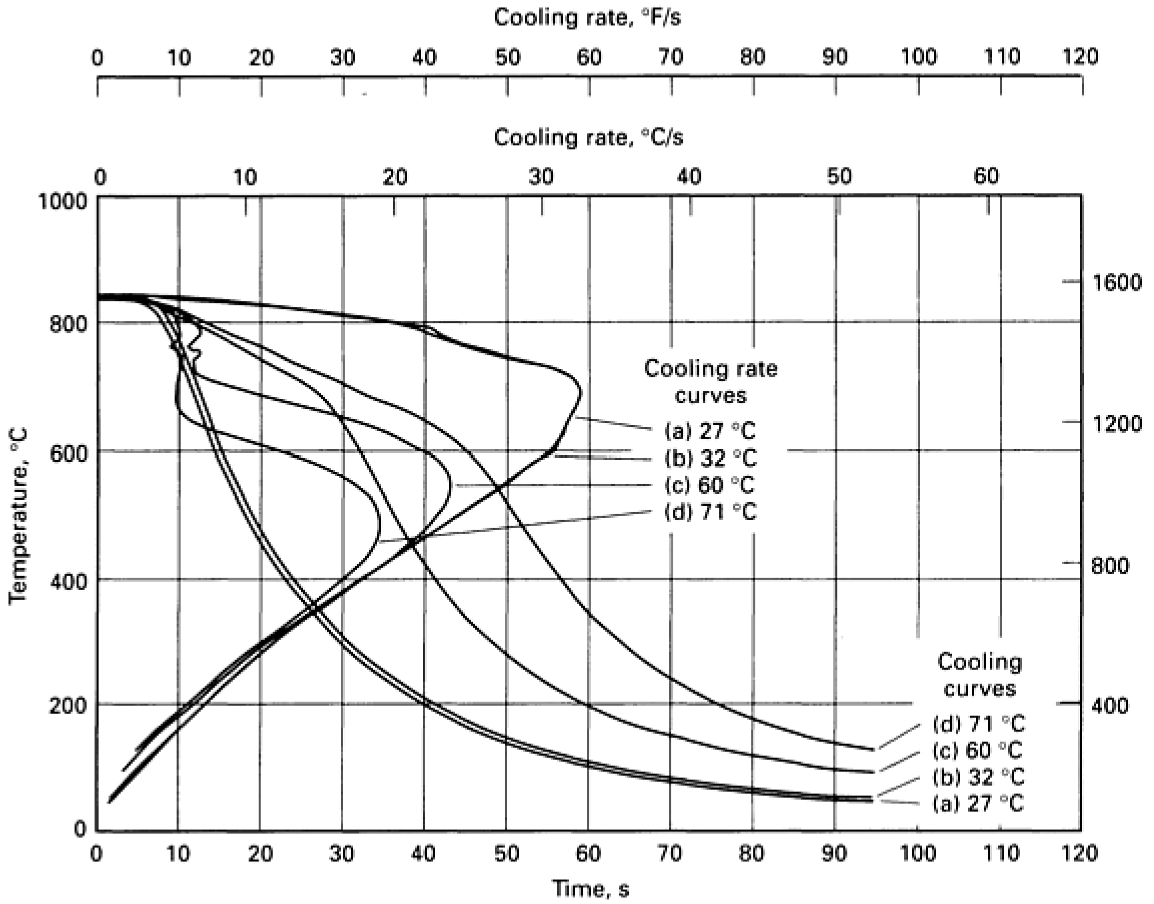

Fig. 13 Cooling curves and cooling rate curves produced by 27, 32, 60, and 71 °C (80, 90, 140, and 160 °F) water that is flowing at 15 m/min (50 ft/min) past a 38 mm (1.5 in.) diameter bar

Quenchant Effects. The type of quenchant used also has a dramatic effect on cooling rates (see Fig. 14). These curves were obtained with a 25.4 mm (1.00 in.) diameter probe quenched into water, a 20% aqueous polyalkylene glycol solution, fast oil, conventional oil, and a martemper oil at temperatures of 32, 49, 65, 65, and 150 °C (90, 120, 150, 150, and 300 °F), respectively. Cooling curves with different shapes were obtained in each solution using the same probe size and quenchant velocity.

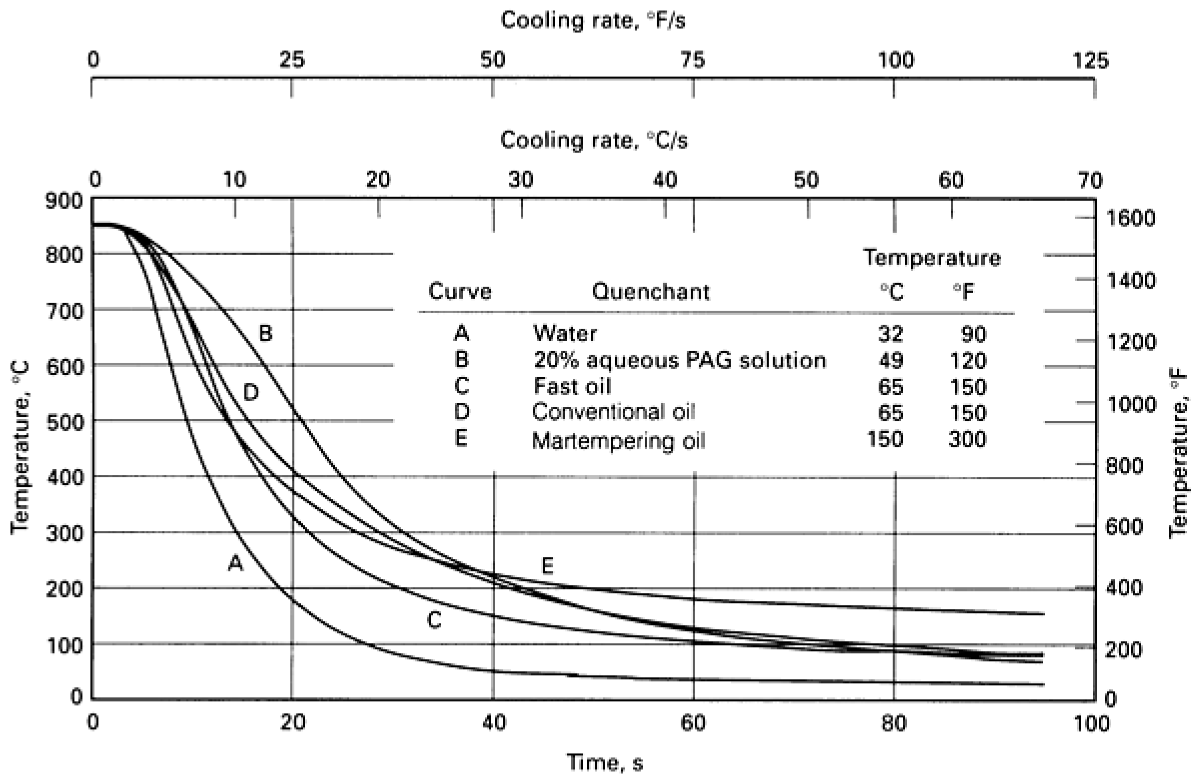

Fig. 14 Effect of selected quenchants on the cooling curve of a 25.4 mm (1.0 in.) diameter steel bar. All quenchants flowing at 0.50 m/s (100 ft/min)

Additional data on the effect of quenchant type, temperature, and quenchant velocity on the Grossmann number and film coefficient produced by water, a fast oil, a conventional oil, a martemper oil, a 25% aqueous polymer solution, and air are presented in Table 3. Water at 27 to 32 °C (80 to 90 °F) can produce film coefficients of over 2800 W/m^2 · K (500 Btu/ft^2 · h · °F) depending on the extent of agitation. The film coefficient decreases rather rapidly however, as the water temperature rises or as the water velocity past the part decreases.

The heat removal characteristics of water at 55 °C (130 °F) are substantially reduced, especially at lower velocities, compared to 27 °C (80 °F) water. The film coefficient of 55 °C (130 °F) water without agitation was only 340 W/m^2 · K (60 Btu/ft^2 · h · °F, but increased to approximately 4100 W/m^2 · K (730 Btu/ft^2 · h · °F with a velocity of 0.75 m/s (150 ft/min).

Thus, without agitation, water at 32 °C (90 °F) can remove heat approximately 5 times faster than water at 55 °C (130 °F) without agitation. At 0.25 m/s (50 ft/min), 55 °C (130 °F) water has less than $\frac{1}{3}$ the heat removal capacity of 32 °C (90 °F) water at the same velocity. At a velocity of 0.50 m/s (100 ft/min), the heat removal capacity of 55 °C (130 °F) water is approximately one-half that of 32 °C (90 °F) water.

The practical implication of this fact is that the temperature of water (and aqueous polymer) quenchants must be carefully controlled to obtain process consistency. Occasionally, some aqueous polymer waterbased quenchants must be agitated more vigorously than oil quenchants to minimize localized bath overheating that could cause a decrease in the cooling rate and produce soft spots on parts.

The temperature of the liquid has a marked effect on its ability to extract heat. Water loses its cooling power as it approaches its boiling point. In oil, this effect is not as pronounced because oil becomes less viscous as the temperature is increased. The reduced oil viscosity offsets the temperature rise by a substantial amount.

Section Size Effects. The effect of section size on cooling rates when 12.7, 25.4, and 38.1 mm (0.50, 1.00, and 1.50 in.) diameter probes quenched in a fast oil at 65 °C (150 °F) and flowing at 0.50 m/s (100 ft/min) is illustrated in Fig. 15.

Cooling rates dramatically decrease with increased section thickness. Under the same operating conditions, the peak cooling rate in a 38.1 mm (1.50 in.) round was 24.5 °C/s (44.1 °F/s) compared to 135 °C/s (245 °F/s) in a 12.7 mm (0.50 in.) round.

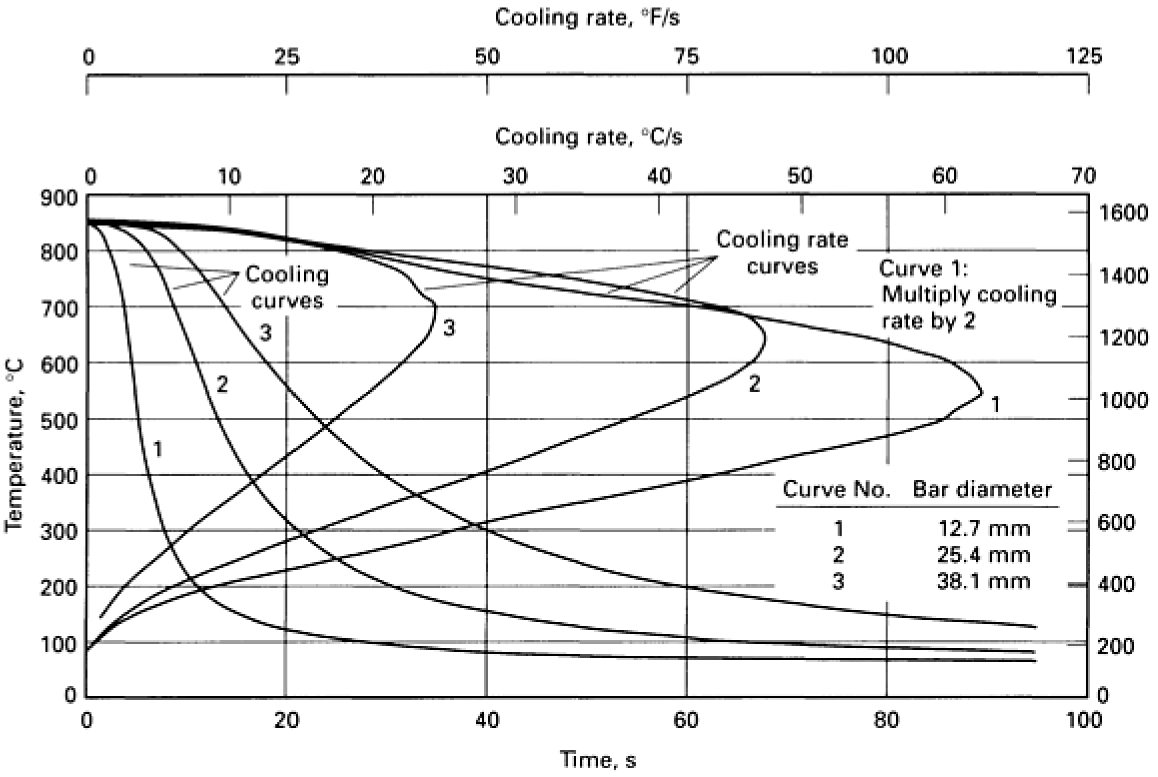

Fig. 15 Effect of section size on cooling curves and cooling rate curves in 65 °C (150 °F) fast oil that is flowing at 0.50 m/s (100 ft/min)

With heavy sections, the cooling rate is limited by the rate of heat conduction from the interior to the surface. Rapid cooling of the center of an extremely large section is impossible by any quenching method because of the mass effect. Therefore, when deep hardening a heavy section, it is necessary to use an alloy steel with higher hardenability.

The data in Fig. 13, 14, and 15 illustrate the fact that many factors, including the section thickness of parts, the characteristics of the quenchant, the type of quenchant, and the quenchant use conditions, affect the shape of cooling rates that can be obtained. Consequently, these factors may also affect the hardness and strength of parts being quenched.

Surface Oxidation Effects. The effects of surface oxidation have been evaluated by magnetic testing, observation of high-speed motion pictures, and cooling curve measurements. The heat transfer rate from nickel balls heated to 885 °C (1625 °F) in an oxidizing atmosphere was compared to that of similar balls heated to the same temperature in a protective, reducing atmosphere. Rates of heat transfer from 885 to 355 °C (1625 to 670 °F), as Shown in Tables 5 and 6, indicate that the balls heated in an oxidizing atmosphere cooled faster than the balls heated in a reducing atmosphere.

Table 5 Comparison of the cooling power of commercially available quenching and martempering oils according to magnetic quenchometer test results

Types of quenching oil	Oil sample	Viscosity at 40 °C (100 °F) SUS[(a)]	Flash point	Quenching duration from 885 °C (1625 °F) to 355 °C (670 °F), s	
				At 27 °C (80 °F)	At 120 °C (250 °F)

			°C	°F	Ni-ball	Chromized Ni-ball	Ni-ball	Chromized Ni-ball
Conventional	1	102	190	375	22.5	27.2	. . .	. . .
	2	105	195	380	17.8	27.9	. . .	. . .
	3	107	170	340	16.0	24.8	. . .	. . .
Fast	4	50	145	290	7.0	[a]	. . .	. . .
	5	94	170	335	9.0	15.0	. . .	. . .
	6	107	190	375	10.8	17.0	. . .	. . .
	7	110	185	370	12.7	19.6	. . .	. . .
	8	120	190	375	13.3	17.8	. . .	. . .
Martempering, without speed improvers	9	329	235	455	19.2	27.6	18.4	22.1
	10	719	245	475	26.9	29.0	25.1	30.4
	11	2550	300	575	31.0	32.0	31.7	32.8
Martempering, with speed improvers	12	337	230	450	15.3	[b]	12.8	[b]
	13	713	245	475	16.4	17.9	14.0	15.6
	14	2450	300	570	19.7	17.0	15.1	15.4

(a) SUS, Saybolt universal seconds.

(b) Not available

Table 6 Comparison of the ranges of cooling power of commercially available quenching and martempering oils according to magnetic quenchometer test results using pure nickel balls

Type of quenching oil	Quenching duration from 885 °C (1625 °F)			
	At 65 °C (150 °F)	At 120 °C (250 °F)	At 175 °C (350 °F)	At 230 °C (450 °F)

Conventional	14-22	14-22	. . .	. . .
Fast	7-14	7-14	. . .	. . .
Martempering without speed improvers	18-34	18-34	22-38	≈47
Martempering with, speed improvers	14-20	13-18	16-22	≈33

High-speed motion-picture techniques have been used to reveal the influence of oxide coatings on the quenching rate of steel in water containing polyvinyl alcohol, trisodium phosphate, or carboxyl methylcellulose. When a steel specimen that had been heated in a protective atmosphere was submerged in the liquid, it was noted that a visible envelope surrounded the specimen preventing contact between the liquid and the steel surface. After a delay of many seconds, the envelope burst and quenching action commenced. The total quenching time in a 0.3% solution of polyvinyl alcohol in water was 37 s, a slower quenching rate than was obtained with conventional quenching oils. When an identical specimen that had been heated in an oxidizing atmosphere was quenched in the same polyvinyl alcohol solution, immediate contact was made between the solution and the specimen surface. The total quenching time was only 2.3 s, a value comparable to the rate obtained in plain water.

Cooling curves, such as those in Fig. 16, also indicate the effect of an oxide scale on quenching characteristics. These curves were obtained by still quenching in fast oil. A scale not more than 0.08 mm (0.003 in.) deep increases the rate of cooling of 1095 steel as compared to the rate obtained on a specimen without scale. However, a heavy scale, 0.13 mm (0.005 in.) deep, retards the cooling rate. A very light scale, 0.013 mm (0.0005 in.) deep, also increased the cooling rate of the 18-8 stainless steel over that obtained on a specimen without scale.

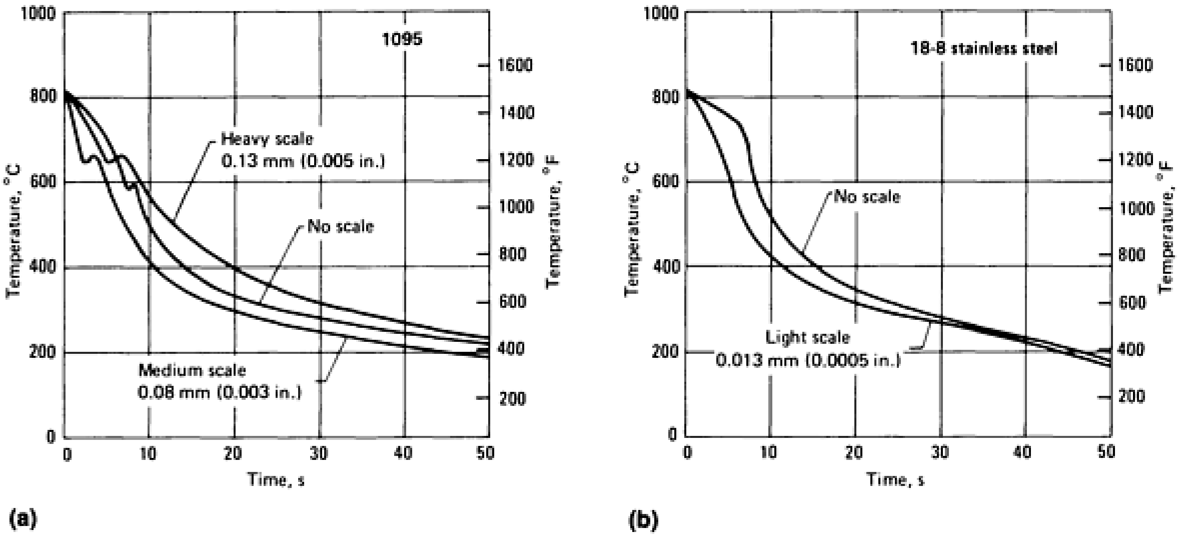

Fig. 16 Center cooling curves showing the effect on scale on the cooling curves of steels quenched without agitation in fast oil. (a) 1095 steel; oil at 50 °C (125 °F). (b) 18-8 stainless steel; oil at 25 °C (75 °F). Specimens were 13 mm ($\frac{1}{2}$ in.) diam by 64 mm ($2\frac{1}{2}$ in.) long.

Distortion and Cracking

Distortion and cracking during quenching limits the severity of the quenchant and equipment that may be used. A more severe quench produces martensite to a greater depth (with a steel of given hardenability), but it also increases the likelihood of distortion and cracking.

Distortion during quenching can be understood by remembering that:

- Steel has a higher strength when cold than when hot
- Steel shrinks while cooling and expands while hardening

Linear dimensional changes occurring during cooling and transformation are shown in Fig. 17 for both slow cooling and fast quenching conditions (Ref 20). Quenching to form martensite results in an expansion of the material compared to that achieved with a slow cooled pearlitic matrix. However, it is recognized that both pearlitic and martensitic materials contract over 1% during cooling from the austenite temperature, but martensitic materials have a lower net contraction.

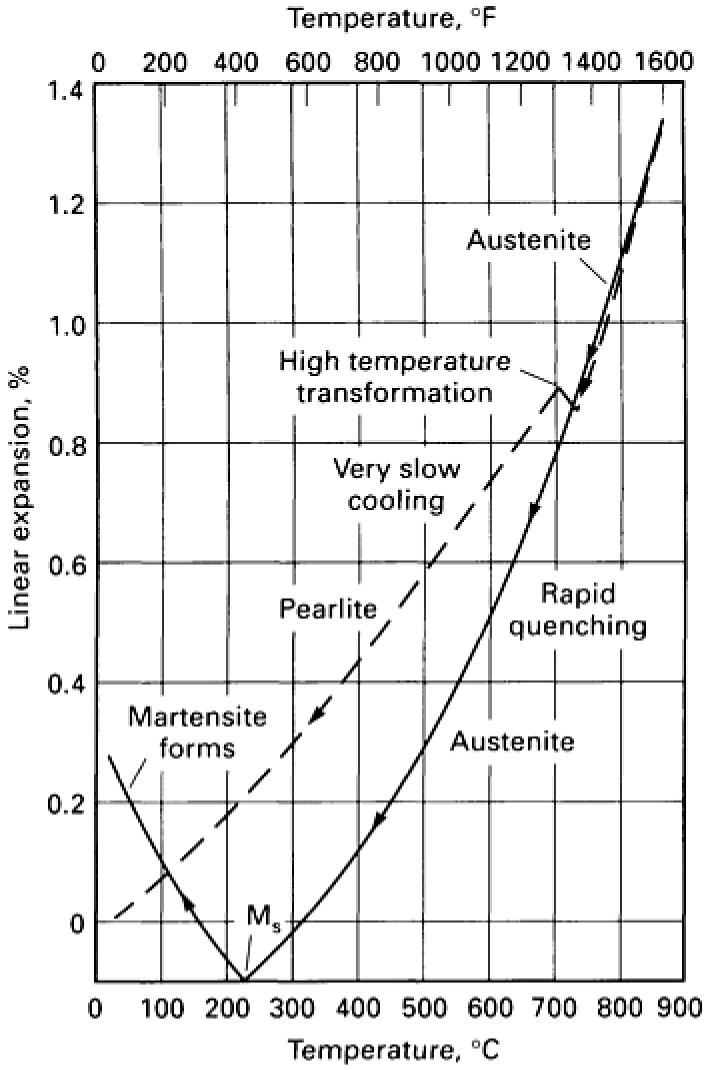

Fig. 17 Dilatometric study of steel cooled from a high temperature to show that the steel undergoes reversals of its dimensional contractions depending on variations in its quenching rate. Source: Ref 12

Distortion is a result of three phenomena: warping, thermally induced deformation, and martensite formation. Warping is the result of nonuniform heating or nonuniform support of a part during heating. Thermal deformation is a result of nonuniform contraction during cooling. These definitions are convenience definitions and there is some overlap in the two phenomena. The expansion associated with martensite formation also induces stresses that cause distortion.

Warping during nonuniform cooling is schematically illustrated in Fig. 18. Assume that the bar was initially at a uniformly high temperature (see Fig. 18a). If the bar were quenched on one side (see Fig. 18b), the more rapidly cooled side would contract earlier and at a higher rate than the opposite side. The rapidly cooled side becomes shorter and

stronger as it cools and causes plastic deformation in the hot side. The deformation is followed by cooling and contraction of the more slowly cooled side.

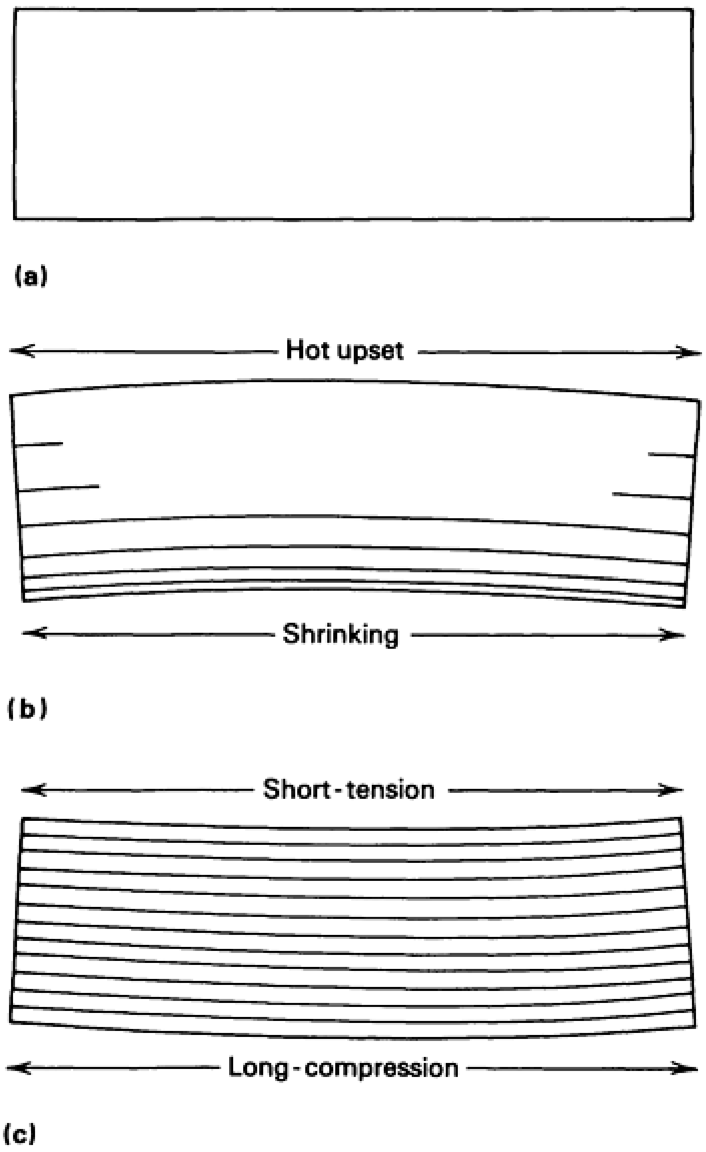

Fig. 18 Warpage caused by nonuniform quenching of a steel block. (a) Uniformly hot. (b) Nonuniform cooling. (c) Uniformly cold. Source: Ref 21

When the part has cooled, it will then be warped (if the stress exceeds the yield strength of the bar) with the slowly cooled side being shorter and warped concave (see Fig. 18c). The plastic deformation on the hot side results in compressive stresses on the rapidly cooled side and tensile stresses on the more slowly cooled side.

Thermally Induced Deformation. Deformation resulting from thermal gradients produced during cooling is illustrated in Fig. 19. If a part is initially uniformly hot, as shown in Fig. 19(a), and is rapidly quenched, the outer surface shrinks while the center is still relatively hot. This process puts the outer surface into tension and the inside into compression, causing internal plastic flow (Fig. 19b). As the center of the part cools and the temperature reaches a uniformly low value, thermal contraction in the center of the bar occurs, which reverses the stress state and places the center in tension (see Fig. 19c). Finish machining of the outer shell removes the tensile stress present in the core (see Fig. 19d).

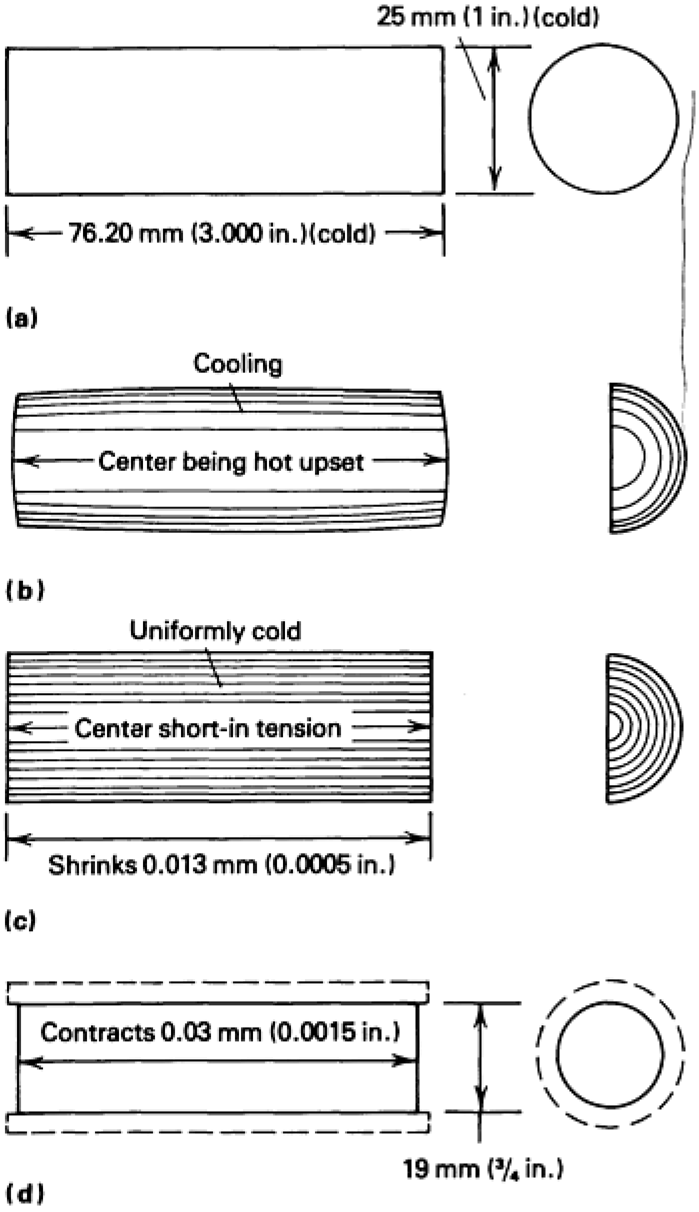

Fig. 19 Effect of quenching on a steel cylinder that was quenched in water from 775 °C (1425 °F). (a) Uniformly hot. (b) Center portion of cylinder is hot upset during quenching. (c) Center portion of cylinder is short in tension when uniformly cold. (d) Machining of the shell removes tensile stress from core to allow cylinder to decrease in length. Source: Ref 21

Martensite Formation. The same deformation processes can occur in a steel part being hardened to produce martensite. The martensitic transformation occurs with a net shrinkage of about 1% during cooling from the austenitizing temperature to room temperature. During rapid cooling, the outer surface is quenched to martensite and the subsequent contraction of the core produces surface compression and center tension (see Fig. 20).

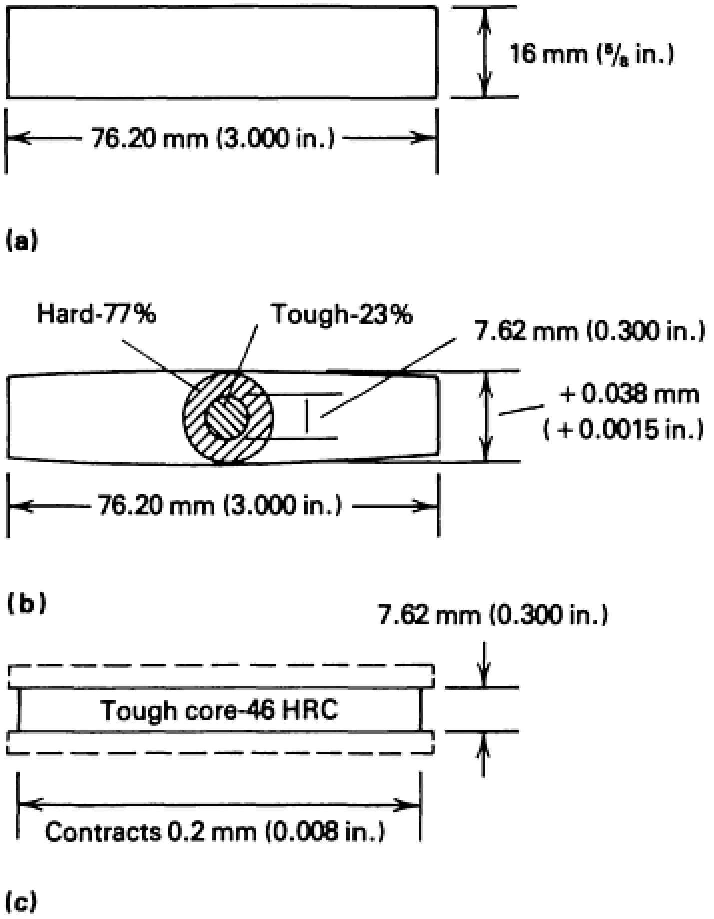

Fig. 20 Strains produced by hardening a cylinder of 1.10% C tool steel. (a) Dimensions of an annealed bar before quenching. (b) Hardness values at selected locations inside cylinder after water quenching at 775 °C (1425 °F) based on surface hardness of 68 HRC. (c) Core hardness after water-quenched cylinder diameter reduced from 16 mm ($\frac{5}{8}$ in.) to 7.62 mm (0.300 in.) by wet grinding. Source. Ref 21

Figure 20 schematically illustrates a bar that was initially 75 mm (3 in.) long and 16 mm ($\frac{5}{8}$ in.) in diameter. During water quenching from 775 °C (1425 °F), deformation occurred in the center of the bar, resulting in a bar diameter 0.038 mm (0.0015 in.) larger than the initial diameter. If the hardened surface of the bar were wet ground to relieve the internal stress and produce a final diameter of 7.62 mm (0.300 in.), the final length of the bar would be 0.2 mm (0.008 in.) less than the as-quenched length. A wide variety of similar experiments have been conducted to demonstrate that the tensile and compressive stress developed during cooling and martensite formation can result in significant deformation of steel parts.

The stress states in a through-hardened 0.6% C steel, an unhardened 0.6% C steel, and a hardened core 0.30% C steel are illustrated in Fig. 21. The length and diameter changes are shown, as well as the stress profiles in 50.0 mm (1.97 in.) bars after water quenching from 850 °C (1560 °F).

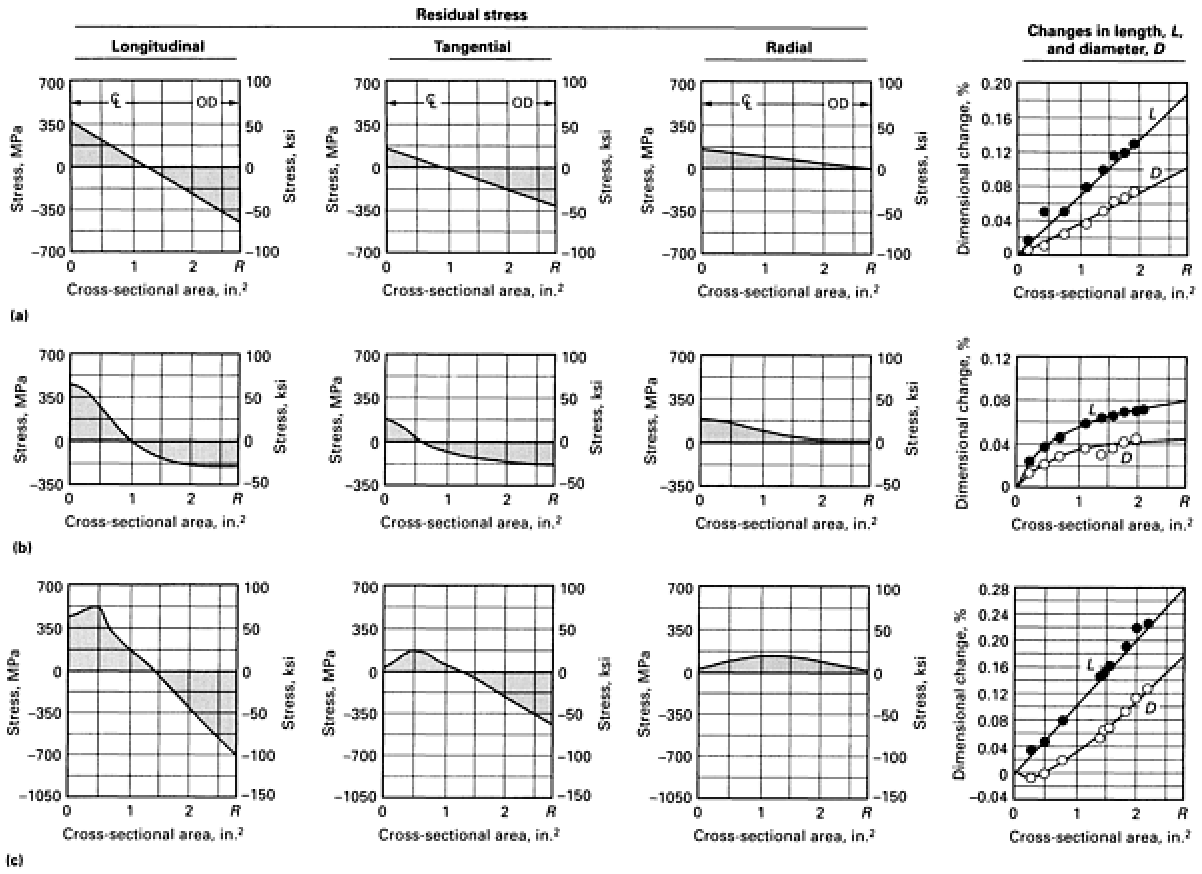

Fig. 21 Residual stress distribution and distortion in 50.0 mm (1.97 in.) diameter carbon steel bars water quenched from 850 °C (1560 °F). (a) Through hardened 0.6% C steel. (b) Unhardened 0.25% C steel. (C) Hardened core 0.30% C steel. OD, outside diameter. Source: Ref 22

Additional Sources of Distortion. In general, the distortion occurring during quenching depends on the size and shape of the bar, bar composition, and the characteristics of the quenchant employed. Parts with section size ratios greater than 1:4; large parts with relatively thin cross sections; and parts containing slots, keyholes, drilled holes, or grooves cause problems because of the difficulty in achieving uniform heating and cooling rates (see Fig. 22(a), 22(b), and 22(c)).

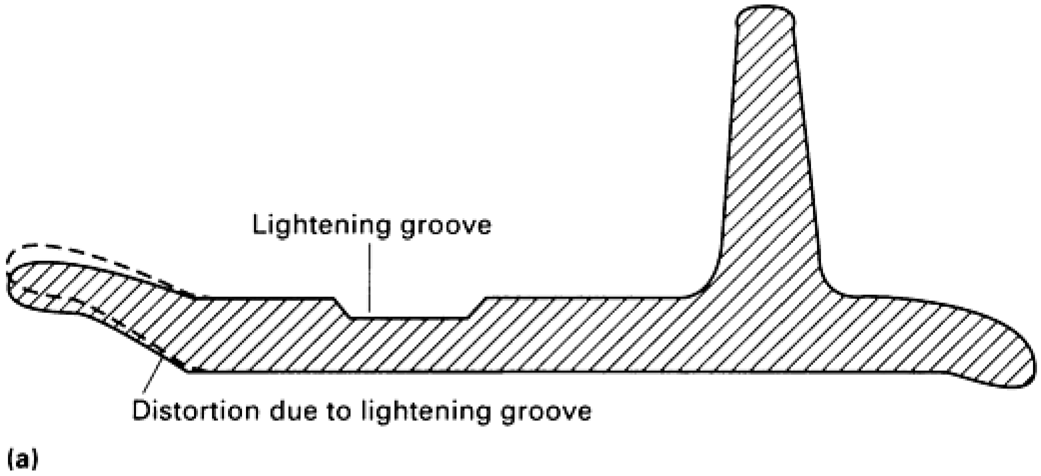

Fig. 22(a) Cross section of a water quenched SAE/AISI 1037 steel track shoe with 0.25 mm (0.010 in.) distortion caused by lightening groove. Redesigning of the shoe to remove the grooves improved uniformity of

the section and reduced the distortion to a maximum of 0.08 mm (0.003 in.). Source: Ref 23

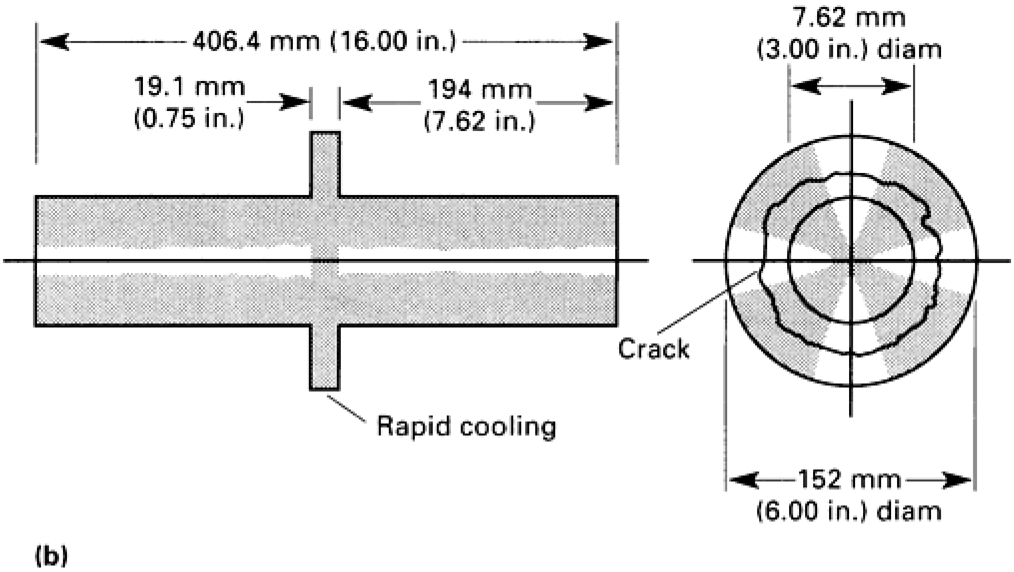

Fig. 22(b) The design of this steel flange on this shaft will cause the flange to crack during quenching. Source: Ref 23

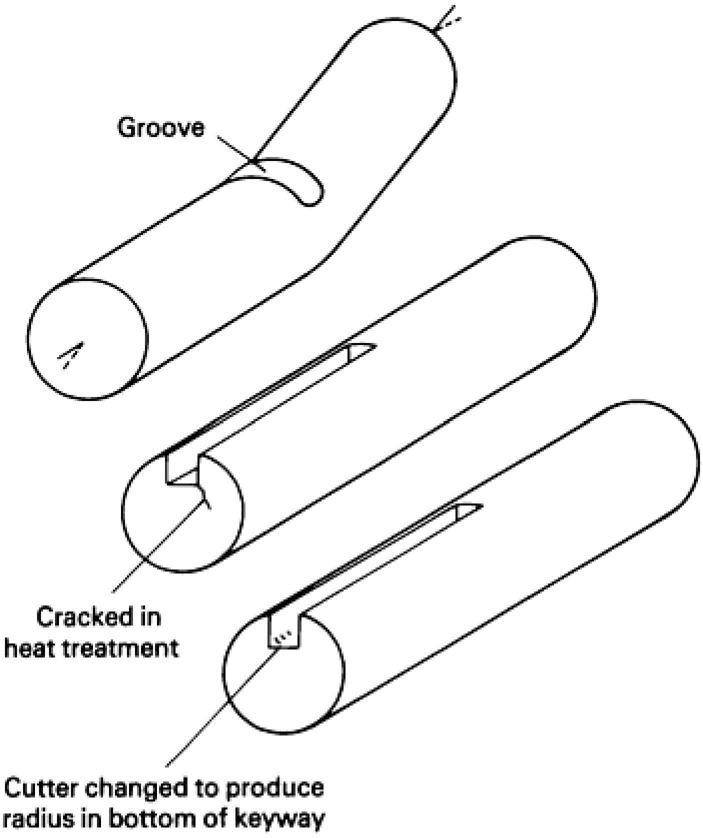

Fig. 22(c) Grooves will cause a shaft to warp in heat treating (top). A keyway with sharp corners often initiates cracks in quenching (center). The keyway crack problem is avoided with a radius (bottom). Source: Ref 23

The distortion that can occur in a track shoe, as a result of the presence of a lightening groove, is illustrated in Fig. 22(a). Flanges and bosses also create conditions that make it difficult to achieve uniform cooling rates (see Fig. 22(b)). The thin,

large diameter flange is very difficult to cool at a rate consistent with the bar, and this almost invariably produces quench cracks.

Keyholes and grooves often cause a shaft to warp during heat treating, and keyways with sharp corners often initiate cracks. The keyway cracking problem can be minimized to some extent with generous radii (see Fig. 22(c)).

The steel composition can also have a significant effect on warping and distortion. High-carbon alloys and those with high hardenability are prone to more distortion than low-carbon with low-hardenability alloys. Similarly, high austenitizing temperatures and low martensite start (M_s) temperatures tend to aggravate distortion.

The characteristics of the quench procedure, particularly conditions promoting high rates of cooling through the transformation range, aggravate distortion and cracking. Rapid quenching to a temperature just above the M_s temperature, followed by slow cooling through the martensite formation range, minimizes distortion. Uniform rates of heat removal per unit of surface area also tend to minimize distortion.

Cracking occurs for the same reasons as distortion, but cracks form when the localized strain exceeds the failure strain in the material. Usually, the cracks follow austenite grain boundaries, but cracking does not appear to be related to the austenite grain size.

The tendency for cracking typically decreases as the M_s temperature increases. The M_s temperature in °C can be approximated by using the following equation (Ref 24):

$$\begin{aligned} M_s = {} & 521 - 353(\%C) - 225(\%Si) \\ & -24.3(\%Mn) - 27.4(\%NI) \\ & - 17.7(\%Cr) - 25.8(\%Mo) \end{aligned} \qquad \textbf{(Eq 11)}$$

The correlation between the occurrence of quench cracks and the M_s temperature in two steels is illustrated in Fig. 23(a).

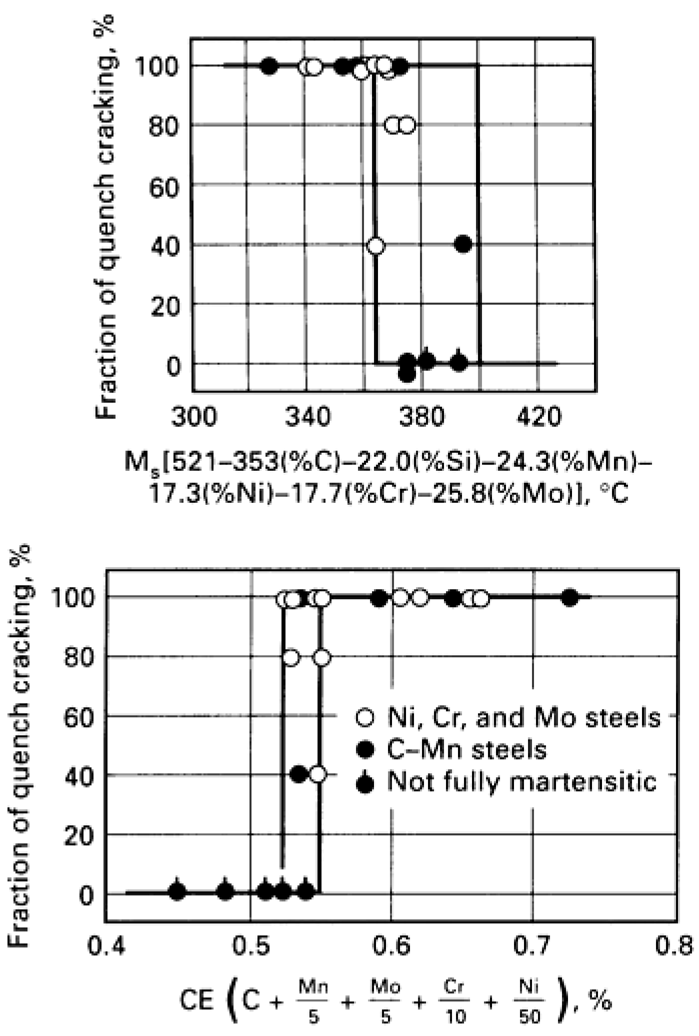

Fig. 23 Effect of M_s, temperature (a) and carbon equivalent (b) on the quench cracking of selected steels

Cracking has also been related to composition using the equation:

$$CE = C + Mn/5 + Mo/5 + Cr/10 + Ni/50 \quad \textbf{(Eq 12)}$$

where CE is the carbon equivalent and the elemental concentrations are expressed in percent by weight.

Quench cracks were prevalent at carbon equivalent values above 0.525, as illustrated in Fig. 23(b).

In general, quenchants must be selected to provide heat rates and cooling rates capable of producing acceptable microstructure in the section thicknesses of interest. However, it is not desirable to use quenchants with excessively high heat removal rates if distortion and cracking are to be minimized. High heat transfer coefficients result in rapid heat loss, high temperature gradients across thick sections, and large temperature differences between thick and thin sections. These conditions aggravate residual stress, distortion, and cracking problems.

High thermal gradients create high thermal stresses as cooler portions of a part try to contract but are restrained by hotter portions. At temperatures above the M_s temperature, steel is quite ductile and some of the stress can be relieved by plastic deformation which results in part distortion. However, when martensite forms, at and below the M_s temperature, the ability of the metal to deform is restricted because of the low ductility of martensite. In addition, there is a volumetric expansion associated with martensite formation that induces additional stress.

Thermal expansion and quench contraction curves for a 4340 steel are illustrated in Fig. 24. During heating, 4340 steel expanded almost linearly until austenite began to form at about 730 °C (1350 °F). After heating to 845 °C (1550 °F), the steel was rapidly cooled with the results shown by the flagged symbol. The volumetric expansion associated with martensite formation beginning at about 315 °C (600 °F), coupled with thermal stress in the austenite, may cause stresses that exceed the fracture stress of the martensite.

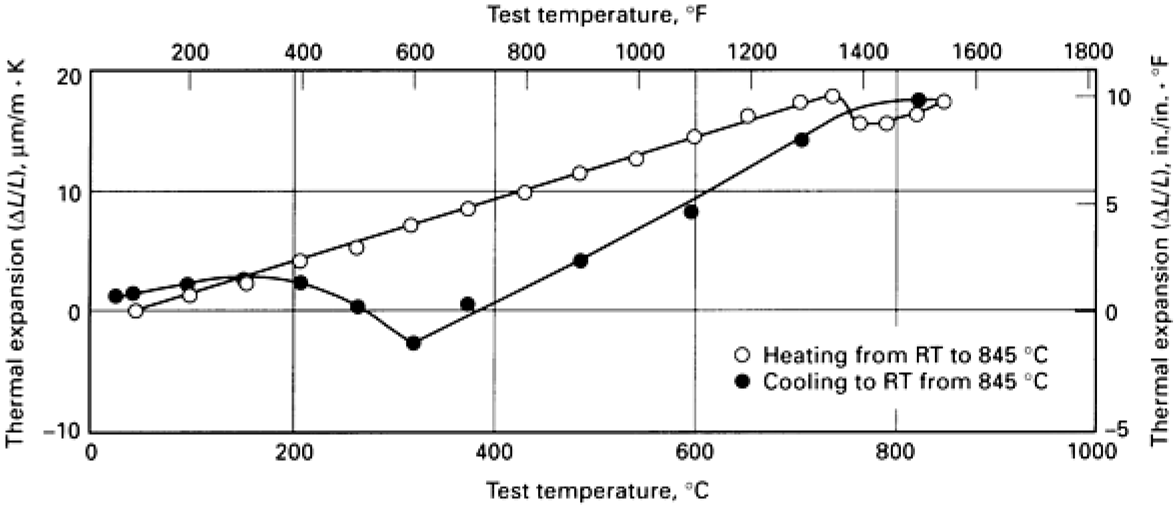

Fig. 24 Thermal expansion and contraction curves for 4340 steel. RT, room temperature

The volumetric changes associated with martensite formation can be controlled only by controlling the carbon concentration of the steel. The data illustrated in Fig. 25, calculated from x-ray diffraction data for fully martensitic microstructures, shows that the volumetric expansion increases linearly with the carbon concentration (Ref 25). Thelning (Ref 26) described volumetric changes occurring during quenching using the following equation:

$$(\Delta V/V) \cdot 100 = (100 - V_c - V_a) \cdot (1.68 \cdot C) + V_a (-4.64 + 2.21 \cdot C) \qquad \textbf{(Eq 13)}$$

where $\Delta V/V \cdot 100$ is the change in volume in %; V_c is the % by volume undissolved cementite; V_a is the % by volume austenite; $100 - V_c - V_a$ is the % by volume martensite; and C is the % by weight of carbon dissolved in austenite and martensite, respectively.

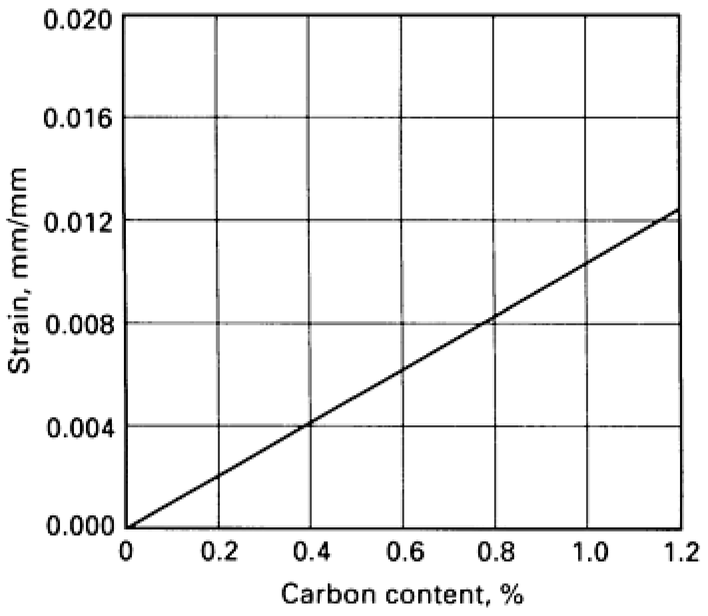

Fig. 25 Linear expansion in steel after quenching to produce fully martensitic microstructures

While low carbon concentrations reduce the probability of cracking, in practice a sufficiently high carbon concentration must be present to produce the desired hardness and strength.

Differential Temperatures in Quenched Probes. Temperature-time curves at two locations in a 50 mm (2 in.) diameter probe quenched in 32 °C (90 °F) water flowing at 0.50 m/s (100 ft/min) and producing an interface heat transfer coefficient of about 1.15 × 10^4 W/m^2 · K (6.53 × 10^4 Btu/ft^2 · h · °F) are illustrated in Fig. 26. These temperature-time curves were obtained with one thermocouple on the probe centerline and the second thermocouple 18 mm (0.7 in.) from the centerline.

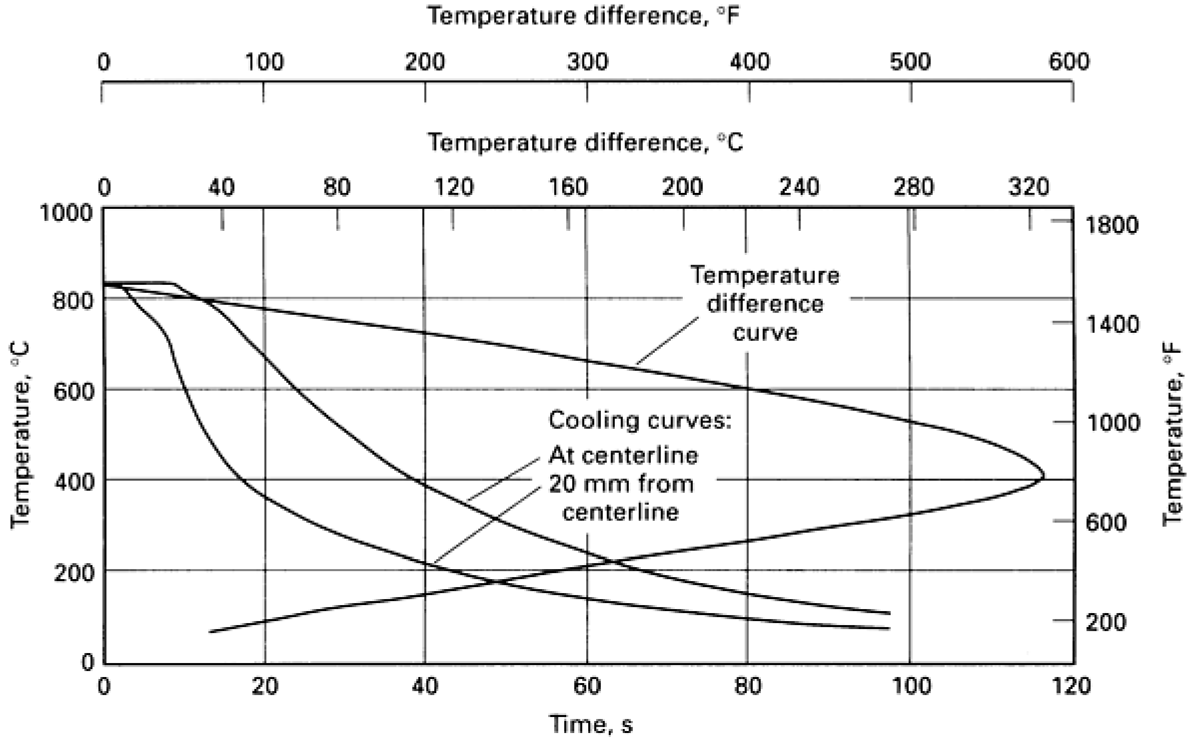

Fig. 26 Cooling curves and temperature difference curve between thermocouple A on centerline and thermocouple B 20 mm ($\frac{25}{32}$ in.) from centerline of 50 mm (2 in.) diameter probe quenched in 32 °C (90 °F) water that is flowing at 0.50 m/s (100 ft/min)

The temperature difference between the two thermocouples, calculated as the center temperature minus the near-surface temperature, is plotted as a function of the near-surface temperature. It is observed that the maximum temperature difference across the bar quenched in water was approximately 320 °C (575 °F) and the maximum value occurred when the near-surface temperature was approximately 420 °C (790 °F).

The maximum gradient occurred when the near-surface temperature was close to 300 °C (570 °F)· The high gradient, which is near the M_s temperature of many steels, coupled with a loss of ductility when martensite forms, can lead to cracking of parts quenched in water.

Similar near-surface and centerline cooling curves in a 50 mm (2.0 in.) diameter bar quenched with an interface heat transfer coefficient of 4300 W/m^2 · K (760 Btu/ft^2 · h · °F), such as produced by an agitated fast oil, are illustrated in Fig. 27. The maximum temperature gradient was 209 °C (376 °F) and occurred at a surface temperature of about 575 °C (1065 °F), substantially above the M_s temperature. The reduced gradient causes oil quenched parts to be less prone to cracking compared to water quenched parts.

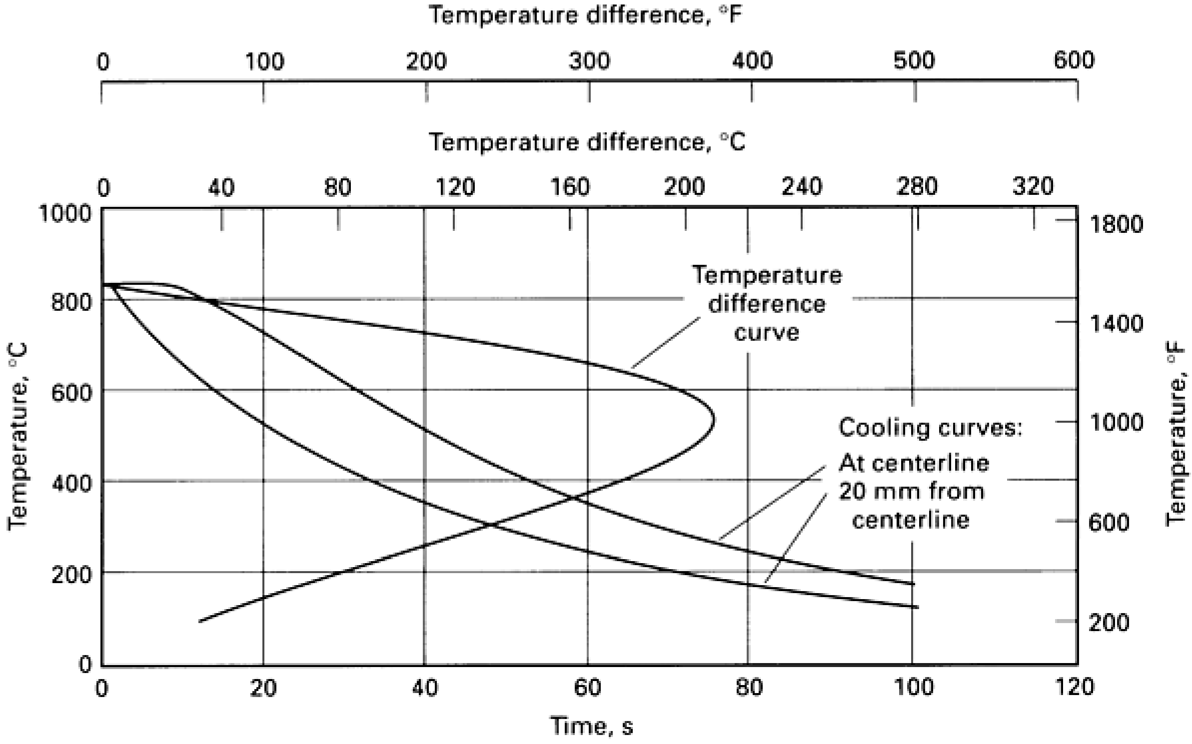

Fig. 27 Cooling curves and temperature difference curve between thermocouple A on centerline and thermocouple B 20 mm ($\frac{25}{32}$ in.) from centerline and thermocouple B 20 mm ($\frac{25}{32}$ in.) from centerline of 50 mm (2 in.) diameter probe quenched in fast oil with film coefficient of 4300 W/m^2 · K (760 Btu/ft^2 · h · °F)

High interface heat transfer coefficients can produce very large differences in temperature between thick and thin sections of a part. Cooling curves associated with a 38 mm ($1\frac{1}{2}$ in.) section and a 25.4 mm (1.00 in.) section quenched in 60 °C (140 °F) conventional oil flowing over the part at a velocity of 0.50 m/s (100 ft/min) are shown in Fig. 28. Oil at this temperature and velocity had an interface heat transfer coefficient of about 3500 W/m^2 · K and produced a maximum

temperature difference between the two sections of approximately 260 °C (470 °F). The peak difference occurred when the smaller section center temperature was about 500 °C (930 °F), which is well above the M_s temperature and unlikely to cause cracking.

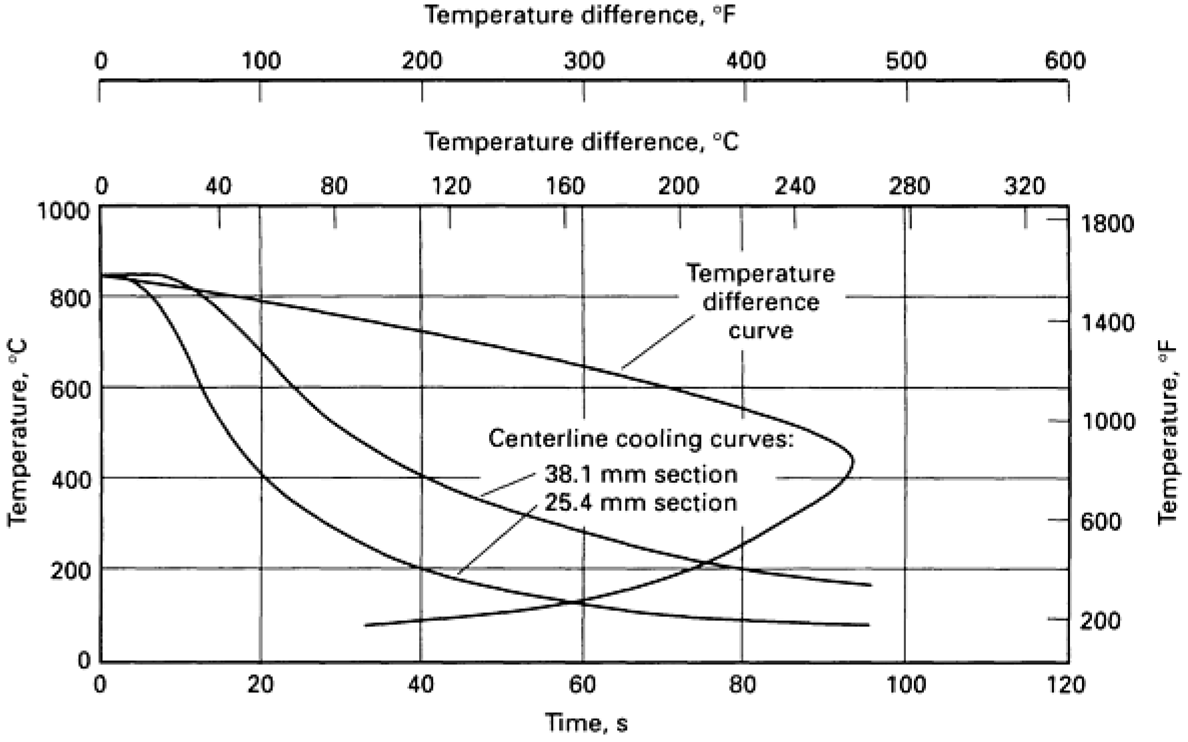

Fig. 28 Cooling curves and temperature differences curves between 38.1 mm(1.5 in.) section and 25.4 mm (1.0 in.) section of steel quenched in conventional oil at 60 °C (140 °F) that is flowing at 0.5 m/s (100 ft/min)

The thermal stress in a part which causes distortion during quenching is a function of the alloy thermal expansion coefficient, elastic modulus, volumetric expansion when martensite forms, and temperature differences within the part. Minimizing the thermal stress requires that temperature differences be minimized because no control can be exercised over either the expansion coefficient or elastic modulus.

When a part is quenched in a solution such as water that produces a high heat transfer coefficient, the temperature in the thin sections drops far more quickly than the temperature in heavier sections. The large temperature differences create high thermal stresses which often cause deformation. The only feasible approach to reducing the stress and cracking tendency is to reduce the heat transfer coefficient and hence minimize temperature differences. The interface heat transfer coefficient should be as low as possible while maintaining a sufficiently high cooling rate to ensure that the required microstructure, hardness, and strength can be obtained in critical sections of the part.

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Hardness and Hardening Characteristics of Steel

Hardenability refers to the ability of a steel to be transformed partially or completely from austenite to martensite at a given depth when cooled under prescribed conditions. This definition reflects the empirical nature of steel hardenability, and many types of experiments have been devised to measure or describe the hardenability of various kinds of steel.

Martensite is the microstructure usually desired in quenched carbon and low-alloy steels. The cooling rate must be fast enough to avoid the nose of the time-temperature-transformation (TTT) curve of the steel being quenched, as indicated by curve A in Fig. 29, to obtain the maximum amount of martensite. If the cooling rate is not fast enough to miss the nose of the TTT curve (curves B, C, and D in Fig. 29), some transformation to bainite, pearlite, or ferrite will take place, with a corresponding decrease in the amount of martensite formed and a decrease in the as-quenched hardness developed.

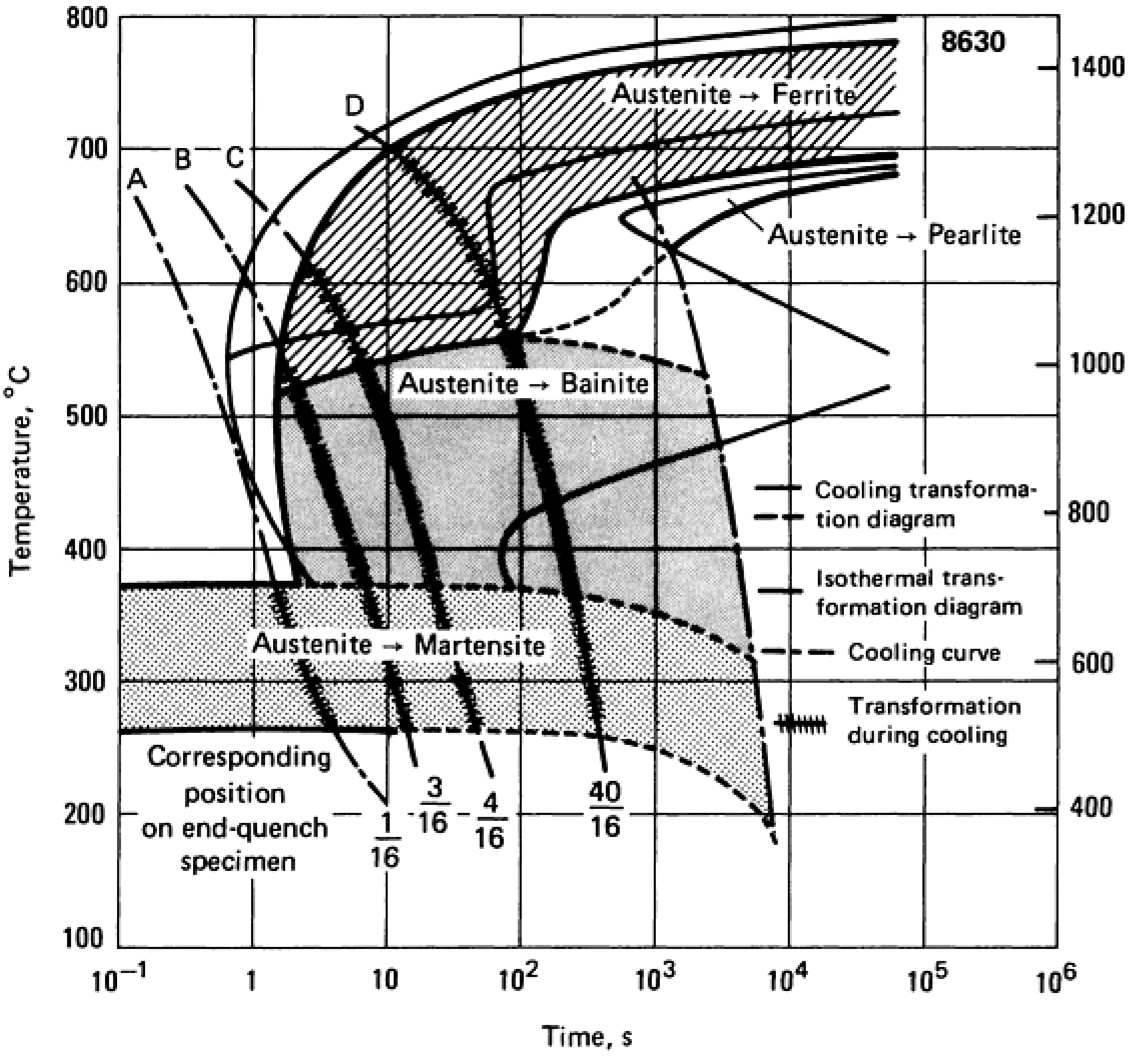


Fig. 29 Transformation diagrams and cooling curves for 8630 steel, indicating the transformation of austenite to other constituents as a function of cooling rate

The cooling rate in quenched parts should be fast enough so that a high percentage of martensite is produced in critically stressed areas of the part. Higher percentages of martensite result in higher fatigue and impact properties after tempering.

The maximum hardness obtainable in a steel depends almost exclusively on the carbon concentration. The relation of carbon concentration and percentage martensite to the approximate maximum as-quenched hardness is shown in Fig. 30 and Table 7.

Table 7 Effect of carbon concentration and % martensite on the as-quenched hardness of steel

Carbon, %	Hardness, HRC				
	99% M	95% M	90% M	80% M	50% M
0.10	38.5	32.9	30.7	27.8	26.2
0.12	39.5	34.5	32.3	29.3	27.3

Carbon, %	Hardness, HRC				
	99% M	**95% M**	**90% M**	**80% M**	**50% M**
0.14	40.6	36.1	33.9	30.8	28.4
0.16	41.8	37.6	35.3	32.3	29.5
0.18	42.9	39.1	36.8	33.7	30.7
0.20	44.2	40.5	38.2	35.0	31.8
0.22	45.4	41.9	39.6	36.3	33.0
0.24	46.6	43.2	40.9	37.6	34.2
0.26	47.9	44.5	42.2	38.8	35.3
0.28	49.1	45.8	43.4	40.0	36.4
0.30	50.3	47.0	44.6	41.2	37.5
0.32	51.5	48.2	45.8	42.3	38.5
0.34	52.7	49.3	46.9	43.4	39.5
0.36	53.9	50.4	47.9	44.4	40.5
0.38	55.0	51.4	49.0	45.4	41.5
0.40	56.1	52.4	50.0	46.4	42.4
0.42	57.1	53.4	50.9	47.3	43.4
0.44	58.1	54.3	51.8	48.2	44.3
0.46	59.1	55.2	52.7	49.0	45.1
0.48	60.0	56.0	53.5	49.8	46.0
0.50	60.9	56.8	54.3	50.6	46.8

Carbon, %	Hardness, HRC				
	99% M	95% M	90% M	80% M	50% M
0.52	61.7	57.5	55.0	51.3	47.7
0.54	62.5	58.2	55.7	52.0	48.5
0.56	63.2	58.9	56.3	52.6	49.3
0.58	63.8	59.5	57.0	53.2	50.0
0.60	64.3	60.0	57.5	53.8	50.7

M, martensite

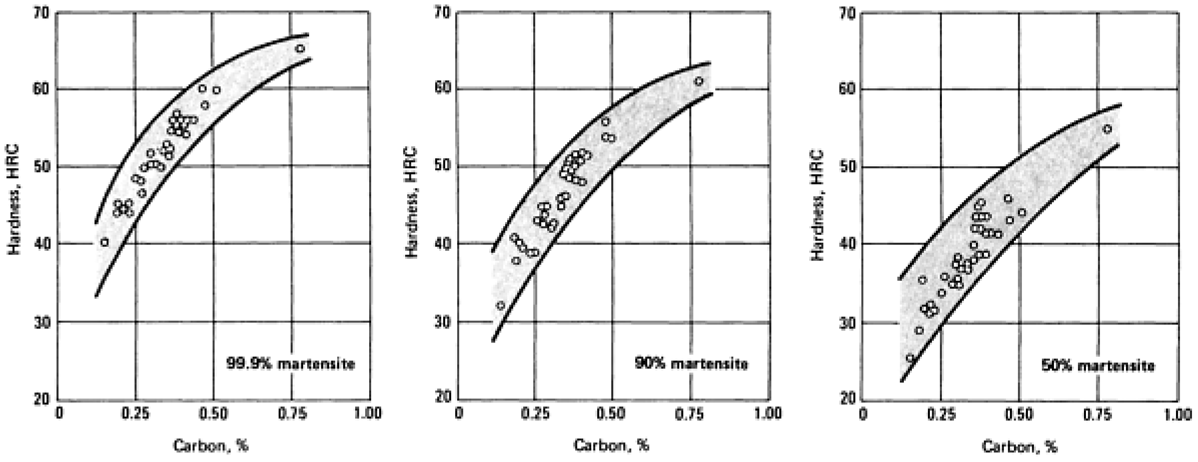


Fig. 30 Relation of carbon content and percentage martensite to HRC hardness

Ideal Critical Diameter

Hardenability is generally calculated in terms of the ideal critical diameter (D_I), and equations most often used for this prediction are base multiplicative factors. The base ideal diameter, DI_{base}, is determined from the carbon content and austenite grain size. The base ideal diameter is then multiplied by the various factors, which take into account the hardenability effects of the other elements present. The following equation is one expression for calculating the ideal critical diameter:

$$D_I = DI_{base} \cdot f_{Mn} \cdot f_{Si} \cdot f_{Cr} \cdot f_{Mo} \cdot f_v \cdot f_{Cu} \quad \textbf{(Eq 14)}$$

where f_x is the multiplicative factor for the particular alloying element.

One set of D_I and alloy factors are presented in Table 8. These alloy factors were developed based on data from medium-carbon steels of medium hardenability, and have been incorporated in a slide rule (Ref 27). An alternative set of alloy factors have also been developed for low-carbon steels and more recently computerized calculators have been developed (Ref 28).

Table 8 Tabulated hardenability factors of steels as a function of carbon content, carbon grain size, and selected alloying elements

Carbon, %	Base ideal diameter, DI_{base}, at following carbon grain size			Alloying factor, f_x, where element, X, is				
	No. 6	No. 7	No. 8	Mn	Si	Ni	Cr	Mo
0.05	0.0814	0.0750	0.0697	1.167	1.035	1.018	1.1080	1.15
0.10	0.1153	0.1065	0.0995	1.333	1.070	1.036	1.2160	1.30
0.15	0.1413	0.1315	0.1212	1.500	1.105	1.055	1.3240	1.45
0.20	0.1623	0.1509	0.1400	1.667	1.140	1.073	1.4320	1.60
0.25	0.1820	0.1678	0.1560	1.833	1.175	1.091	1.54	1.75
0.30	0.1991	0.1849	0.1700	2.000	1.210	1.109	1.6480	1.90
0.35	0.2154	0.2000	0.1842	2.167	1.245	1.128	1.7560	2.05
0.40	0.2300	0.2130	0.1976	2.333	1.280	1.146	1.8640	2.20
0.45	0.2440	0.2259	0.2090	2.500	1.315	1.164	1.9720	2.35
0.50	0.2580	0.2380	0.2200	2.667	1.350	1.182	2.0800	2.50
0.55	0.273	0.251	0.231	2.833	1.385	1.201	2.1880	2.65
0.60	0.284	0.262	0.241	3.000	1.420	1.219	2.2960	2.80
0.65	0.295	0.273	0.251	3.167	1.455	1.237	2.4040	2.95
0.70	0.306	0.283	0.260	3.333	1.490	1.255	2.5120	3.10
0.75	0.316	0.293	0.270	3.500	1.525	1.273	2.62	3.25
0.80	0.326	0.303	0.278	3.667	1.560	1.291	2.7280	3.40
0.85	0.336	0.312	0.287	3.833	1.595	1.309	2.8360	3.55

0.90	0.346	0.321	0.296	4.000	1.630	1.321	2.9440	3.70
0.95	. . .	. . .	. . .	4.167	1.665	1.345	3.0520	. . .
1.00	. . .	. . .	. . .	4.333	1.700	1.364	3.1600	. . .

The general procedure for calculating the hardenability of a steel from the composition includes the following steps:

- *Step 1:* Determine the ASTM grain size
- *Step 2:* Obtain a chemical composition
- *Step 3:* Determine DI_{base} from the carbon content and the grain size (see Table 8)
- *Step 4:* Determine alloy factors (see Table 8)
- *Step 5:* Multiply the factors according to the above equation to provide the calculated ideal critical diameter

These methods for determining the ideal critical diameter of an alloy from the composition and grain size have been compared for a large number of steels (Ref 29). In general, the United States Steel (USS) calculator has been found to predict hardenability well in medium- and high-carbon steels of high hardenability. The Climax Molybdenum calculator is reported to more accurately predict the hardenability in low- to medium-carbon steels.

Jominy Hardenability

The most familiar and commonly used procedure for evaluating the hardenability of steel is the Jominy end-quench test (ASTM A 255). In this test, a 100 mm (4 in.) long by 25 mm (1 in.) diameter bar is austenitized at the proper temperature for the alloy, dropped into a fixture, and one end rapidly cooled with 27 °C (80 °F) water. The end quenching process produces a range of cooling curves with progressively lower cooling rates with increasing distance from the water quenched surface. After cooling to room temperature, parallel flats are ground on opposite sides of the bar and hardness measurements are made at 1.6 mm ($\frac{1}{16}$ in.) intervals along the bar length. This process provides hardness values associated with various positions on the bar that are cooled at different rates. Additional information is available in the articles "Hardenability of Carbon and Low-Alloy Steels" and "Hardenability Curves" in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.*

In general, the Jominy test is considered to provide valid data on steels having an ideal diameter in the range of from about 25 to 150 mm (1 to 6 in.). D_I can be less than 25 mm (1 in.), but this normally requires that Vickers hardness readings be taken closer to the quenched end of the bar and closer together than is possible using standard Rockwell hardness measuring equipment.

Jominy data for an AISI 4130 steel austenitized and quenched from 855 °C (1575 °F) are illustrated in Fig. 31. This steel contained 0.29% C, 0.25% Si, 0.55% Mn, 0.16% Ni, 1.02% Cr, 0.15% Mo, and 0.15% Cu and had a calculated ideal critical diameter of 68.3 mm (2.69 in.). The ideal critical diameter (D_I) is the diameter of a bar that can be quenched to 50% martensite in the center when given a sufficiently severe quench that the heat removal rate is controlled by the thermal diffusivity of the metal and not by the surface heat transfer rate.

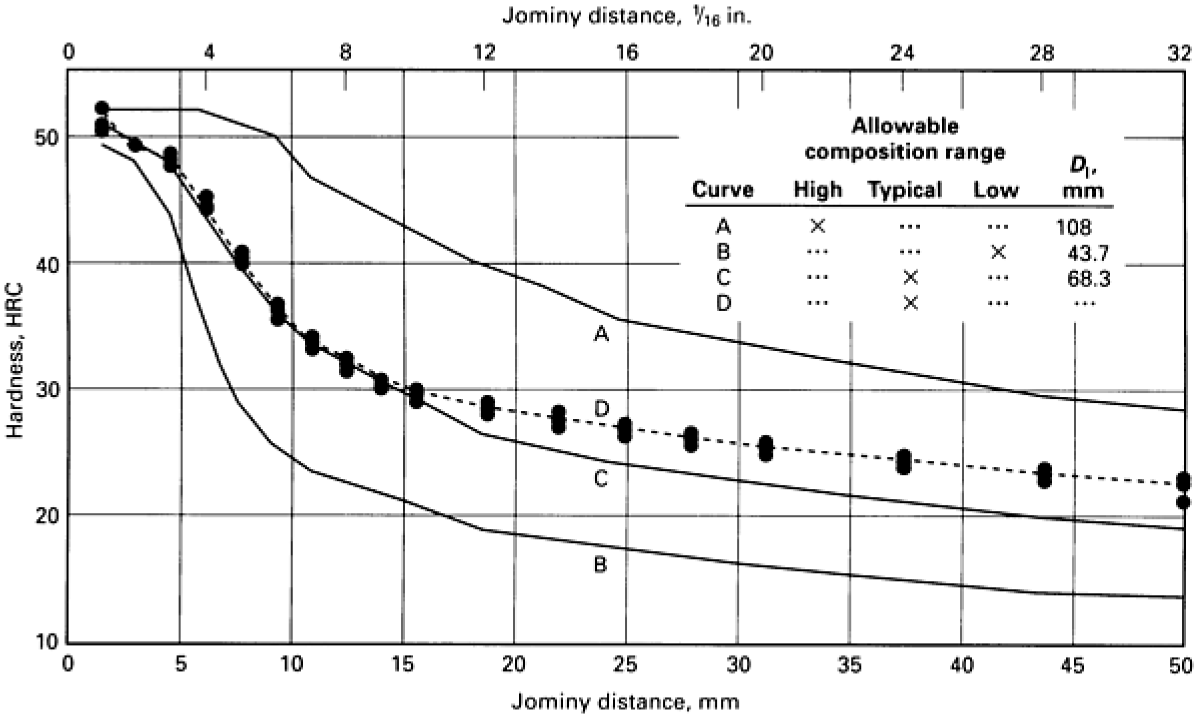


Fig. 31 Calculated and experimental Jominy hardness values of AISI 4130 steel that was austenitized and quenched from 855 °C (1575 °F). Curves A, B, and C were calculated from D_I values; curve D obtained from measured hardness values

The solid curves in Fig. 31 represent calculated hardness distributions. The lower solid curve represents the calculated Jominy hardness distribution assuming all elements to be at the low end of the allowable composition range, and the top curve represents the calculated hardness distribution if all of the elements are assumed to be on the high end of the range. The intermediate curve represents the calculated Jominy hardness distribution for a sample of 4130 steel. The stars represent measured hardness values after end quenching.

This representation of Jominy data provides hardness as a function of distance from the water quenched end of the bar which is related to the cooling rate and hardenability of the alloy. The hardness at the water quenched end of the bar should correspond to the maximum hardness attainable in the steel based on the carbon concentration. The hardness usually decreases with increasing distance from the quenched end. Steels of low hardenability will drop in hardness rather quickly. Steels with higher hardenability will drop less rapidly because higher hardenability steels are able to maintain their hardness at lower cooling rates.

For example, the cooling rate 1.6 mm ($\frac{1}{16}$ in.) from the end of the bar is reported to be about 270 °C/s (490 °F/s) through 700 °C (1290 °F), and this cooling rate is associated with a hardness of HRC 52 in this steel. Similarly, the cooling rates are reported to be about 110 °C/s (195 °F/s) 4.75 mm ($\frac{3}{6}$ in.) from the end and 43 °C/s (77 °F/s) 7.9 mm ($\frac{5}{16}$ in.) from the end of the bar (Ref 30). The hardness values associated with those locations were HRC 52, 49, and 40, respectively. The approximate cooling rates in a Jominy specimen are given in Table 9 as a function of distance from the quenched end (Ref 30).

Table 9 Typical cooling rates at 705 °C (1300 °F) in a Jominy specimen as a function of distance from the quenched end

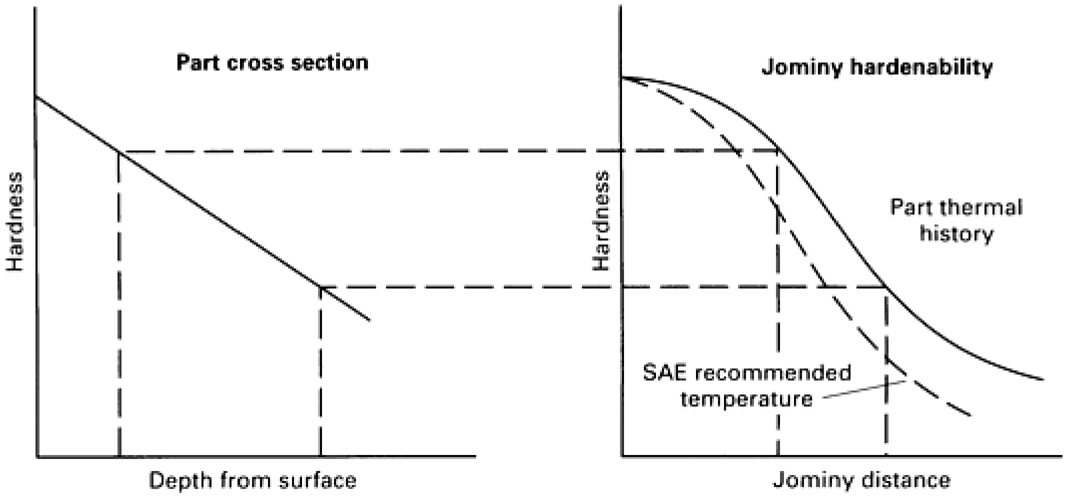
Distance from water	Cooling rate

quenched end, $\frac{1}{16}$ in.	°C/s	°F/s
1	270	490
2	170	305
3	110	195
4	70	125
5	43	77
6	31	56
7	23	42
8	18	33
9	14	26
10	11.9	21.4
12	9.1	16.3
14	6.9	12.4
16	5.6	10.0
18	4.6	8.3
20	3.9	7.0

The cooling rates, as a function of distance from the quenched end, are approximate and vary with the conductivity and transformation products of the particular alloy being quenched. Cooling rates at 705 °C (1300 °F) cannot reliably be used to predict hardness in carbon and low-alloy steels because the critical temperature range moves to higher or lower temperatures as the concentration of alloy elements changes between the different grades (Ref 12).

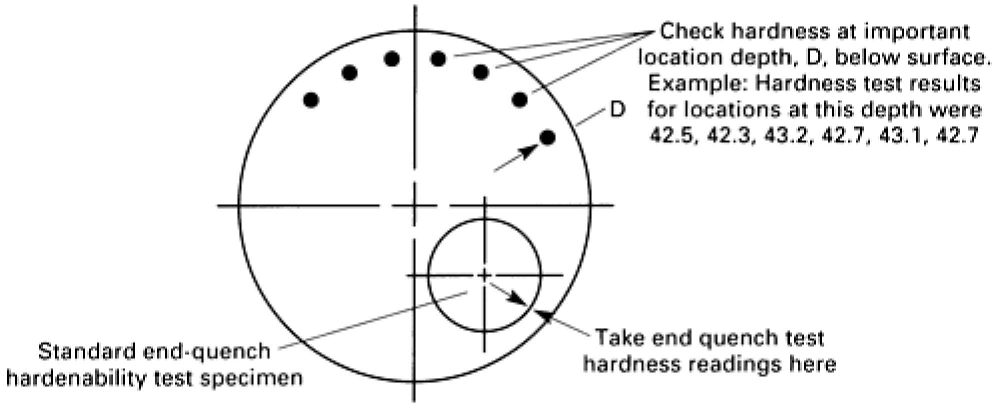
Jominy Equivalence

Once the Jominy curve has been determined, the cooling rate in critical areas of quenched parts must be estimated. One method of establishing the cooling rate is to determine the Jominy equivalent (J_{eq}). The procedure for determining the Jominy equivalent distance is outlined in Fig. 32.



Procedure to determine quench cooling rates at important locations in a workpiece:

- *Step 1:* Obtain at least two test parts (a) made from the same heat of steel and manufactured as close as possible to the proposed production method. Castings will do if forging dies are not available
- *Step 2:* Machine parts to condition in which they will be hardened. Copper plate or otherwise protect parts from any carburizing or decarburizing action. Process parts through heat-treating operations for times estimated to be approximately that for the production part. Quench part No. 1 in a manner as close to production as possible (no temper)
- *Step 3:* Cut, grind, and polish hardened sections from part No. 1 so hardness readings may be taken as shown on example below:



- *Step 4:* Machine end-quench hardenability test specimens from part No. 2 test location on hardenability specimens to correspond to depth D, below surface. Harden end-quench specimens from same temperature as part No. 1. Example test results as follows:

Distance from quenched end, $\frac{1}{16}$ in.	1	2	3	4	5	6	8
Hardness, HRC	56	55	55	54	52	48	43

- *Step 5:* By comparing hardness results obtained at reference location of step 3 (HRC 42.7) to end-quench results (step 4), it can be seen that this hardness occurs at $\frac{8}{16}$ in. on end-quench curve. Quench cooling rate at reference point is approximately equal to $\frac{8}{16}$ in. in end-quench test
- *Step 6:* Confirm cooling rate subsequently on a number of different heats of production parts and adjust material or heat treatment or both to obtain the engineering requirements more precisely

(a) Can be used on gear teeth, roots of splines, and other part shapes. If section in which cooling rate must be determined (such as a gear tooth) is too small for an end-quench hardenability specimen, test results from a separate test may be used. An attempt should be made to make end-quench hardness tests on metal of same location in cross section as gear tooth.

Fig. 32 Determination of Jominy equivalent condition (J_{eq}). Source. Ref 31

The cooling rate can be determined based on a knowledge of the quenchant and the cross section of the part. Approximate cooling rate data through 705 °C (1300 °F) are illustrated in Fig. 33(a) and 33(b) for various bar diameters ranging from about 13 to 100 mm ($\frac{1}{2}$ to 4 in.). The cooling rates at the surface, three-quarter radius, half-radius, and center, are related to the cooling rates at an equivalent distance from the end of a quenched Jominy bar. Thus, the cooling rate at the center of a 50 mm (2 in.) diameter bar quenched in water has a cooling rate equivalent to the value at a distance of about $\frac{6}{16}$ in. from the end of the Jominy bar. The cooling rate at the center of a 50 mm (2 in.) diameter bar quenched in oil has a cooling rate comparable to a point $\frac{10}{16}$ in. from the water quenched end of a Jominy bar.

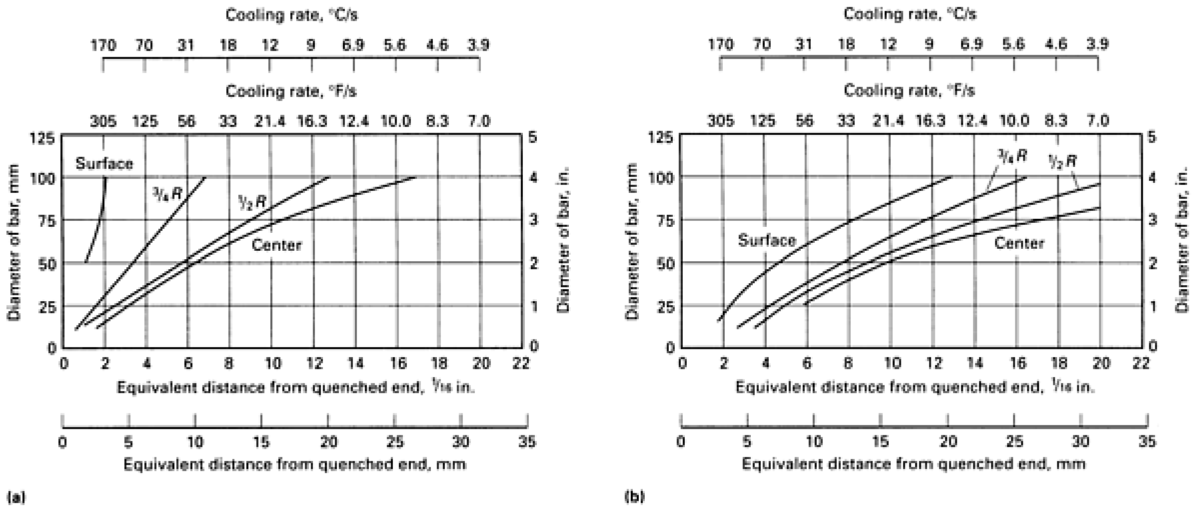


Fig. 33 Equivalent cooling rates at 705 °C (1300 °F) for round bars quenched in (a) water and (b) oil. Fluid viscosity is 1.0 m/s (200 ft/min). Correlation of equivalent cooling rates in the end-quenched hardenability specimen and quenched round bars free from scale. Data for surface hardness are for mild agitation.

Relationships between bar diameter and other simple part geometries such as squares and plates are shown in Fig. 34.

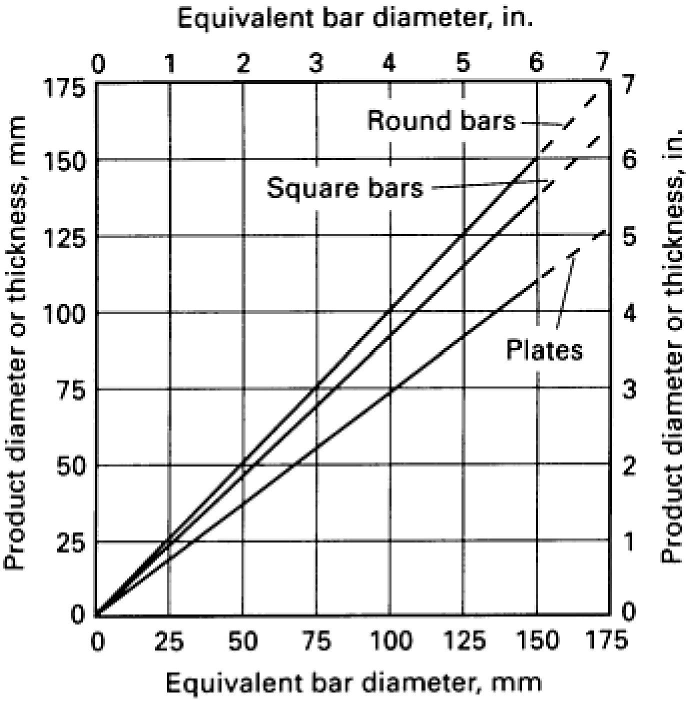


Fig. 34 Relation between through-quenched bar diameter and the through-quenched thickness of plates and square bars

Basically, the Jominy equivalence technique involves:

- Choosing an equivalent bar diameter for estimating the necessary cooling rate from Fig. 34
- Using the equivalent bar diameter to choose the J_{eq} distance for a water quenchant from Fig. 33(a) and an oil quenchant from Fig. 33(b)

TTT and CCT Diagrams

The cooling rates required to achieve particular microstructures are often represented by time-temperature-transformation (TTT) diagrams and continuous-cooling-transformation (CCT) diagrams.

TTT Diagrams. TTT curves are usually produced by solution treating (austenitizing) small samples of steel at the appropriate temperature for the alloy, quickly transferring samples to a lead or salt bath, holding for selected periods of time, and water quenching. The microstructure of each sample after quenching is examined to determine the point in time when the transformation to ferrite, pearlite, or bainite began and the rate at which the transformation progressed with increasing isothermal holding time. The start of transformation in TTT curves is usually defined as the time required to produce 0.1% transformation at the specified holding temperature.

The TTT curve for 4130 steel (see Fig. 35) is usually interpreted to mean that the steel must be cooled past 540 °C (1000 °F) and to the start of the martensitic transformation (M_s) in less than about 1.5 s to produce a fully martensitic structure or must be cooled from the austenitizing temperatures and to the M_s in about 10 s to produce a 50% martensitic structure. Slower cooling rates may result in less than 50% hardening.

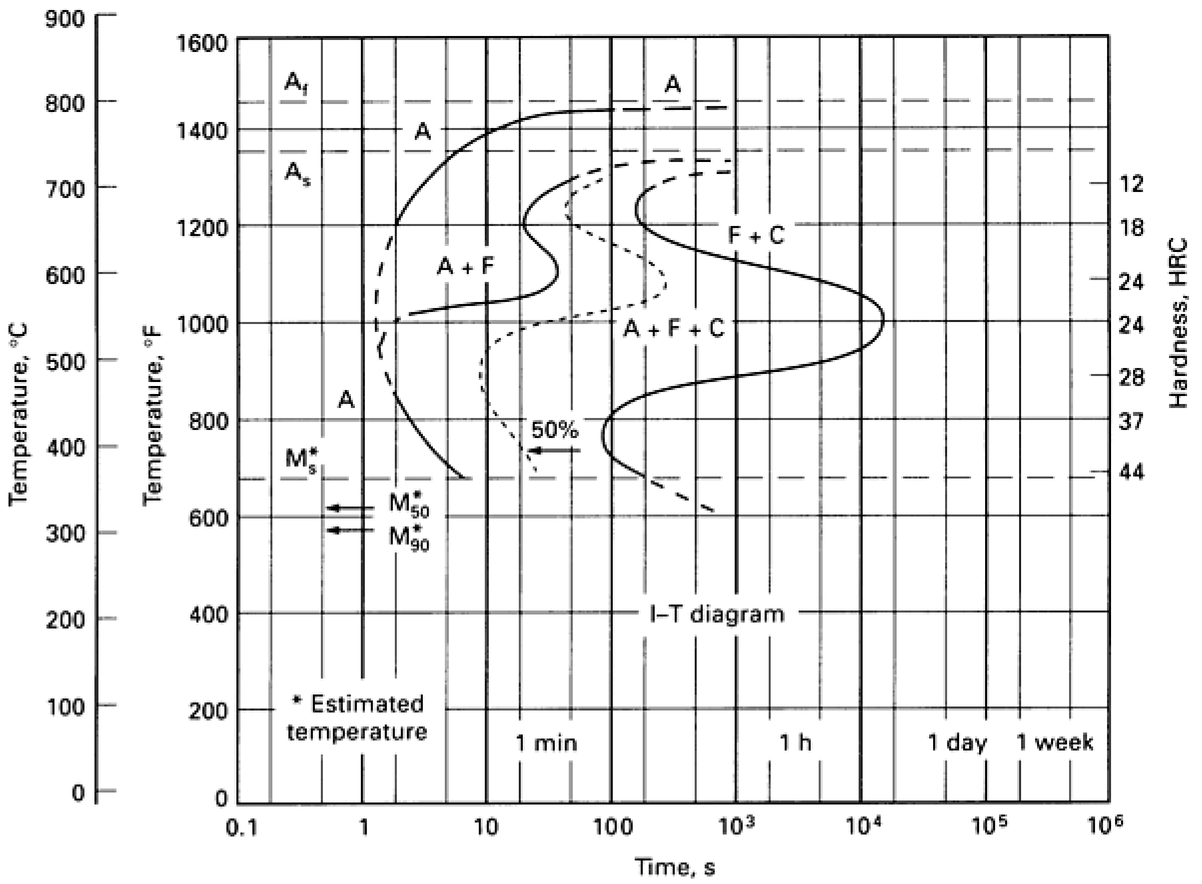


Fig. 35 TTT diagram for 4130 low-alloy steel

Many TTT curves have been published and provide valuable assistance to metallurgists regarding the relative hardenability of different alloys (Ref 31, 32). However, it is difficult to quantitatively determine from a TTT curve whether a steel of a particular composition and section size can be hardened in a particular quenchant.

CCT diagrams are constructed by cooling samples of alloys and examining the resulting microstructures to determine the phases associated with particular cooling rates. CCT diagrams for a wide variety of alloys have also been published (Ref 33, 34).

The CCT diagram for an AISI 4130 steel is shown in Fig. 36. This diagram indicates that a fully martensitic microstructure in this alloy requires a cooling rate above 170 °C/s (300 °F/s) at 705 °C (1300 °F). Achieving a 50% martensitic microstructure requires a minimum cooling rate of about 65 °C/s (120 °F/s) at 705 °C (1300 °F).

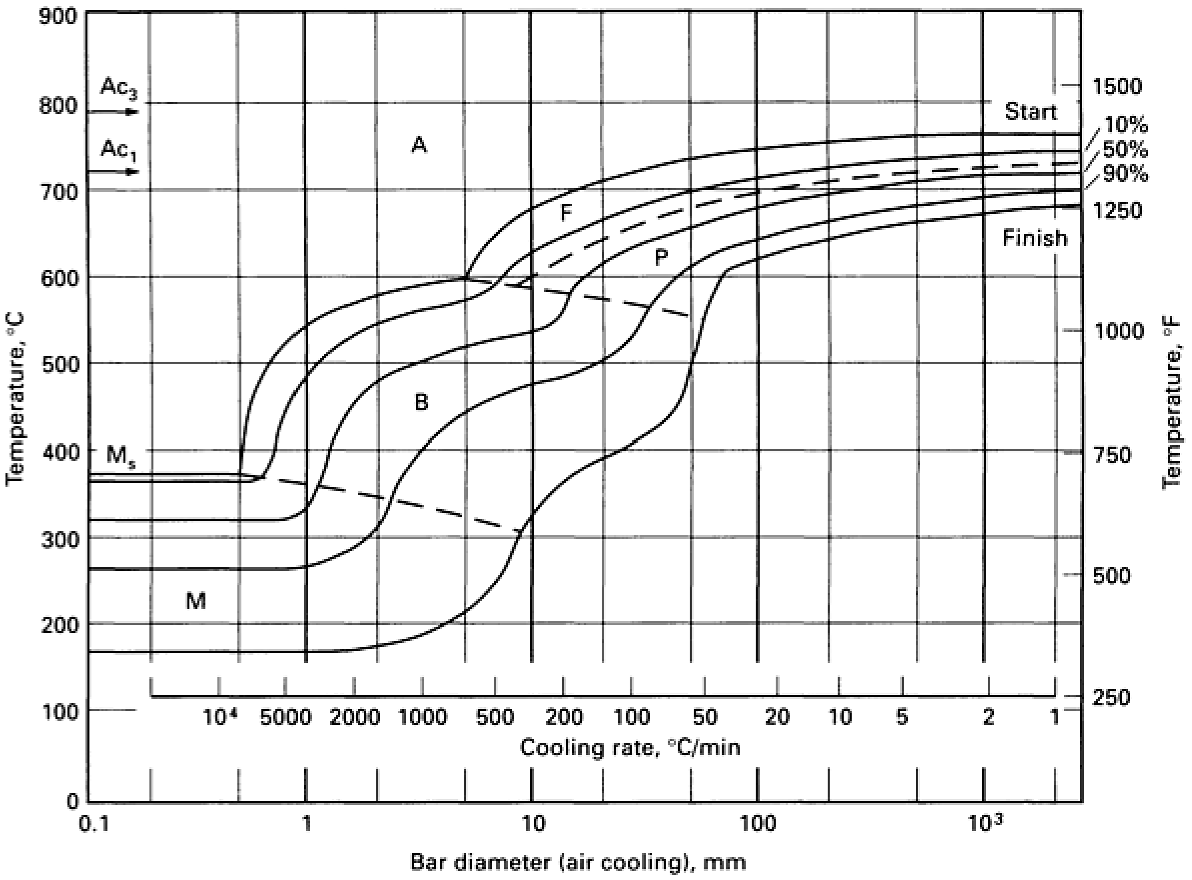


Fig. 36 CCT diagram for 4130 low-alloy steel with 0.30C-0.25Si-0.50Mn-0.020P-0.020S-1.00Cr-0.20Mo composition tested at 750 °C (1380 °F). Calculated critical cooling rate is 143 °C/s (258 °F/s).

These and other published diagrams present approximate cooling rates needed during quenching various alloys to obtain desired microstructures (Ref 15, 35). The actual rates depend to some extent on the specific composition of the steel being quenched. Quenching facilities rely on the quenchant, alloy composition, and attainable quench rates to achieve hardness levels in critical sections of parts without inducing cracks.

Quench Factor Analysis

Jominy, CCT, and TTT curves have been used to represent hardenability of various grades of steel for many years. A more recently introduced concept is that of quench factors (Ref 12, 36, 37).

Quench factor analysis provides a single number, *Q*, that interrelates the cooling rate in a part and the transformation kinetics of the particular alloy being quenched. Cooling rates used in the analyses may be experimentally measured or calculated from heat transfer data.

Alloy hardening characteristics are described by the time-temperature-property (TTP) function, which is the mathematical expression relating transformation temperatures and times to as-quenched properties, usually as-quenched hardness.

The basic hypothesis behind the quench factor concept is that the hardening behavior of steel during continuous cooling can be predicted by dividing a cooling curve into discrete temperature-time increments and determining the ratio of the amount of time the steel was at each temperature divided by the amount of time required to obtain a specified amount of transformation at that temperature. The sum of the incremental quench factor values over the transformation range between the A_3 and the M_s temperatures is the quench factor, *Q*. This approach is usually referred to as the Avrami or additivity rule.

Scheil first proposed the additivity rule to describe incubation or nucleation during phase transformations (Ref 38). Avrami continued the analysis and showed that when the nucleation rate is proportional to the growth rate, the additivity rule is applicable (Ref 39, 40). Avrami developed different expressions to describe the rate of transformation during phase changes depending on whether there were a few or many nuclei present and depending on the type of phase growth that occurred. Transformation rate laws were derived for transformations that nucleated on grain boundary surfaces, grain edges, and grain corners.

Cahn showed that transformations that nucleate heterogeneously often obey the Avrami rule according to rate laws that could be calculated from isothermal transformation data (Ref 41, 42).

Kirkaldy used the Avrami principle and compared the predicted start of the transformation curve with the experimental start of the transformation curve for nine different steels. Good agreement was found in most cases, especially in view of uncertainties in the experimental curves and the assumptions made to calculate the theoretical curves (Ref 43). Kirkaldy has used the Avrami principle to develop computer programs for predicting the transformation rates and hardness of steel under a wide variety of cooling rates (Ref 44).

Tamura studied effects of section size and austenite grain size on the transformation rate of steel and found the additivity rule to be approximately correct during step quenching (Ref 45). Tamura applied the additivity rule to the transformation of a eutectoid steel and was able to obtain equations describing the hardenability that gave predictions similar but slightly lower than those of Grossmann (Ref 46). The basic principles have also been used for several years to predict properties in quenched and tempered aluminum alloys (Ref 47, 48).

Quench factors can be calculated relatively easily from digitally recorded time-temperature curves (cooling curves) obtained in instrumented parts and the equation describing the C curve for the alloy of interest (C_T function).

The C_T function for the alloy of interest is usually described with an equation of the form:

$$C_T = -K_1 \cdot K_2 \cdot \exp\left[\frac{K_3 \cdot K_4^2}{R \cdot T(K_4 - T)^2}\right] \cdot \exp\left(\frac{K_5}{R \cdot T}\right) \quad \textbf{(Eq 15)}$$

where C_T is the critical time required to transform a constant amount of ferrite, pearlite, or bainite, typically 0.1 or 0.5% (the locus of the critical times is the start of the transformation C-curve); K_1 is the constant which equals the natural logarithm of the volume fraction austenite not transformed above the M_s during cooling, that is, the fraction defined by the C-curve, typically ln 0.999 or ln 0.995; K_2 is the constant related to the reciprocal of the number of nucleation sites; K_3 is the constant related to the energy required to form a nucleus for a diffusion controlled transformation; K_4 is the constant related to the carbon solvus temperature (A_3); K_5 is the constant related to the activation energy for diffusion; R is the 8.3143 J/K · mol (gas constant); and T is the average temperature between successive time steps (K).

When making a quench factor calculation, an incremental quench factor, q, for each time step in the transformation range is first calculated using the following equation:

$$q = \frac{\Delta t}{C_T} \quad \textbf{(Eq 16)}$$

where Δt is the time step used in data acquisition, and C_T is the time for the start of transformation at the sample temperature.

The incremental quench factor values are summed over the transformation range between Ar_3 and M_s to produce the cumulative quench factor, Q, according to the equation:

$$xQ = \sum q = \sum_{T = M_s}^{T = Ar_3} \frac{\Delta t_i}{C_{T_i}} \quad \text{(Eq 17)}$$

The cumulative quench factor reflects the heat extraction characteristics of the quenchant as a function of the quenchant type, velocity, and temperature over the transformation range of the steel being quenched. This factor includes section thickness effects, agitation, and surface finish effects on cooling rate as well as the transformation rate of the alloy. The calculation process is schematically illustrated in Fig. 37.

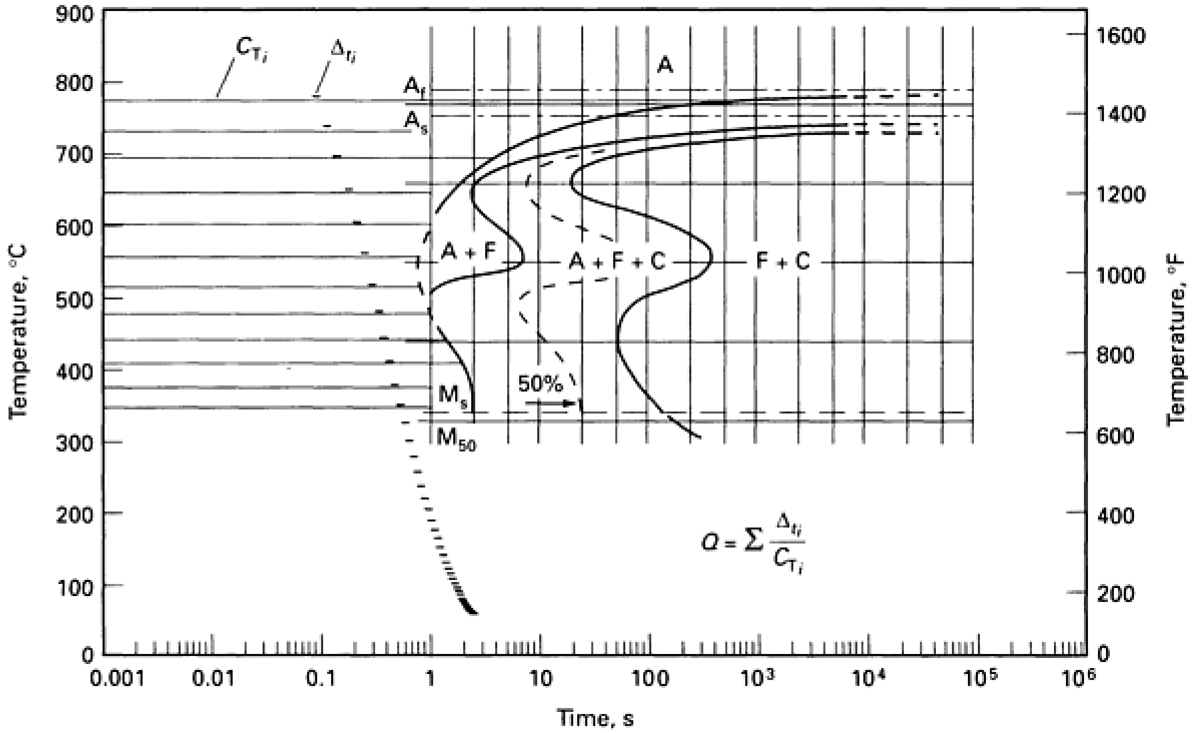


Fig. 37 Schematic illustration showing method for calculating a quench factor

The quench factor can be used to predict the as-quenched hardness in steel using the following equation:

$$H_P = H_{min} + (H_{max} - H_{min}) \exp (K_1 Q) \quad \text{(Eq 18)}$$

where H_P is the predicted hardness; H_{min} is the minimum hardness for alloy; H_{max} is the maximum hardness for alloy; exp is the base of the natural logarithm; K_1 is the ln (0.995) = -0.00501; and Q is the quench factor.

The critical value of the quench factor is the maximum value that will produce the desired as-quenched hardness in the particular steel being quenched. Maximum hardness and strength values are obtained with low quench factors, but minimum quenching stresses are obtained with high quench factors. Minimum residual stress and distortion consistent with the desired hardness is achieved when the quench factor is just below the critical value.

The goal of quench factor analysis is to interrelate alloy hardenability and quenching variables and allow predictions to be made about hardness and strength in specific alloys and specific locations in parts. Once a quench factor is established that will provide the required hardness and strength, a quenchant should be selected and used in such a way that thermal stress and the tendency for distortion and quench cracking is minimized.

Approximate TTP curves have been developed for the compositions of 4130 steel in Table 10. These TTP curves are illustrated in Fig. 38. These C curves are plotted for times to 1000 s (16.7 min) rather than the usual 10^6 s (20 days) used

in many published diagrams. Transformations that occur over a 20 day period are of little interest in heat-treating operations. At 595 °C (1100 °F), the transformation begins in about 0.15 s in the low specification composition, in 1 s in the actual composition, and after about 3 s in the high specification composition. The C curves illustrate the shift in the start of transformation with alloy content. The mathematical expression describing the curves allows hardness predictions to be made under a wide variety of quenching conditions.

Table 10 Comparison of actual chemical composition with chemical composition limits of AISI 4130 steel

Steel designation	Composition, wt%						
	C	Si	Mn	Ni	Cr	Mo	Cu
Low specification	0.280	0.150	0.400	0.160	0.800	0.150	0.150
Actual composition	0.290	0.240	0.550	0.160	1.020	0.150	0.150

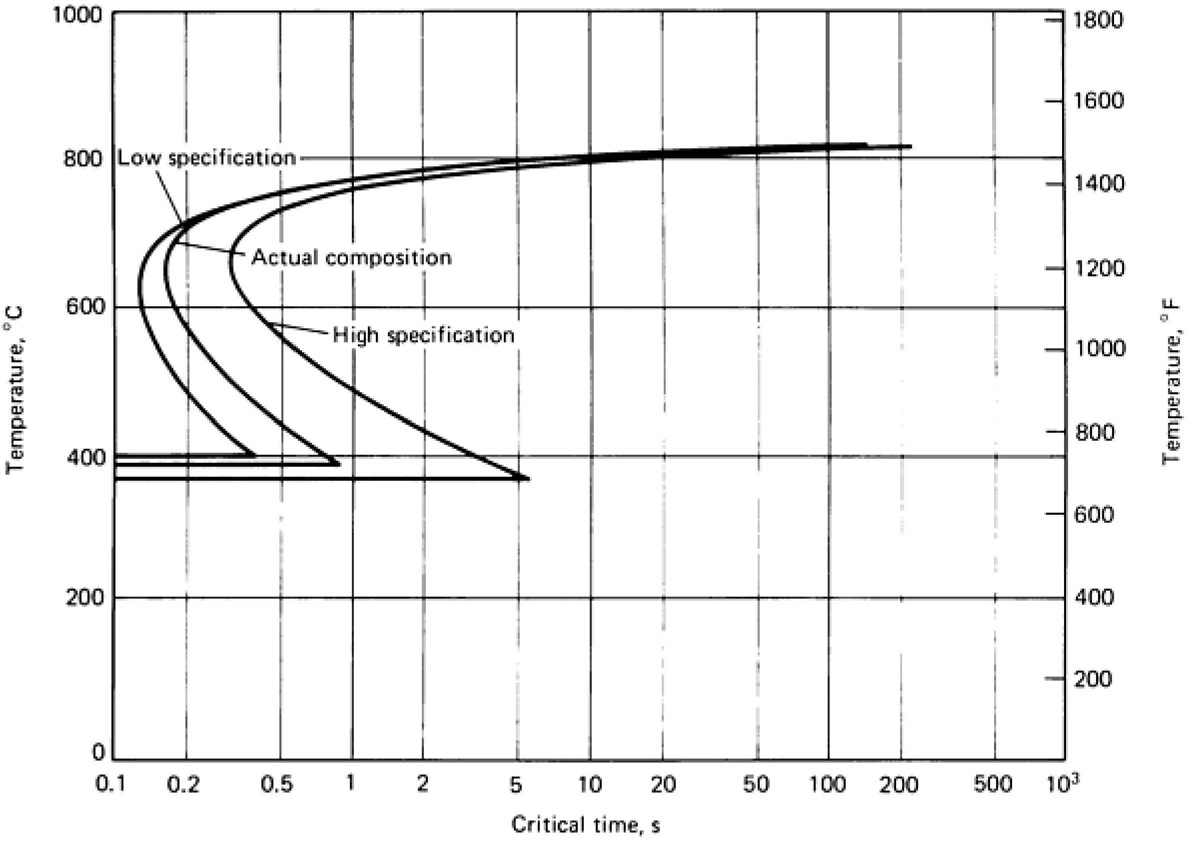


Fig. 38 Approximate TTP curves for 4130 low-alloy steel compositions in Table 10

Some correlations between quench factor, predicted hardness, and measured hardness in cast 4130 are presented in Table 11 and the results are graphically illustrated in Fig. 39. The solid line in Fig. 39 represents the predicted hardness as a function of quench factor, and the data points are measured hardness values at locations in a quenched part where cooling curves were available.

Table 11 Measured and predicted hardness at 17 positions in a water quenched 4130 low-alloy steel casting

Casting position	Cooling rate at 705 °C (1300 °F)		Quench factor, *H*	Hardness, HRC	
	°C/s	°F/s		Predicted	Measured
1	114.2	205.4	7.2	51.8	52
2	67.7	121.7	12.4	50.9	51
3	40.1	72.1	18.5	49.9	50
4	29.4	52.9	25.6	48.8	50
5	21.6	38.8	33.1	47.7	49
6	17.4	31.3	41.5	46.4	47
7	13.2	23.8	50.1	45.2	45
8	11.1	19.9	58.7	44.1	42
9	9.5	17.0	67.3	43.0	42
10	7.1	12.7	86.8	40.7	39
11	5.4	9.8	103.1	38.9	38
12	4.5	8.1	119.1	37.3	36
13	3.8	6.8	134.8	35.8	35
14	3.3	5.9	150.1	34.5	34
15	2.6	4.6	175.3	32.5	33
16	2.2	3.9	197.6	31.0	31

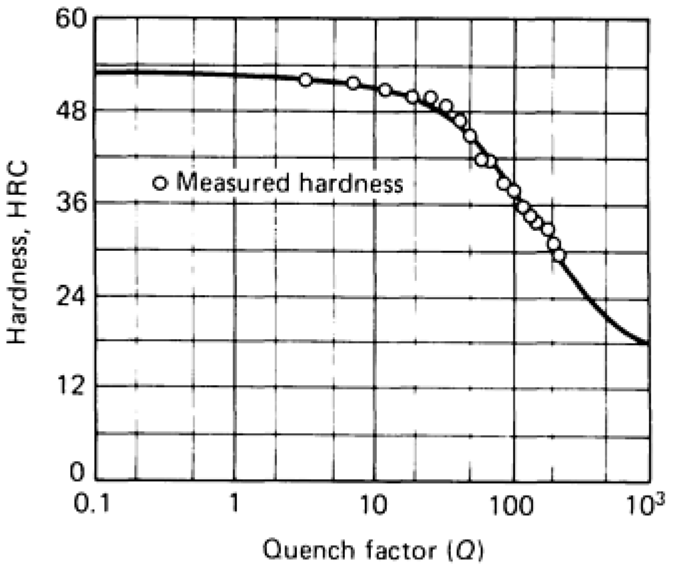


Fig. 39 Correlation between predicted hardness, H_p, and measured hardness at 18 locations in a quenched 4130 low-alloy steel casting

While quench factor analysis appears to be an excellent technique of correlating cooling curves with metallurgical response, it suffers from a lack of availability of constants for the C_T function. However, these can be determined experimentally. Once computerized, this technique is one of the simplest to use by both the heat treater and metallurgical researcher.

Grossmann Quench Severity

A practical method for evaluating quench severity and determining the response of a steel to the imposed quenchant conditions is to determine the Grossmann quench severity or *H* value (Ref 49). The *H* value reflects the ability of the quenching medium to extract heat from a hot steel workpiece. If the *H* value of still water is taken as 1.0, the *H* values of oil, water, and brine are as presented in Tables 1 and 3.

The relations between bar diameter, inherent hardenability, and *H* value may be plotted as shown in Fig. 40, which is referred to as a Grossmann chart. The *H* values of a material are plotted as follows: If a 25 mm (1 in.) diameter part is quenched in oil with good agitation (0.50 *H* value), the chart shows that, reading across the 25 mm (1 in.) diameter horizontal line to the 0.50 *H* value and then down, a value of 8 mm ($\frac{5}{16}$ in.) on the end-quench hardenability specimen is obtained. This means that the center of the bar can be expected to have the same hardness as that shown at 8 mm ($\frac{5}{16}$ in.) from the quenched end of a standard Jominy hardenability specimen made from the steel being quenched.

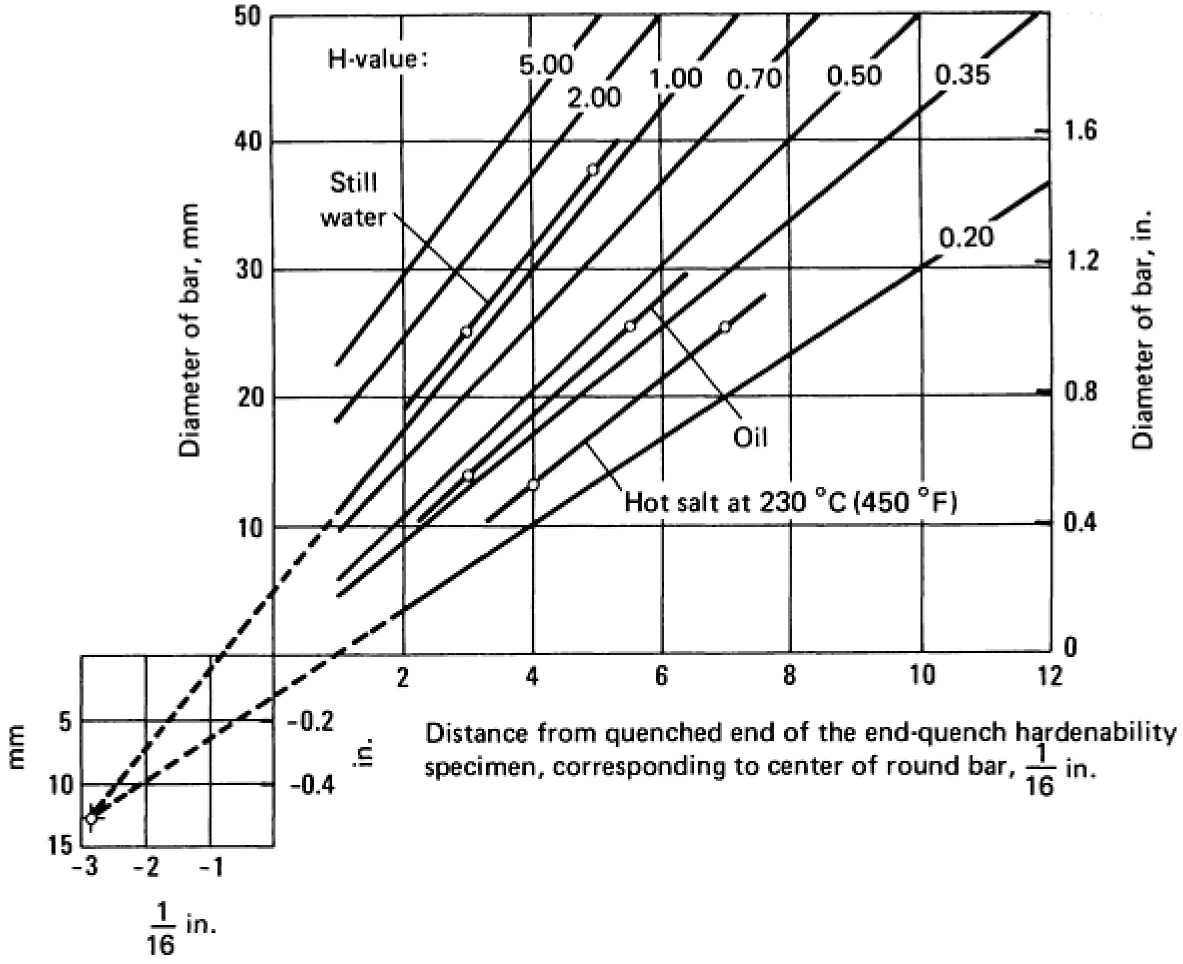


Fig. 40 Grossmann chart relating bar diameter, hardenability of steel, and severity of quench. *H*-value (severity of quench): 5.00, strong brine quench, violent agitation; 2.00, poor brine quench, no agitation; 1.00, poor water quench, no agitation; 0.70, strong oil quench, good agitation; 0.50, good oil quench, good agitation; 0.35, good oil quench, moderate agitation; and 0.20, poor oil quench, no agitation

The cooling power of a quench bath under any loading condition can also be determined using Fig. 40. If the hardenability of the steel and the bar diameter are known, it is possible to plot a point on the quench-severity curve. For example, if the 8 mm ($\frac{5}{16}$ in.) point on the end-quench specimen shows a hardness of 45 HRC, and a 25 mm (1 in.) diameter bar of the same steel quenched in the bath to be evaluated has a center hardness of 45 HRC, the result indicates a quench severity of 0.50.

Regardless of the hardness obtained at the center of the 25 mm (1 in.) diameter test bar, it can be plotted on Fig. 40 at the correct location. If the center hardness had been 48 HRC, and if the hardenability curve for the bar of steel tested had shown 48 HRC at 6 mm ($\frac{1}{4}$ in.), the 6 mm line and the 25 mm diameter line would intersect at a quench severity of 0.70.

The various quench severity lines of the Grossmann chart converge at a point outside the normal chart range. The point of intersection can be used as a second point in drawing new quench-severity lines. An example is illustrated by the line labeled oil. The two experimental points on this line were obtained by quenching a stepped bar of steel of known hardenability having two different diameters, 25 and 12.5 mm (1 and $\frac{1}{2}$ in.). The use of a bar with two diameters offers a means of checking results because it provides three points on the line. The results obtained from hot salt, oil, and still water, as determined with stepped test bars, are plotted on Fig. 40.

The principal advantage of this test is that the specimen can be treated along with other work just as if it were a production part; thus, the quench is evaluated under the conditions of temperature and agitation that actually prevail in production quenching of a load of parts. The test bar should be of such diameter that the as-quenched hardness at the center of the bar falls on the sloping portion of the Jominy hardenability curve for the steel being quenched. The test can be performed most conveniently with a shallow-hardening steel because this type of steel permits the use of smaller diameter test bars, which are easier to prepare and section after being quenched. The use of shallow-hardening steel in no way detracts from the validity of the test results, because severity of quench is an inherent characteristic of the bath and is not affected by part size or hardenability.

The Rushman-Lamont method is a variation of the bar quenching technique. Two bars having the same composition, intermediate hardenability (typically 1141), and different diameters are quenched in the facility of interest. The bars are then cut in two and the hardness at the bar center or mid-radius measured. Using the bar diameter and the equivalent Jominy distance based on the hardness achieved when the two bars were quenched, the data points are placed on a Lamont diagram, illustrated in Fig. 41 (Ref 30, 50).

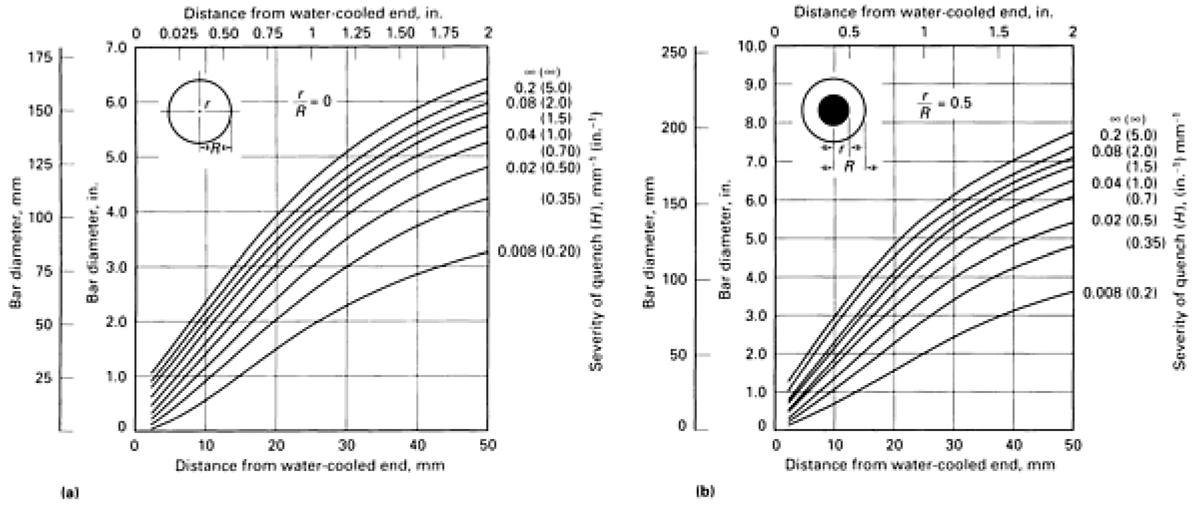


Fig. 41 Location in end-quenched Jominy hardenability round bar specimen corresponding to (a) center position and (b) half-radius position. Source: Ref 30, 50

This procedure involves:

- *Step 1:* Quenching 2 bars (typically 1141) of different diameters (typically 13 mm and 25 mm, or $\frac{1}{2}$ and 1 in.) in the quenchant or quench facility of interest
- *Step 2:* Determining the Jominy curve for the steel used in the bars
- *Step 3:* Comparing center or mid-radius hardnesses in the bar with the Jominy curve and assigning a Jominy distance to the cooling rate
- *Step 4:* By comparison with Fig. 41 or Table 12, an *H* value for the quenchant can be assigned

Table 12 Effect of end-quench distance and Grossmann quench severity, *H*, on the equivalent bar diameter of 1141 resulfurized carbon steel

Distance from end in end-quench test	Equivalent bar diameter when quenched[(a)]			
	Oil	Water	Still brine, H = 2.0	Infinite or idealized

mm	$\frac{1}{16}$ in.	in.	Still, *H*=0.25	Circulated, *H*=0.45	Still, *H*=1.0	Circulated, *H*=1.5	*H* = 2.0	quench, *H* = ∞
1.5	$\frac{1}{16}$	. . .	0.1	0.15	0.3	0.35	0.4	0.7
3	$\frac{2}{16}$	$\frac{1}{8}$	0.2	0.3	0.5	0.65	0.75	1.15
. . .	$\frac{3}{16}$	. . .	0.35	0.55	0.85	1.0	1.25	1.6
6	$\frac{4}{16}$	$\frac{1}{4}$	0.5	0.80	1.15	1.3	1.5	1.9
. . .	$\frac{5}{16}$	. . .	0.6	0.95	1.4	1.6	1.75	2.2
10	$\frac{6}{16}$	$\frac{3}{8}$	0.8	1.2	1.6	1.8	2.0	2.4
. . .	$\frac{7}{16}$	. . .	1.0	1.4	1.8	2.0	2.3	2.7
13	$\frac{8}{16}$	$\frac{1}{2}$	1.1	1.5	2.1	2.3	2.5	2.9
. . .	$\frac{9}{16}$	. . .	1.3	1.7	2.3	2.5	2.7	3.2
16	$\frac{10}{16}$	$\frac{5}{8}$	1.4	1.9	2.5	2.7	2.9	3.4
. . .	$\frac{11}{16}$	. . .	1.6	2.1	2.8	3.0	3.2	3.6
19	$\frac{12}{16}$	$\frac{3}{4}$	1.7	2.2	3.0	3.2	3.4	3.8
. . .	$\frac{13}{16}$	. . .	1.9	2.4	3.2	3.4	3.5	4.0
22	$\frac{14}{16}$		2.0	2.5	3.3	3.5	3.7	4.2
. . .	$\frac{15}{16}$	. . .	2.1	2.7	3.5	3.7	3.9	4.4
25	$\frac{16}{16}$	1	2.3	2.8	3.7	3.9	4.1	4.6

. . .	$\frac{17}{16}$	. . .	2.4	3.0	3.9	4.1	4.2	4.7
29	$\frac{18}{16}$	$1\frac{1}{8}$	2.5	3.1	4.0	4.2	4.4	4.9
. . .	$\frac{19}{16}$	. . .	2.6	3.3	4.1	4.4	4.5	5.0
32	$\frac{20}{16}$	1	2.7	3.4	4.3	4.5	4.7	5.1
. . .	$\frac{21}{16}$	. . .	2.8	3.5	4.4	4.7	4.8	5.3
35	$\frac{22}{16}$	1	2.9	3.6	4.5	4.8	4.9	5.4
. . .	$\frac{23}{16}$	. . .	3.0	3.7	4.7	5.0	5.1	5.5
38	$\frac{24}{16}$	1	3.1	3.8	4.8	5.1	5.2	5.6
. . .	$\frac{25}{16}$	. . .	3.2	4.0	4.9	5.2	5.3	5.8
41	$\frac{26}{16}$	1	3.3	4.0	5.0	5.3	5.4	5.9
. . .	$\frac{27}{16}$	. . .	3.4	4.1	5.1	5.4	5.5	6.0
44	$\frac{28}{16}$	1	3.5	4.2	5.2	5.5	5.6	6.1
. . .	$\frac{29}{16}$	. . .	3.6	4.3	5.3	5.6	5.6	6.2
48	$\frac{30}{16}$	1	3.6	4.4	5.4	5.7	5.7	6.2
. . .	$\frac{31}{16}$	. . .	3.7	4.5	5.5	5.8	5.8	6.3
51	$\frac{32}{16}$	2	3.8	4.5	5.5	5.8	5.9	6.4

(a) When the end-quench hardness curve of a steel has been found, this table enables the user to estimate the hardnesses that would be obtained at the centers of quenched round bars of different diameters, when that same steel is quenched with various severities of quench. For each

successive in. position, the hardness obtained in the end-quench test would be found at the center of the bar size shown.

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Quenching Media

Many different media have been used for quenching. Most are included in the list that follows, but some (indicated by *) are used only to a limited extent:

- Water
- Aqueous brine solutions
- Aqueous caustic solutions*
- Oils
- Aqueous polymer solutions
- Molten salts
- Molten metals*
- Gases
- Fluid beds*
- Fogs*
- Sprays
- Dry dies*

Water

Vigorously agitated water produces cooling rates approaching the maximum rates attainable with liquid quenchants. Water is inexpensive, readily available, and, unless contaminated, it is easily disposed of with a minimum of pollution or health hazard. Water is also effective in breaking scale from the surface of steel parts quenched from furnaces without protective atmospheres.

Water, therefore, is used wherever a severe quench does not result in excessive distortion or cracking. Water is widely used for quenching nonferrous metals, austenitic stainless steels, and other metals that have been solution treated at elevated temperatures.

One disadvantage of water is that its rapid cooling rate persists at lower temperatures where distortion and cracking are more likely to occur. Consequently, water quenching is usually restricted to the quenching of simple, symmetrical parts made of shallow hardening grades of steel. A second disadvantage of using plain water is that it may have an extended vapor blanket stage. Complex parts encourage vapor entrapment which may produce an uneven hardness and unfavorable stress distribution leading to distortion or soft spots. Water quenched steel parts may also rust unless immediately treated with a rust preventative.

Facility Operation. To obtain reproducible results by water quenching, the temperature, agitation, and extent of contamination must be controlled. Generally, water will provide uniform quenching speed and reproducible results if maintained at a temperature of 15 to 25 °C (55 to 75 °F) and agitated to produce velocities greater than 0.25 m/s (50 ft/min).

The effects of water temperature on cooling curves and cooling rate curves in an Inconel 600 probe (12.5 mm diameter), are illustrated in Fig. 42 (a) and (b), respectively. Similar cooling curves and cooling rate curves obtained at a water temperature of 55 °C (130 °F) using quenchant velocities between 0 and 0.75 m/s (0 and 150 ft/min) are illustrated in Fig. 43.

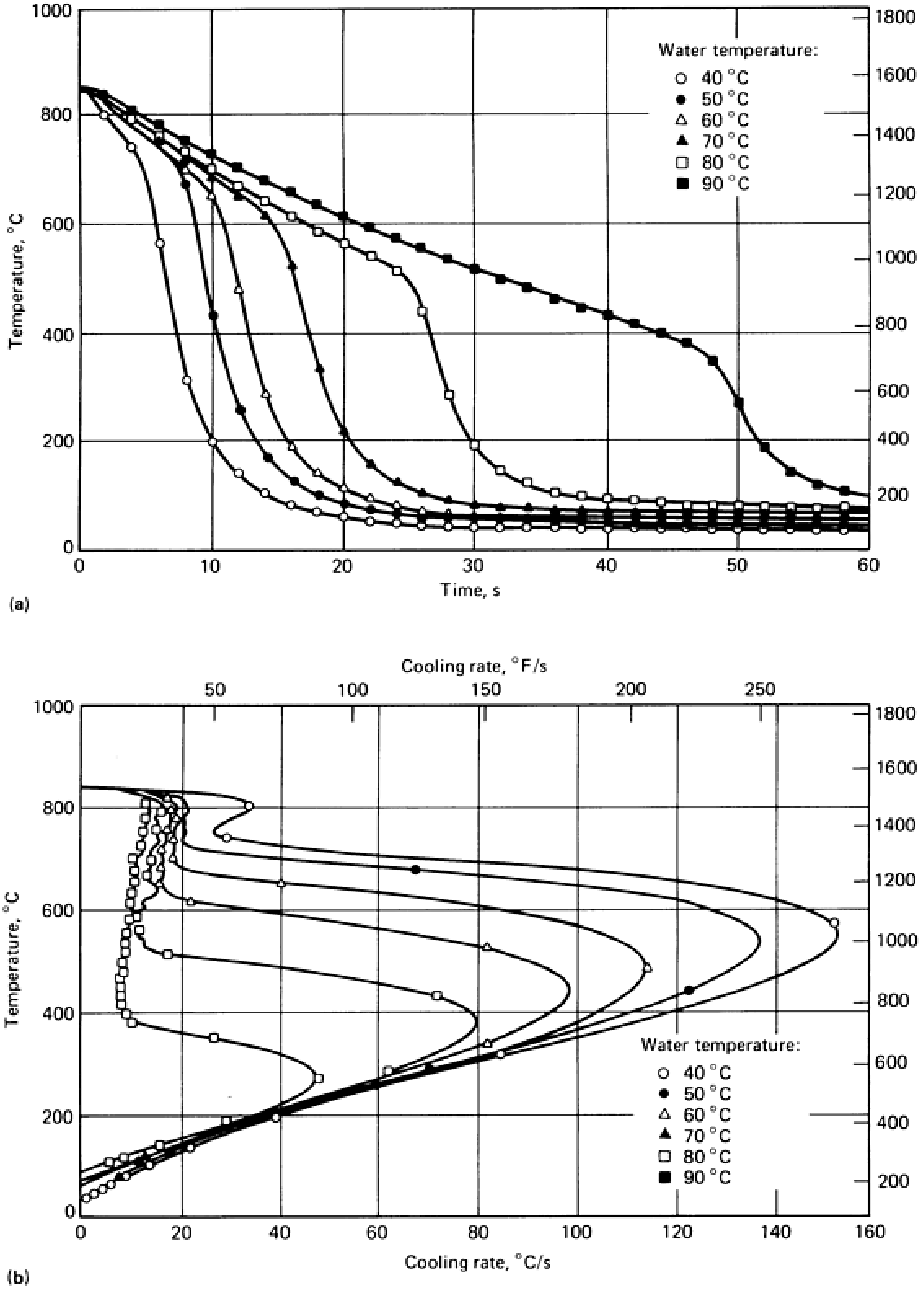


Fig. 42 Effect of bath temperature on heat removal in a Wolfson probe. (a) Cooling curves. (b) Cooling rate curves. Quenchant is water having 0.25 m/s (50 ft/min) velocity.

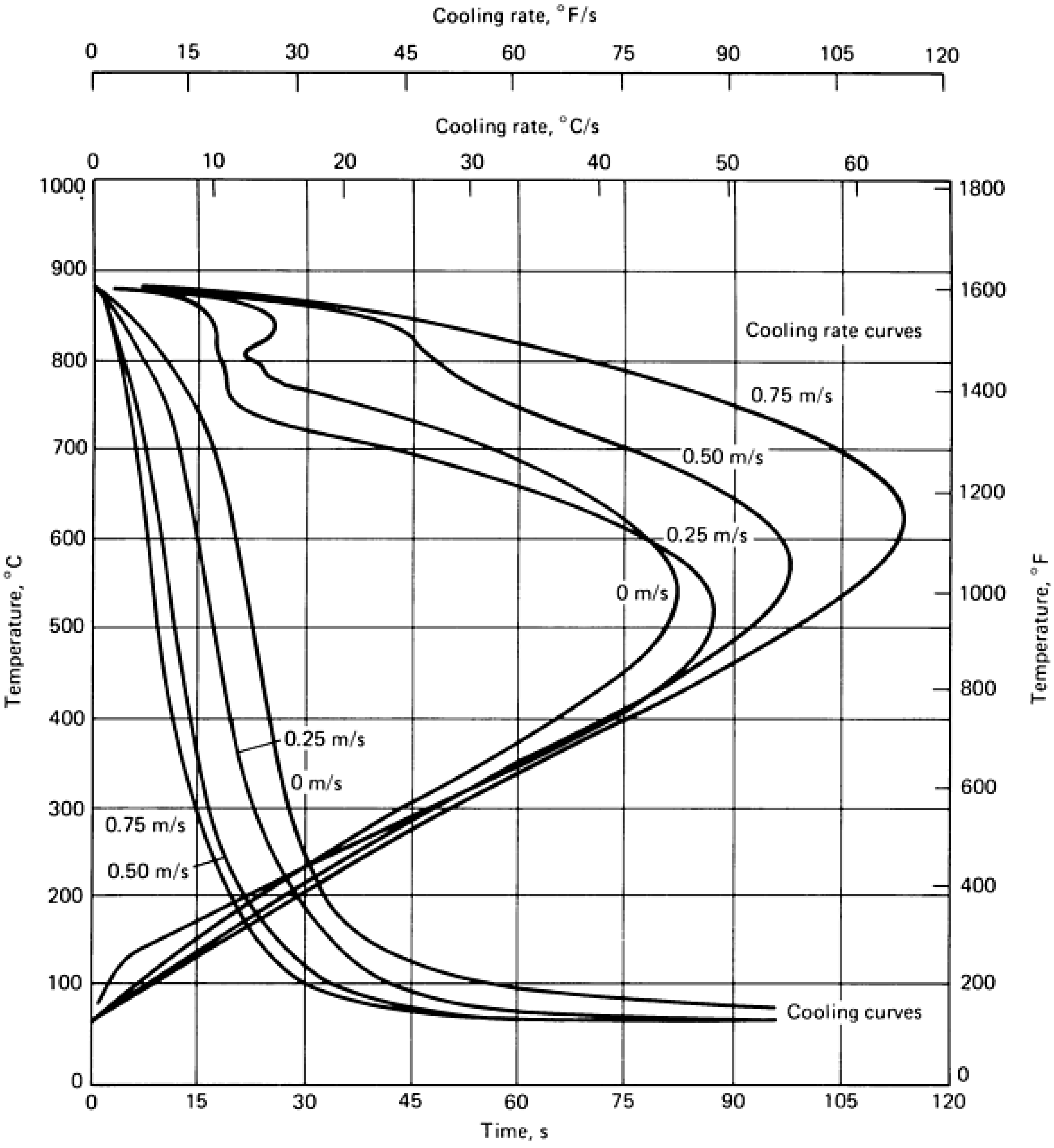


Fig. 43 Cooling curves and cooling rate curves for a 25 mm (1 in.) diameter stainless steel probe quenched in 55 °C (130 °F) water that is flowing at selected velocities from 0 to 0.75 m/s (0 to 150 ft/min)

The time-temperature and rate curves shown in Fig. 42 also illustrate that quenching into water of increasing temperature increases the duration of A-stage cooling and decreases the A- and B-stage cooling rates. Both of these effects will increase the difficulty of achieving desirable as-quenched hardness values.

There is relatively little impact of increasing water temperature on C-stage cooling rates. Since the objective of raising the water temperature is to decrease cracking and distortion and since the tendency for cracking to occur is often proportional to C-stage cooling rates, these figures show that raising the water temperature is a relatively ineffective procedure. This data explains why alternative quenchants such as oils and aqueous polymers are used. Another reason for the use of these quenchants as alternatives to hot water is that these media produce much more uniform wetting of the metal surface during the quenching. This is critically important if localized surface cracking and distortion are to be avoided.

In some applications, it is desirable to increase the quench severity of water and avoid the use of caustic and brine quenchants. This may be done by increasing the agitation rate. The cooling rate data shown in Table 3 and Fig. 43 show

that substantial increases in cooling rates are attainable by increasing the agitation rate. At least some agitation is recommended in order to improve the uniformity of the quenching process. The cooling power of water decreases rapidly as water temperature increases, as indicated in Fig. 44. Agitation is especially important during water quenching because it disperses vapor bubbles and directs cooler water against the workpiece.

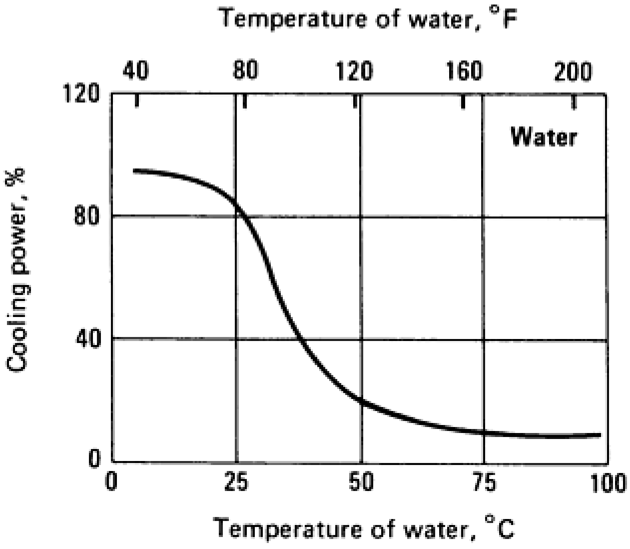


Fig. 44 Relation of the surface cooling power of moderately agitated water to water temperature

Contamination Effects. Contamination of quench baths with heat-treating salts is likely to further increase the cooling rate because salts reduce the duration of the vapor blanket stage. Insoluble salts carried into the quench tank from activated salt baths may interfere with the operation of the pumping system and reduce the volume of water in the quench tank. Periodic desludging or replacement of the quench water is therefore recommended. Contaminants such as soaps, algae, slimes, or emulsion-formers reduce the cooling rate by creating films that retard heat transfer from the surface and prevent cooler water from contacting the part.

Brine Solutions

The term brine, as applied to quenching, refers to aqueous solutions containing various percentages of salts such as sodium or calcium chloride. The cooling rates produced by brine are higher than provided by water for the same degree of agitation, or alternatively, less agitation is required to achieve a given cooling rate. The higher cooling rates reduce the possibility of soft spots from steam pockets. However, the higher cooling rates generally increase the likelihood of distortion or cracking. Complex baffling patterns in the quench tank and propeller agitation, both of which are often necessary with oil and water quenchants, are not always required with a brine quench, but may be required for steels with very low hardenability.

Brine quenching is used only where oil or water quenchants do not provide desired hardness due to insufficient quench severity. Some of the disadvantages of brine are that it is corrosive, and for reasonable service life, the quench tank, pumps, conveyors, and other equipment in contact with the brine must be either protected by a coating, or made of corrosion-resistant metals such as copper-base alloys or stainless steels. In addition, a hood may be needed to carry off the corrosive fumes to protect nearby equipment from attack. The cost of brine quenching is higher than water because of the required use of special pumps, quenching facilities, and corrosion inhibitors.

Concentration Effects. The concentration of the brine can be expressed in several ways (see Table 13). Although brine solutions containing up to 24% NaCl progressively reduce the vapor stage, such high concentrations are generally impractical.

Table 13 Relation of brine density to brine concentration

Salt, %	Specific gravity		Salt concentration	
	Direct reading hydrometer	°Bé[a]	g/L	lb/gal
NaCl solutions				
4	1.0268	3.8	41.1	0.343
6	1.0413	5.8	62.4	0.521
8	1.0559	7.7	84.5	0.705
9	1.0633	8.7	95.9	0.800
10	1.0707	9.6	107.1	0.894
12	1.0857	11.5	130.3	1.087
NaOH solutions				
1	1.0095	1.4	10.1	0.0842
2	1.0207	2.9	20.4	0.1704
3	1.0318	4.5	31.0	0.2583
4	1.0428	6.0	41.7	0.3481
5	1.0538	7.4	52.7	0.4397

(a) °Bé, Baumé; specific gravity for liquids heavier than water is 145/(145 - *n*), where *n* is reading on Bé scale in °Bé

In conventional quenching, it has been found that a 10% NaCl solution is quite effective from the viewpoint of hardening. The value of the 10% NaCl solution in developing maximum surface hardness in conventional quenching is illustrated in Fig. 45. It should be noted that although end-quench values are used in Fig. 45, the specimen was not quenched as in the standard end-quench test but was quenched in still water with only the end face contacting the water to simulate surface quenching.

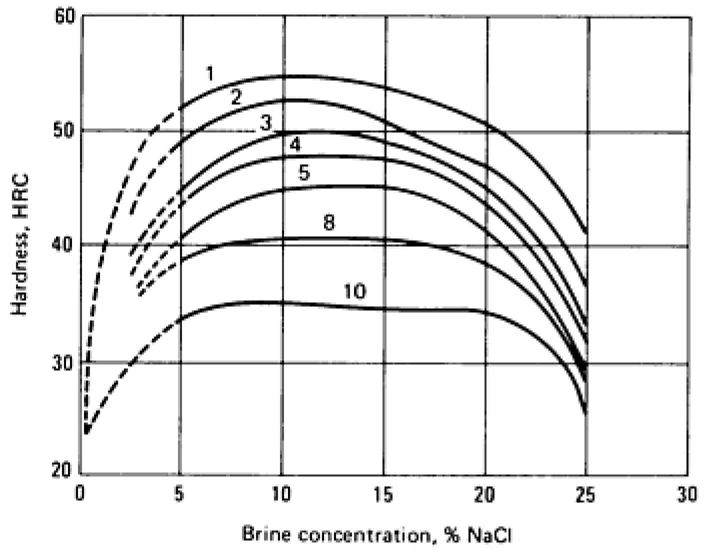


Fig. 45 Relation of hardness to brine concentration when still-quenching end-quench specimens in a 99 °C (210 °F) brine solution. Numbers above curves indicate distance from quenched end in units of $\frac{1}{16}$ in.

Kobasco characterized the quenching performance of aqueous brines by determining the heat transfer coefficients from cooling curve analysis. The results of this study, illustrated in Fig. 46, also showed that the optimal level of both aqueous NaCl and caustic (sodium hydroxide) solutions was approximately 10% (Ref 51). These results emphasize the point that it is important to monitor the concentration of the brine if reproducible results are to be obtained.

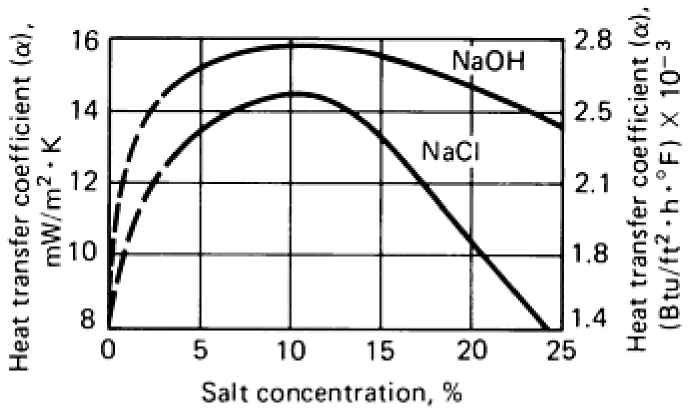


Fig. 46 Effect of salt concentration on the heat transfer coefficient of sodium hydroxide and sodium chloride brine solutions

Temperature Effects. The cooling power of brine solutions is not critically affected by small variations in operating temperature. Although such solutions can be used at or near the temperature of boiling water, they provide maximum cooling power at about 20 °C (70 °F). The relatively small effect of temperature on cooling power of brine compared with water is illustrated in Fig. 47.

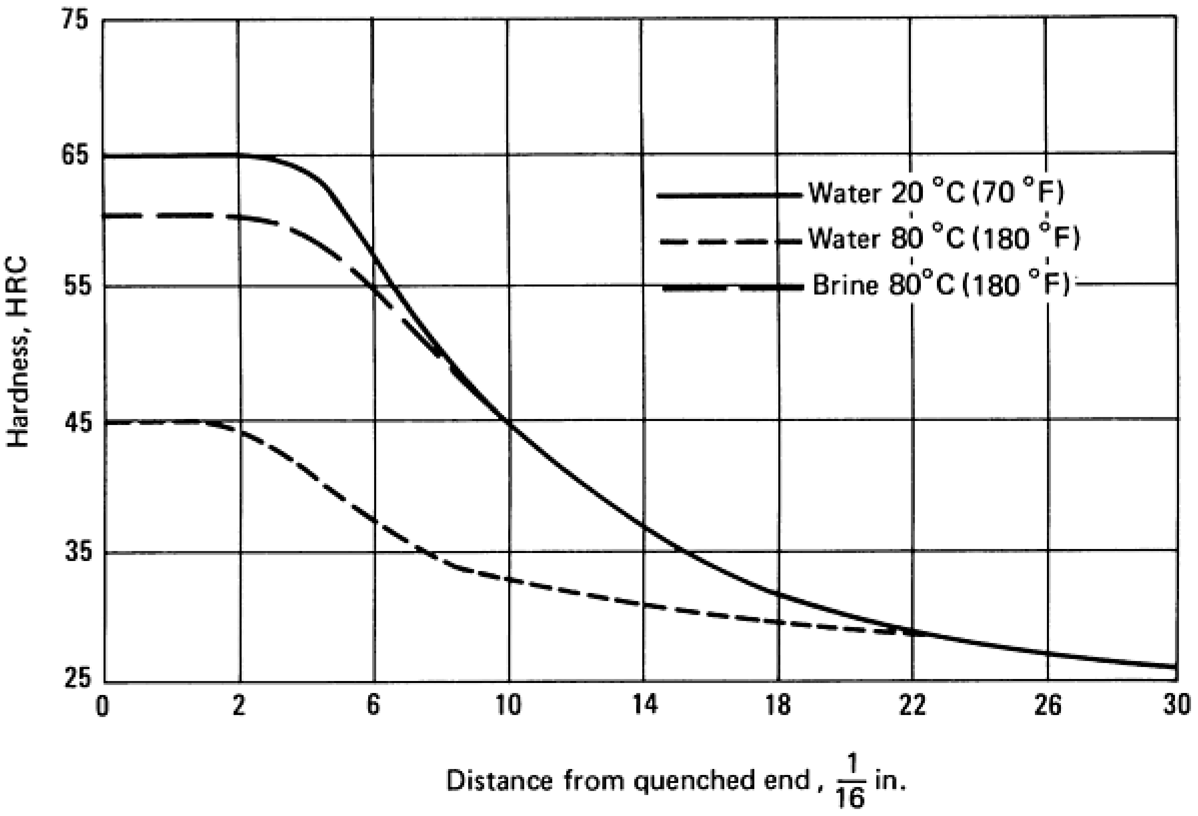


Fig. 47 Relation of hardness to the distance from quenched end of specimens quenched in water and brine. Cooling power of brine is greater than water at 80 °C (180 °F).

Contamination Effects. Sludge and scale should be removed periodically, because both act to clog pumps and recirculating systems as well as reduce the volume and cooling rate of the brine quench bath. Excess water reduces the solution strength and quenching power of the brine.

Caustic Solutions

Aqueous solutions of 5 to 10 wt% sodium hydroxide (NaOH) are also sometimes used for quenching. The performance of such solutions is similar to brine solutions sharing about the same advantages as a quenchant (Ref 51). The main shortcoming of caustic solutions is its high alkalinity which is harmful to human skin.

Cooling curves indicate that at 20 °C (70 °F) and moving at 0.9 m/s (3 ft/s), a solution containing 5 wt% NaOH can cool the surface of a cylinder 12.5 mm ($\frac{1}{2}$ in.) in diameter and 50 mm (2 in.) long from 870 to 200 °C (1600 to 390 °F) in 0.31 s. Under the same conditions, a 5% NaCl solution required 0.48 s, while plain water requires 1.2 s. However, a sodium chloride solution is safer, less costly, and easier to handle than a sodium hydroxide solution, and may be preferred even though the latter provides faster cooling rates.

Oils

Quenching oils can be divided into several distinctive groups based on composition, the presence of additives, and application temperature.

Classification. Quenching oils are usually categorized as slow, conventional, fast, and martempering or hot quenching oils. An additional group of oil-base quenchants are oil-in-water emulsions. These find only limited use because of their unpredictable quenching characteristics.

Mineral-oil-base quenchants are often classified by their quench severity according to the GM Quenchometer (nickel ball) test (ASTM A 235). In this test, a standard nickel ball is quenched into an oil at 25 °C (80 °F) and the time for the nickel

ball to cool to its Curie point is recorded. Shorter times for cooling to the Curie temperature imply an increase in the quench severity. The oils are classified in Table 14.

Table 14 Oil classification by the magnetic quenchometer test per ASTM D 3520

Oil classification	Cooling time, s
Fast	8-10
Medium	11-14
Slow	15-20

All modern quenching oils are based on mineral oils, usually paraffin-base, and do not contain fatty oils formerly used. The mineral oils have better aging stability and some of the historically used fatty oils are now unavailable. Sperm oil, which has been used successfully as quenchant for bright quenching of small workpieces, is banned from importation and use in the United States.

Slow and conventional quenching oils sometimes contain antioxidants but are free of additives that might accelerate their quenching effects. The typical viscosity lies in the range of 100 to 110 Saybolt universal second (SUS) at 40 °C (100 °F) but can reach about 200 SUS at 40 °C (100 °F).

Fast quenching oils are mineral oil blends with a viscosity between 50 and 110 SUS at 40 °C (100 °F) but more typically with a viscosity between 85 and 105 SUS. They contain proprietary additives to enhance quenching and often contain antioxidants and wetting agents.

Martempering or hot quenching oils are solvent-refined paraffin-base mineral oils with good thermal stability and oxidation resistance. They are used at temperatures between about 95 °C (200 °F) and 230 °C (450 °F) for modified and actual martempering of ferrous metals. Martempering oils may also contain antioxidants to improve their aging stability. They are available with comparatively high quenching effects, even at high use temperatures, because of the addition of effective speed improvers. Also, the increased viscosity has a tendency to eliminate vapor phase cooling.

Emulsions of soluble oils, usually employed as coolants in metal-working processes such as grinding, cutting, and sometimes forming, are used for quenching with concentrations of 3 to about 15%. Oil emulsions, when used as quenchants, provide a quench similar to water. However, it is difficult to maintain a constant severity over time since the emulsion is usually unstable under quenching conditions.

Typical physical and chemical properties of several commercially available quenching oils are listed in Table 15. This table shows the appropriate ASTM test methods for the determination of the properties listed. These tests are commonly used by vendors for quality control of new and used quenching oils. Oils from different producers may differ in general properties and quenching effects as a result of variations in composition and additives present.

Table 15 Typical properties of commercially available quenching and martempering oils

Type of quenching oil	No.	API gravity[(a)]	Flash point[(b)]		Pour point[(c)]		Viscosity at 40 °C (100 °F), SUS[(d)]	Saponification[(e)]	Ash[(f)], %	Water[(g)], %
			°C	°F	°C	°F				
Conventional, no additives	1	33	155	315	-12	10	107	0.0	0.01	0.0

	2	27	185	365	-9	15	111	0.0	0.03	0.0
Fast, with speed improvers	3	33.5	190	370	-12	10	95	0.0	0.05	0.0
	4	35	160	320	-4	25	60	0.0	0.20	0.0
Martempering, without speed improvers	5	31.1	235	455	-9	15	329	0.0	0.02	0.0
	6	28.4	245	475	-9	15	719	0.0	0.05	0.0
	7	26.6	300	575	-7	20	2550	0.0	0.10	0.0
Martempering, with speed improvers	8	28.4	230	450	-9	15	337	2.0	1.1	0.0
	9	27.8	245	475	-9	15	713	2.2	1.1	0.0
	10	25.5	300	570	-7	20	2450	2.5	1.4	0.0

ASTM specifications:

(a) D 287.

(b) D 92.

(c) D 97.

(d) D 445, D 2161.

(e) D 94.

(f) D 482.

(g) D 95, D 1533

Cooling Characteristics. The ideal quenchant would produce low cooling rates from the solution treating temperature to the A_3 temperature, fast cooling rates from the A_3 to near the M_s, and low rates from the M_s temperature to room temperature. Cold water, and especially aqueous solutions containing inorganic salts, show the highest quenching speeds in the A_3 to A_1 range, but they also quench very fast toward the end of the quenching process. Thus, they are restricted to quenching simple shapes and steels of comparatively low hardenability. For complex workpieces, water and brine solutions usually cause intolerable distortion, warpage, and quench cracks.

Almost all quench oils produce lower quench rates than water or aqueous inorganic salt solutions. However, heat removal is more uniform than typically achievable with water. As a result, the dangers of distortion or cracking are considerably diminished.

Slow and conventional quenching oils exhibit comparatively long A-stage cooling times, during which period the quenching speed is relatively low. The rate of cooling increases during B-stage cooling, followed again by slow cooling in the C-stage or convective cooling stage. The quench severity of conventional oils is substantially less than that of water and, therefore, may be inadequate for steels of lower hardenability.

The effect of bath temperature, agitation rate, and cross-section size on the maximum cooling rates and the cooling rate at 345 °C (650 °F) for a slow oil quenchant are illustrated by contour plots in Fig. 48. The data show that the maximum cooling rate and the cooling rate at 345 °C (650 °F) increase with increasing circulation rate and decreasing cross-section size. As expected, both parameters are essentially independent of bath temperature.

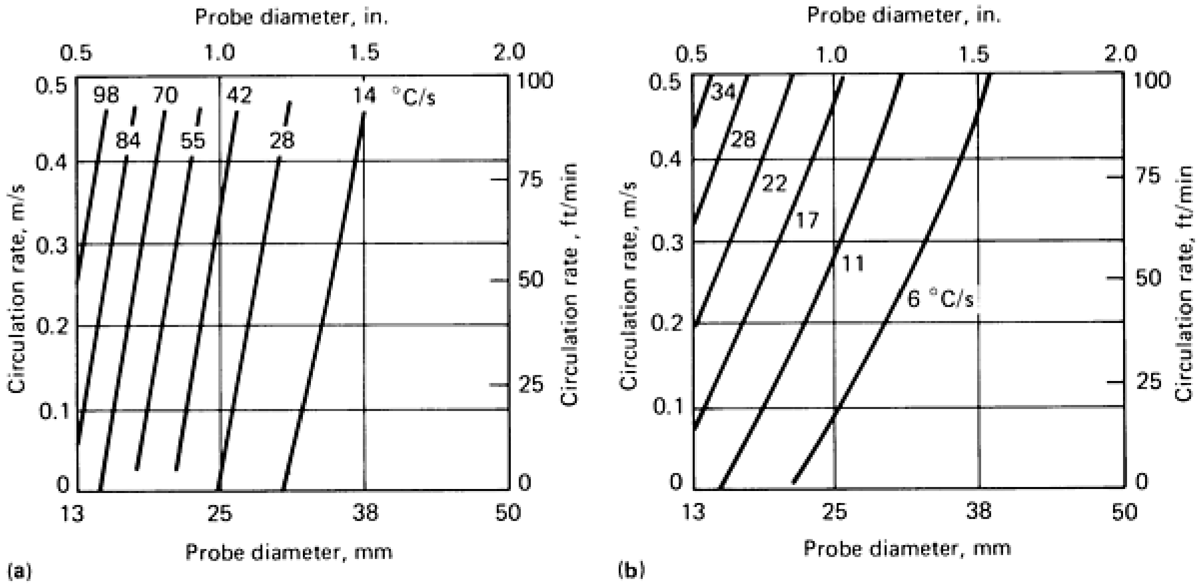


Fig. 48 Contour plots that show quenching properties of a typical slow quench oil. (a) Maximum cooling rate. (b) Cooling rate at 345 °C (650 °F), Data are independent of bath temperature.

Contour plots illustrating the effect of probe diameter and circulation rate on maximum cooling rate, cooling rate at 345 °C (650 °F), predicted hardness in AISI 1045 and 4140 steels, and Grossmann *H* values as produced by a conventional oil are illustrated in Fig. 49. Again, modest changes in oil temperature had no effect on quenchant performance.

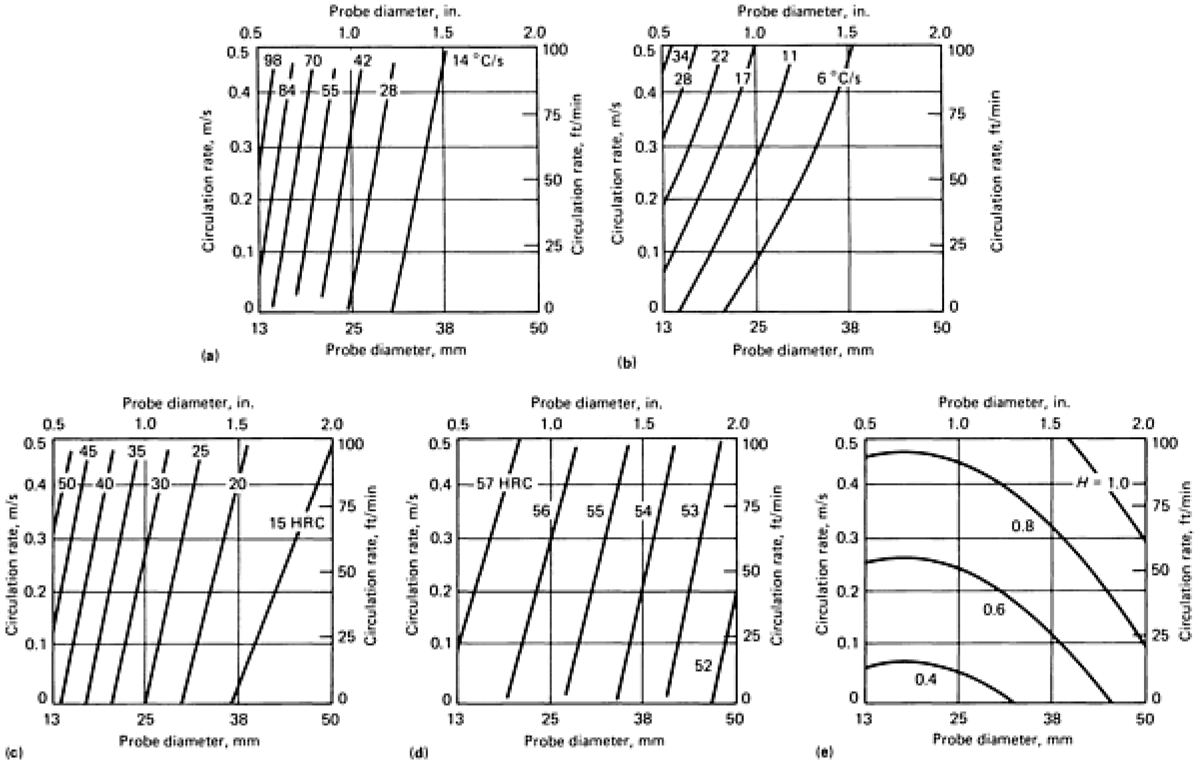
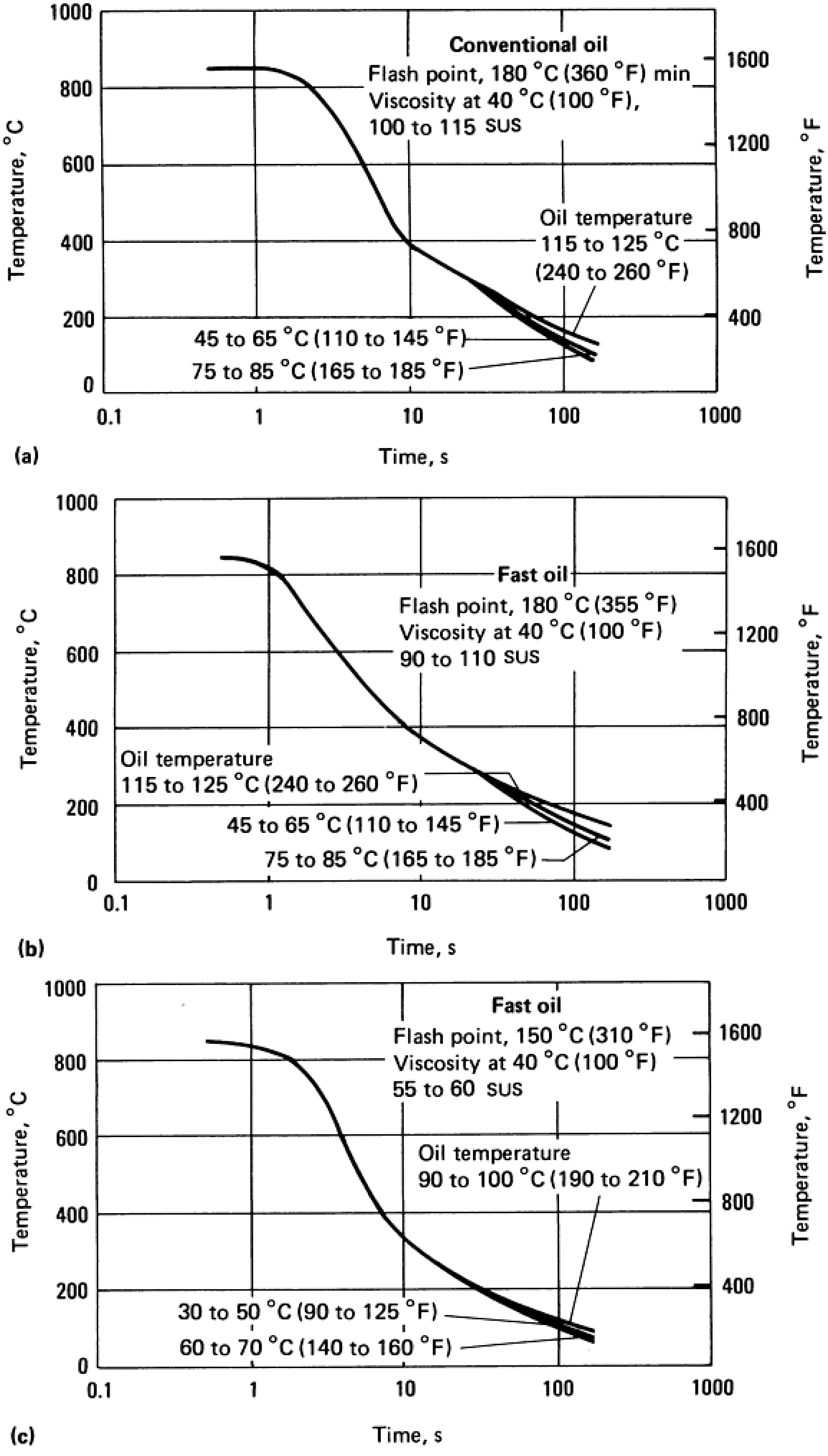


Fig. 49 Plots of probe size versus circulation rate for a conventional mineral oil. (a) Maximum cooling rate. (b) Cooling rate at 345 °C (650 °F). (c) Predicted hardness for 1045 steel. (d) Predicted hardness for 4140 steel. (e) Grossmann *H* factor values. Data are independent of bath temperature.

Fast quenching oils exhibit higher quenching speeds, especially during A-stage cooling and, in some situations, approach the rates exhibited by water. Fast oils exhibit a moderately fast cooling rate in the nucleate boiling range. C-stage cooling rates are usually about the same as provided by conventional quenching oils but substantially slower than those provided by water (see Fig. 50). However, some fast quenching oils contain special additives that provide faster C-stage cooling rates that result in slightly better through-hardening effects, as illustrated by the curves in Fig. 50(c). The cooling characteristics of quenching oils, particularly fast quenching oils, are critically dependent on the concentration of some of the additives. Therefore, it is essential that the quality of quench oil be monitored over time if consistent quench severity is to be maintained.



Conventional oil
Flash point, 180 °C (360 °F) min
Viscosity at 40 °C (100 °F),
100 to 115 SUS
Oil temperature
115 to 125 °C
(240 to 260 °F)
45 to 65 °C (110 to 145 °F)
75 to 85 °C (165 to 185 °F)
Temperature, °C
Temperature, °F
1000
800
600
400
200
0
1600
1200
800
400
0.1
1
10
100
1000
Time, s
(a)
Fast oil
Flash point, 180 °C (355 °F)
Viscosity at 40 °C (100 °F)
90 to 110 SUS
Oil temperature
115 to 125 °C (240 to 260 °F)
45 to 65 °C (110 to 145 °F)
75 to 85 °C (165 to 185 °F)
Temperature, °C
Temperature, °F
Time, s
(b)
Fast oil
Flash point, 150 °C (310 °F)
Viscosity at 40 °C (100 °F)
55 to 60 SUS
Oil temperature
90 to 100 °C (190 to 210 °F)
30 to 50 °C (90 to 125 °F)
60 to 70 °C (140 to 160 °F)
Temperature, °C
Temperature, °F
Time, s
(c)

Fig. 50 Effect of oil type and oil temperature on center cooling curves for type 304 stainless steel specimens still quenched in a conventional oil and in two fast oils. Thermocouples were placed at geometric centers of specimens, which were 13 mm (0.5 in.) in diameter and 100 mm (4 in.) long. See text for discussion of significance of these data.

The data summarized in Fig. 51 show that the quench rates of a fast oil may decrease over time. This is due to selective drag-out of the quench accelerating additives. Thus, the residual oil becomes more like an unaccelerated conventional or slow oil.

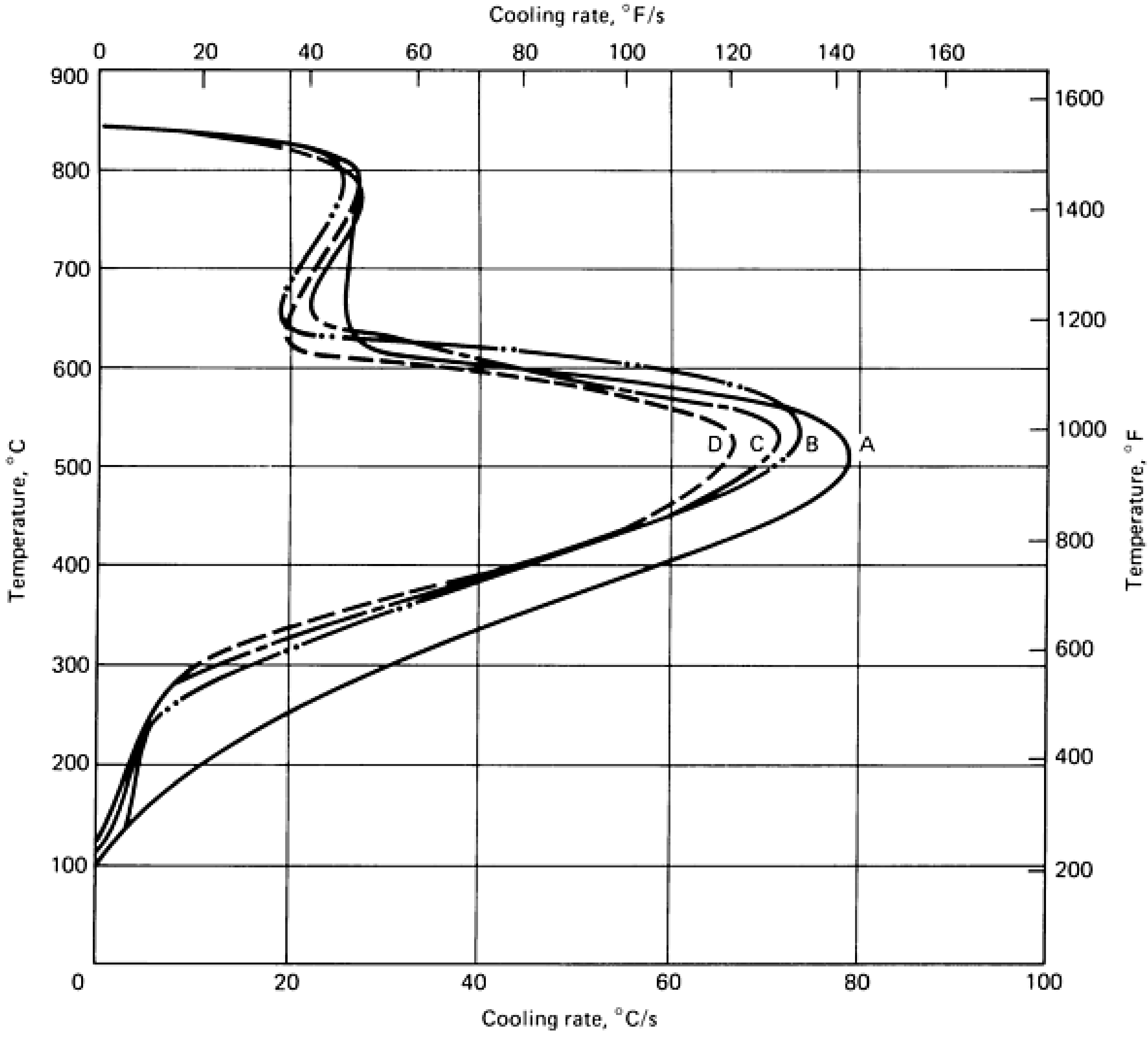


Fig. 51 Variation in cooling rate of a fast quench oil as a function of time used. A, new oil; B, 3-month old oil; C, 6-month old oil; D, 9-month old oil. Data are for oil having a bath temperature of 40 °C (105 °F).

However, oils do not always react in this manner. In some systems, the conditions cause the quench oil to shear, thus causing the oil to increase its quenching severity. In almost all systems, the oil initially speeds up due to the initial contamination with solids which, in suspension, act as a speed-improving additive. As contamination increases and the oil begins to degrade, the quenching severity begins to decrease. The makeup oil added to replace the dragout and evaporated oil usually stabilizes the quenching severity.

If quenching oils are reclaimed from wash systems and returned to the quench system, care must be taken that other fluids and solids are not carried back into the tank.

The variation in quench severity of eight compounded (speed-improving additive-containing) fast quenching oils is shown in Fig. 52 as a shaded band with a reference curve for a conventional additive-free 100 SUS at 40 °C (100 °F) mineral quenching oil. These cooling curves show the difference in quench severity that may be exhibited by conventional and fast quenching oils. These curves were obtained without agitation using a cylindrical austenitic stainless steel test probe with a diameter of 13 mm (0.5 in.) and a length of 64 mm (2.5 in.) containing a thermocouple in its geometric center. The oil temperature was 50 °C (125 °F)

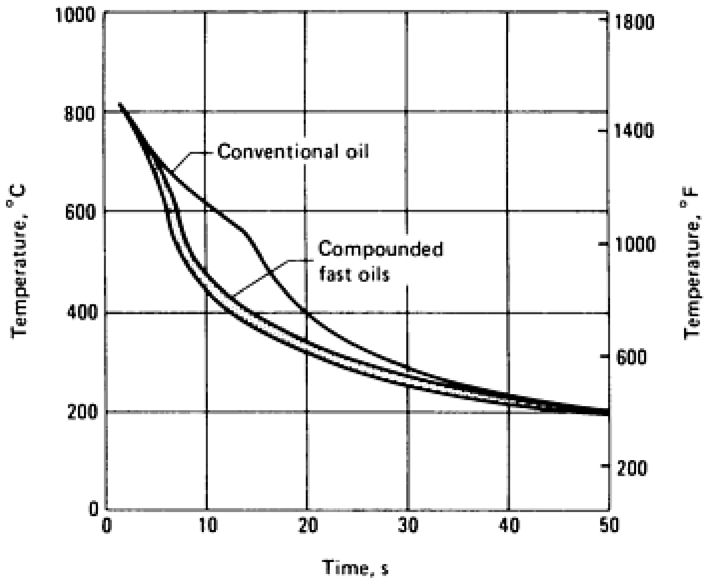


Fig. 52 Center cooling curves for austenitic stainless steel quenched in conventional oil and compounded oils with fast quenching capacities. All oils at 52 °C (125 °F). Specimens were 13 mm (0.5 in.) in diam by 64 mm (2.5 in.) long.

Test results from magnetic quenchometer test methods were presented in Table 5 and show the difference in quenching effect between conventional and fast quenching oils at Various temperatures. Table 5 also shows that martempering oils with speed improvers have, at 120 °C (250 °F), quenching effects close to the upper range of fast oils. The martempering oils quench as fast as conventional 100 SUS quenching oils when used at about 175 °C (350 °F). Thus, the martempering oils permit modified or actual martempering of steel parts that are either thicker or lower in hardenability than previously permissible when using martempering oils without speed-improving additives.

Temperature Effects. The typical ranges for the magnetic quenchometer speeds of the different quenching oil groups are listed in Table 6 as a function of their actual use temperature. Table 6 clearly illustrates that the quenching effect of quenching oils does not change with moderate changes in oil temperature. Significant decreases in quench severity only occur for temperatures over about 150 °C (300 °F) where martempering oils are preferred.

The cooling curves in Fig. 50 also show that the cooling characteristics of quenching oils are not substantially changed over a modest range of operating temperatures. The only differences are found in the last stage of cooling when the temperature of the quenched part approaches the oil temperature. During this stage, the cooling rate decreases with higher quenching oil temperatures. Slower cooling rates reduce temperature gradients between surface and core and result in lower internal stresses. This is especially beneficial while the steel part is passing through the temperature range of martensite formation, below about 260 °C (500 °F).

The cooling curves presented in Fig. 53 show that emulsions of water and soluble oil combine the poorest features of water and oil quenchants. The center-cooling curves of an oil-water emulsion, consisting of 10% soluble oil and 90% water at 25 °C (75 °F) and 50 °C (125 °F), show that stable vapor envelopes are formed at the beginning of the quenching cycle. Thus, at the higher bath temperature, the initial quench severity is below that of a conventional oil. As the cooling process continues, the quench severities approach those for water.

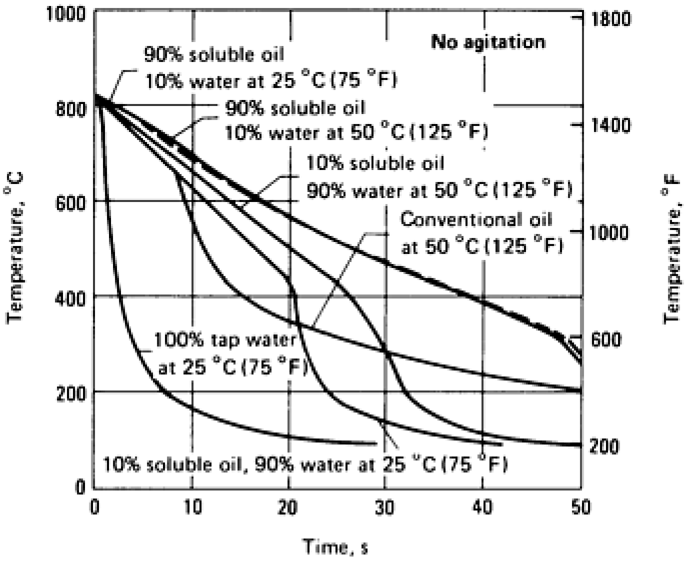


Fig. 53 Comparison of center cooling curves for still-quenched 18-8 stainless steel treated in water, oil, and emulsions of water and soluble oil at temperatures of 25 and 50 °C (75 and 125 °F). Specimen dimensions were 13 mm (0.5 in.) in diameter by 64 mm (2.5 in.) long.

Water-in-oil emulsions containing 90% soluble oil and 10% water have much lower cooling rates than conventional oil. For these reasons, oil and water emulsions are generally inferior to other quenchants, but they are sometimes used for spray quenching of induction or flame-heated parts. Even in these instances, aqueous polymer quenchants would be more desirable.

Oil-in-water emulsions are effective as a final coolant for tempered parts to provide a black surface and rust protection. Such emulsions commonly contain about 3 to 10% soluble oil and are used at temperatures between about 30 and 80 °C (85 and 175 °F) However, in the application, the primary purpose is to produce the desired black color and not to alter the metallurgical properties.

The quenching effects of conventional and fast oils are only slightly affected by their use temperatures under normal quenching conditions. For practical reasons, these oils are generally maintained at temperatures between 40 and 95 °C (100 and 200 °F), most often at 50 to 70 °C (120 to 160 °F) Higher or lower oil temperatures are possible without any substantial change in the as-quenched hardness but are rarely utilized. Higher temperatures will cause faster aging of the oil and can lead to increased fuming. For safety purposes, the maximum oil use temperature should be at least 50 °C (120 °F) below the flash point of the oil. Lower oil temperatures may increase the fire hazard because the higher viscosity of cold oil leads to localized heating above the oil flash point.

The advantage of a lower viscosity quenching oil is illustrated in Fig. 54. The viscosity of an oil will decrease with increasing temperature. However, when a hot part is immersed into a low-viscosity oil, the fire hazard may be lower even if the oil's flash point is lower. This effect occurs because heat extracted from the part is distributed rapidly by the thermosyphon effect (convective currents in the oil). Thus, oil contacting the hot metal at the air interface does not exceed its flash point. The depth of a quenched part or load must be sufficient to allow the heated oil above the hot work to distribute the heat to the bath before the oil reaches its auto ignition temperature.

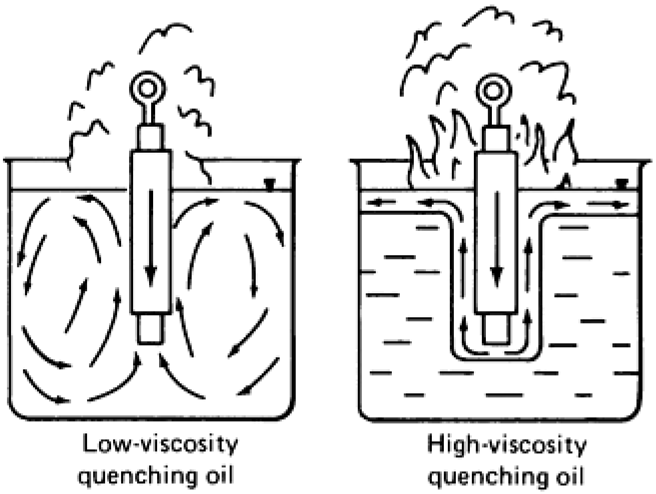


Fig. 54 Advantage of low-viscosity quenching oil over high-viscosity oil. See text for discussion.

Quenching oils with comparatively high viscosities (for example, cold oils) do not distribute heat as rapidly. Instead, a comparatively thin layer of oil is heated at the part surface, and the oil gets hotter as it rises through the load. The oil can reach the air-oil interface at a temperature in excess of its auto ignition temperature and cause an immediate fire.

In one test, two similar parts, each weighing 80 kg (175 lb) and at a temperature of about 870 °C (1600 °F), were partially immersed in separate baths containing 180 kg (395 lb) of oil at 20 °C (70 °F) with no circulation. One oil had a flash point of 205 °C (400 °F) with a viscosity of 120 SUS at 50 °C (120 °F), and the oil ignited immediately. The second tank contained oil with a lower flash point of 120 °C (250 °F), but the oil had a lower viscosity of 46 SUS at 50 °C (120 °F) and it took 20 s to ignite.

Two precepts are apparent from these test results. First, cold viscous oils should be preheated to decrease their viscosities, and second, higher-flash-point oils are preferred. Typical conventional or fast quenching oils have minimum flash points of 125 °C (260 °F) and average flash points of 175 °C (350 °F).

Martempering oils are designed for use at higher temperatures. The typical use temperature ranges for commercially available martempering oils are given in Table 16.

Table 16 Typical bath temperatures for commercially available martempering oils

Viscosity at 40 °C (100 °F), SUS[(a)]	Flash point[(b)]		Temperature range			
			In open air		Under protective atmosphere	
	°C	°F	°C	°F	°C	°F
250-550	220	430	95-150	205-300	95-175	205-345
700-1500	250	480	120-175	250-345	120-205	250-400

(a) SUS. Saybolt universal seconds.

(b) Minimum

Martempering oils, when covered by an inert, neutral, or reducing atmosphere in an integral quench furnace are largely protected from oxidation by air. Thus, they may be used at higher temperatures and closer to their flash points than similar oils used in open air.

The dragout loss of a quenching oil depends mainly on its viscosity, which is dependent on its temperature. Because oils of higher viscosities are usually used at higher temperatures, the actual viscosities and dragout losses of different quenching oils do not vary significantly. Table 17 shows the viscosities of a conventional, a fast, and two martempering oils as a function of the temperature.

Table 17 Viscosity of a conventional oil, a fast oil, and two selected martempering oils as a function of temperature

Oil temperature		Oil viscosity, SUS[(a)]			
		Conventional	Fast	Martempering	
°C	°F			Oil no. 1	Oil no. 2
40	105	100	95	720	2630
65	150	55	60	190	555
95	205	40	40	85	180
120	250	35	35	55	90
150	300	30	35	45	60
175	345	. . .	. . .	40	45
205	400	. . .	. . .	35	40

(a) SUS, Saybolt universal seconds

Quench loads in relation to the oil volume determine the temperature rise in the quenching oil, but uniform hardening usually can be maintained despite moderate temperature increases. However, the danger of fire must be considered when the oil temperatures approach the flash point. Parts with high ratio of surface area to volume increase the fire hazard because they transfer heat more rapidly to the oil. As a consequence, parts with a high surface to volume ratio require

lower quenching oil temperatures, larger oil volumes, or oils of higher flash point. A commonly used rule is that the capacity of an oil quench tank (in gallons) should equal the weight of the quench load in pounds. This rule includes the weight of fixtures, trays, and so on, that are at the temperature of the parts and enter the quenchant.

For more massive parts, the oil volume can be lower since large parts transfer the heat comparatively slowly to the oil. However, it is still necessary to install coolers and provide circulation from tank to cooler in order to maintain the oil temperature at a safe value.

All quenching oils should have as little contact with air as possible to minimize oxidation. For this reason, it is recommended that the surface of open-air quench baths be kept as small as possible. Exposure to the air should be as short as possible for oil baths under controlled atmospheres.

Oil Flow. Quenching oils should be agitated to distribute heat quickly and uniformly and to maintain a uniform bath temperature, which maintains a uniform quenching effect throughout the quench cycle. Only mechanical agitation should be used (pumps or impellers). Compressed air should *never* be bubbled through oil for agitation! Heating elements used for pre-heating quenching oils should have less than 1.5×10^4 W/m^2 (10.0 W/in.^{2}) to prevent local overheating, unnecessary aging, and the formation of an insulating carbonaceous layer on the heater elements with the possible result of heating element burn-outs.

Measurements of the rate of flow from pipes into tanks or from mechanical stirrers usually have too much variation to provide quantitative information on the effects of oil flow rate. However, flow rate data such as those plotted in Fig. 55, 56, and 57 obtained in specially designed equipment, are of more general applicability. The data in Fig. 55 were obtained on scale-free bars of 9445 alloy steel (0.46C-1.05Mn-0.040P-0.040S-0.27Si-0.40Cr-0.45Ni-0.12Mo) heated in an exothermic atmosphere and quenched in a mineral oil at 50 °C (120 °F), viscosity at 40 °C (100 °F), 79 SUS. Figure 56 shows the relationship between bar diameter and equivalent locations on the end-quench hardenability specimen, both for scale-free bars and for those scaled by heating in air. The criteria listed in Table 18 were used to develop the data in Fig. 55, 56, and 57.

Table 18 Quenching temperature data used to compile plots shown in Figs. 55, 56, 57 for 9445 alloy steel

Position in quenched bar	Temperature range	
	°C	°F
Surface	730-315	1350-600
$\frac{3}{4}$-radius	730-370	1350-700
$\frac{1}{2}$-radius	730-425	1350-800

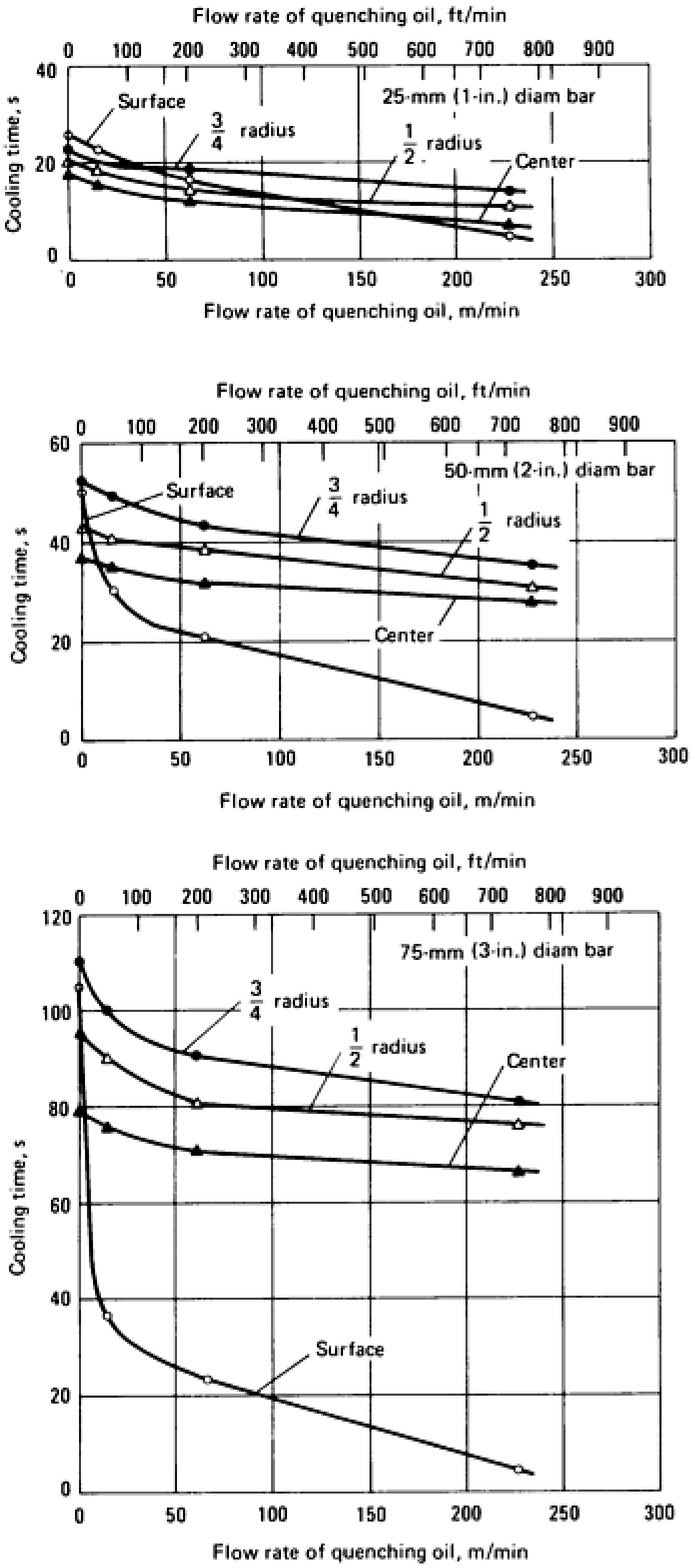


Fig. 55 Fffect of flow rate of quenching oil on cooling time of scale-free bars of 9445 alloy steel. Bars were heated in an exothermic atmosphere, and were quenched in a mineral oil at 50 °C (120 °F). Saybolt universal viscosity of the oil at 40 °C (100 °F) was 79 SUS.

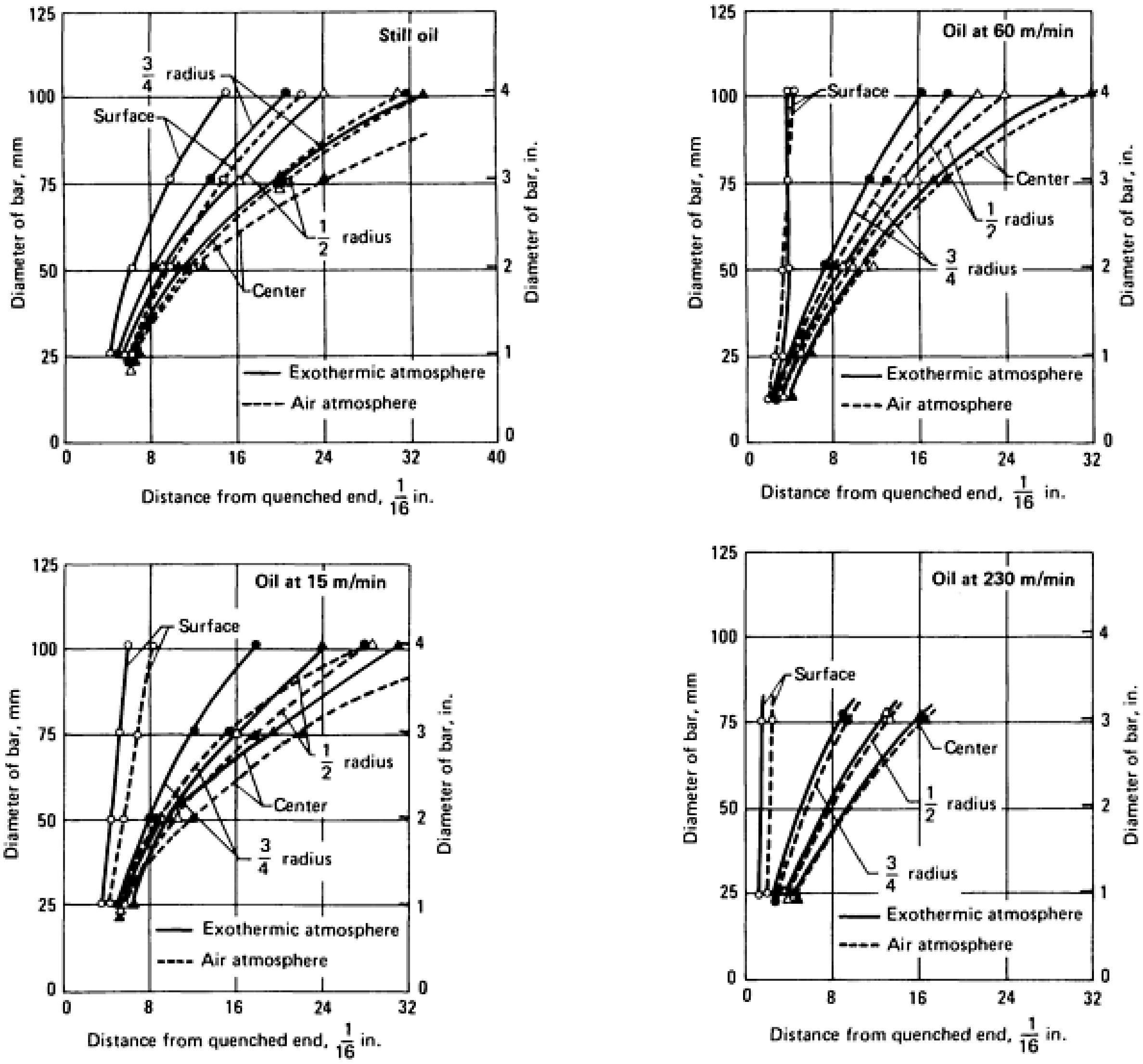


Fig. 56 Curves for identical cooling times in 9445 alloy steel end-quench hardenability specimens and round bars quenched in oil. Mineral oil used for quenching had a Saybolt universal viscosity at 40 °C (100 °F) of 79 SUS.

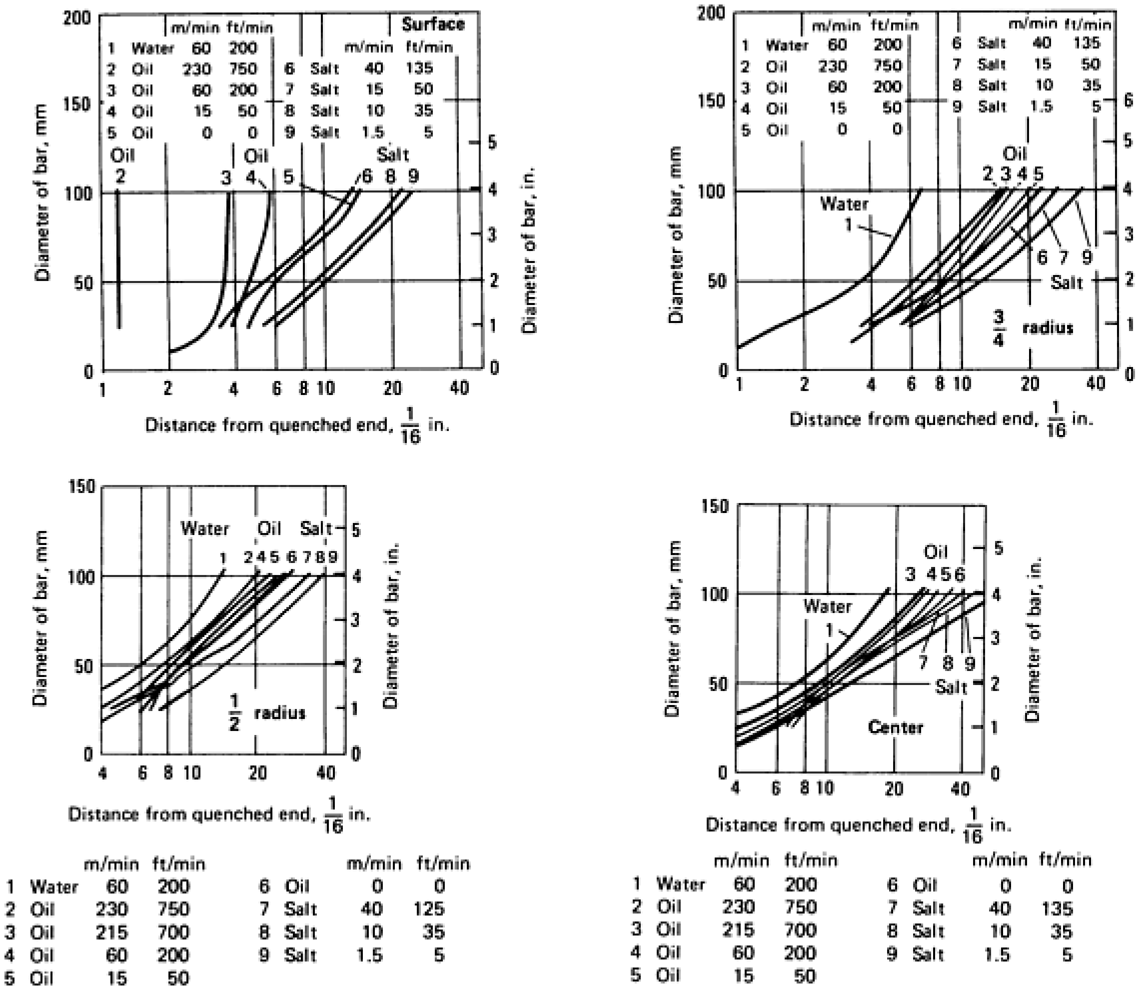


Fig. 57 Correlation curves for identical cooling times in 9445 alloy steel end-quench hardenability specimens and round bars quenched in hot salt, oil, and water. Water was at 25 °C (75 °F); mineral oil at 50 °C (120 °F), Saybolt universal viscosity at 40 °C (100 °F) was 79 SUS; molten salt, at 205 °C (400 °F)

The smaller temperature ranges used for $\frac{3}{4}$-radius, $\frac{1}{2}$-radius, and the center of the bar distort the relationships somewhat, but it is evident that increasing the rate of flow has the greatest influence on the cooling rate at the surface and that the surface of a 75 mm (3 in.) bar can be cooled almost as fast as the surface of a 25 mm (1 in.) bar when the velocity of the oil is above about 150 m/min (500 ft/min). It is evident also that the major advantage from agitation lies in the range between still oil and a velocity of 60 m/min (200 ft/min).

The oil quenching system, particularly heating elements and coolers, should not be composed of copper or copper alloys. These metals act as catalysts to accelerate the oxidation and polymerization of mineral oils. Steel, stainless steel, nickel-plated, and tin-plated materials are recommended instead. Existing copper or brass equipment should be tin plated.

Water Contamination. Contamination and oxidation may also produce critically important effects on quenchant performance. For example, the effect of increasing oil oxidation on a conventional oil may result in substantial quench rate variation (see Fig. 58).

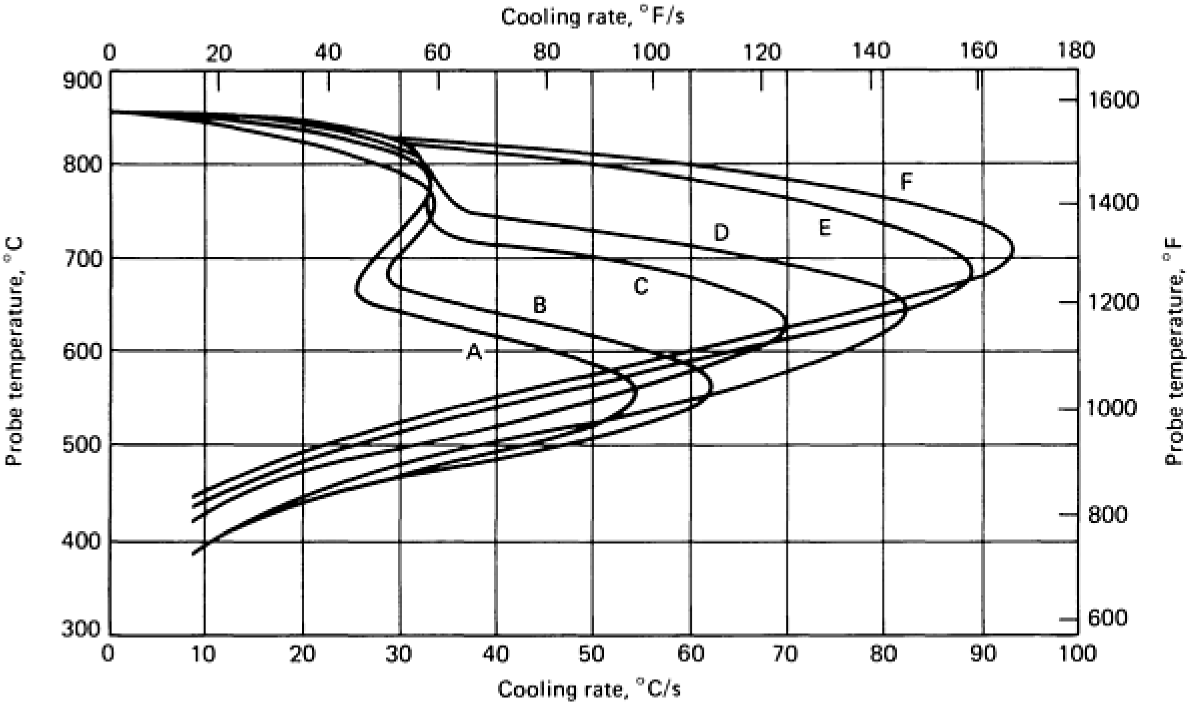


Fig. 58 Variation in cooling rate of a martempering oil as a function of time in use: A, new oil; B, 3-month old oil; C, 7-month old oil; D, 25-month old oil. Source: Ref 52

Water in quenching oils is dangerous, particularly in martempering oils used at temperatures above 100 °C (212 °F). Not only does water cause nonuniform as-quenched hardnesses, but it also causes foaming that increases the fire hazard. Oil foam that develops in an integral-quenching chamber can cause an explosion if the foam level reaches the hot furnace chamber.

The effect of water in quenching oils on cooling curves is shown in Fig. 59. These results were recorded by quenching a cylindrical stainless steel probe in a fast quenching oil free of water and after water additions of 0.06 to 2.0%. At water concentrations below 0.12%, the initial quenching speed was increased. Higher water concentrations caused a more stable vapor blanket around the probe resulting in a lower initial quenching speed.

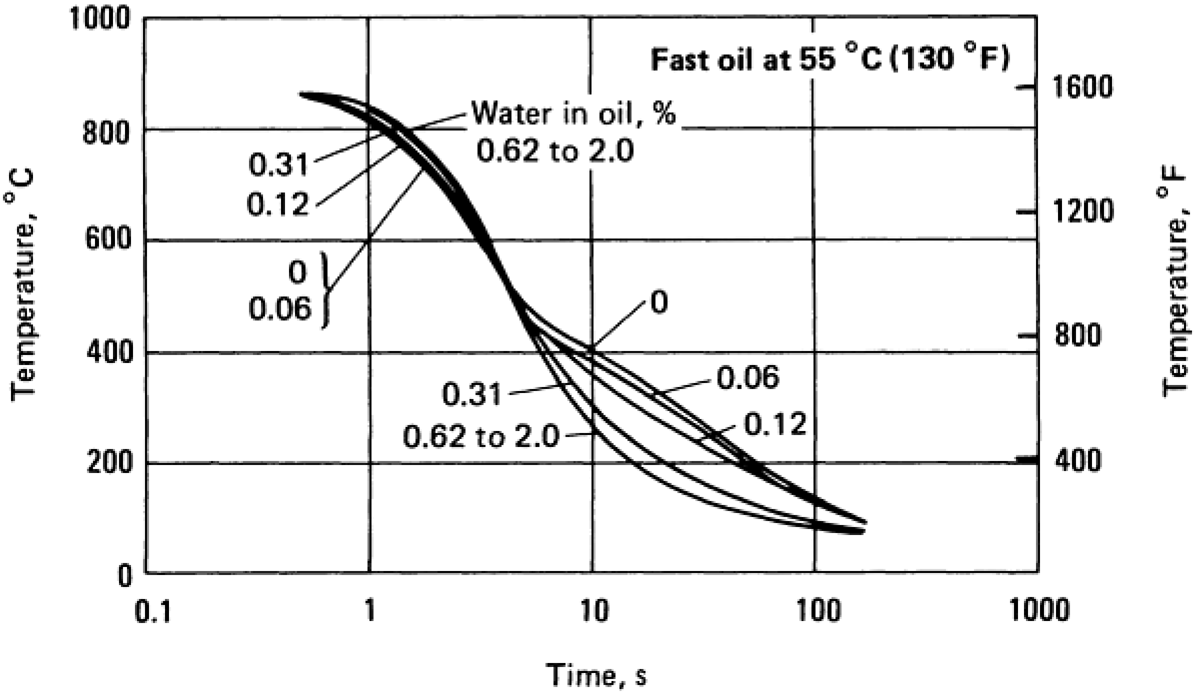


Fig. 59 Effect of water contamination on the quenching power of fast oil at 55 °C (130 °F) in quenching type 304 stainless steel. Specimens measured 13 mm (0.5 in.) in diam by 100 mm (4 in.) long. Oil was not circulated, and specimens were not agitated. Thermocouples were located at the geometric center of specimens.

All oil samples containing water quenched faster than a water-free fast oil during boiling and convection ranges. Because of the higher cooling rates in the convection range, which overlaps with the martensite formation range of most common steels, increased distortion and cracking can be expected when using water-contaminated quenching oils.

Water entrapment in an oil bath can result in an explosion from the sudden formation of large volumes of steam. Normal bath circulation dispenses the water, however, and minimizes the risk.

Water can be removed from an oil bath by several methods including: (a) raising the temperature above the water boiling point; (b) allowing the water to settle and draining it off; and (c) passing the bath through a centrifuge. However, used quenching oils may sometimes emulsify the water. Emulsions cannot be treated by using the method described in (b). The other two methods will work. The effect of boiling off the water on cooling curves is illustrated in Fig. 60.

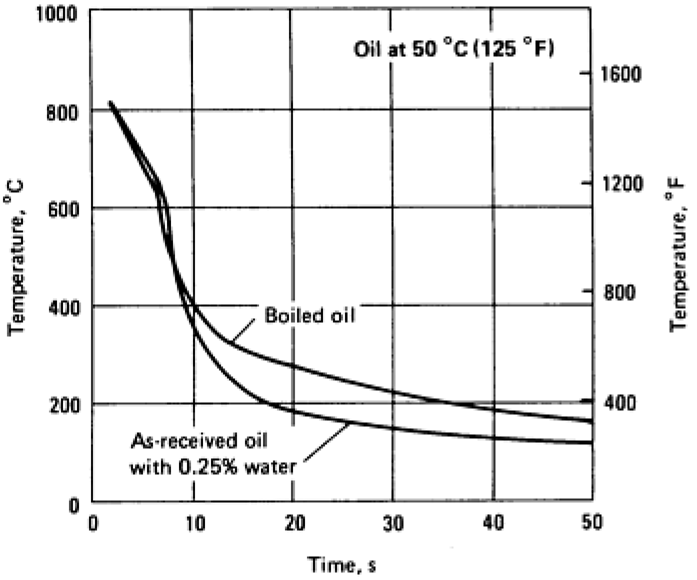


Fig. 60 Effect of boiling off water that has contaminated an oil quenchant on the center cooling curves of austenitic stainless steel. Specimens measured 13 mm (0.5 in.) in diam by 64 mm (2.5 in.) long. Plot shows the effects of quenching in as-received oil containing 0.25% water and in the same oil after it had been freed of water contamination by being boiled at 120 °C (250 °F) for 5 h. Quenching temperature of oil for both conditions was 52 °C (125 °F).

Staining. In order to attain clean quench-hardened parts, the quenching oil must retain its nonstaining features. This is best accomplished by minimizing oxidation or oil degradation.

Carbonaceous deposits (sludging) on quenched parts are symptomatic of oil breakdown. Normally, an oil does not reach this stage of degradation without detection, except in unprotected systems. Carbonaceous deposits are objectionable because they are difficult and costly to remove. However, they do not adversely affect hardening of the steel because the deposits develop at low temperatures after hardening has already occurred.

Control of Quenching Oils. Routine analyses to determine the state of a used quenching oil should be performed regularly. Used quenching oils are usually checked as follows:

- Cooling curve test
- Crackle test (water, qualitative)
- Water content (quantitative, only if above test is positive) by ASTM test method D 95
- Viscosity at 40 °C (100 °F) by ASTM test methods D 445, D 2161
- Sludge test by ASTM test method D 2273
- Magnetic quenchometer speed, using plain nickel balls, at 25 °C (80 °F) for conventional and fast quenching oils; at 120 °C (250 °F) for martempering oils
- Hot wire test

Selection of a Quenching Oil. The quenching of steel involves unsteady heat flow and solid-state transformations, both of which are difficult to handle quantitatively. As a consequence, the selection of oils for specific applications has historically been based largely on trial and error.

The most important criterion in selecting a quenching oil is that it provide a cooling rate that will harden the part without cracking it. Other considerations are degree of distortion and cost for the finished part.

If a steel has sufficient hardenability to be fully hardened by being quenched in a conventional oil, there is probably no advantage to using more costly fast oils.

For example, consider 4135 and 4140 steels that have been quenched using both conventional and fast oils. Specimens of 4140 steel having 19 mm ($\frac{3}{4}$ in.) diameter were quenched in both types of oil at 855 °C (1575 °F) and tempered at 595 °C (1100 °F). Average mechanical properties after several tests are given in Table 19. The less expensive conventional oil provided equivalent properties in this application.

Table 19 Mechanical properties of 4140 steel quenched in selected quenching oils

Property	Oil type	
	Conventional	Fast
Tensile strength, MPa (ksi)	1035 (150)	1035 (150)
Yield strength, MPa (ksi)	940 (136)	940 (136)
Elongation in 50 mm (2 in.), %	19.75	19.25
Reduction in area, %	59.1	59.4
Charpy impact, J (ft · lb)	43 (32)	46 (34)

Tubular sections of 4135 steel, 120 mm (4.75 in.) OD, 70 mm (2.75 in.) ID, were also quenched in the conventional and fast oils. A comparison of hardness traverses through the 25 mm (1 in.) wall sections showed uniform values of 46 to 47 HRC in both cases.

In other applications, a steel may have such low hardenability that full hardening is difficult to obtain even in a water quench. Under these conditions, it is unlikely that a fast oil will provide adequate hardening. However, there are many applications where it is advantageous to make discriminating selections between competing oil types.

In many instances, oil selection is based entirely on practical results and plant experience with various quenching oils. Factors that affect oil selection are detailed in Examples 1, 2, 3.

Example 1: Elimination of Hardness Nonuniformity in 1050 Steel Transmission Shifter Shafts by Replacing Conventional Oil with Cost-Effective Fast Oil.

Transmission shifter shafts, 14.3 mm (0.562 in.) diameter by 91 mm (3.6 in.) long, made of 1050 steel were carbonitrided at 815 °C (1500 °F) and quenched in conventional oil (86 to 110 SUS) at 40 °C (100 °F), and tempered at 250 °C (480 °F) They were loaded vertically in baskets (1800 pieces per load), using a stabilizing screen. A minimum hardness of 50 HRC was required. Nonuniform hardness (within individual parts and from part to part) was encountered and caused excessive rejection.

Replacing the conventional oil with a fast oil eliminated the nonuniformity in hardness. Although the initial cost for the fast oil was higher than the conventional oil, the net cost of the heat-treated parts was lower because rejects were eliminated.

Example 2: Switching from Conventional to Fast Oil Results in Uniform Hardness of 1064 Steel Spring Clips and Fasteners.

Nonuniform hardness values ranging from 50 to 60 HRC were experienced while heat treating spring clips and fasteners made of 1064 steel having section thicknesses ranging from 0.25 to 1.55 mm (0.010 to 0.062 in.). The parts were heated in a shaker-hearth furnace at 870 °C (1600 °F) and continuously dropped at a rate of 90 kg/h (200 lb/h) into an 1890 L (500 gal) quenching tank. The temperature of the conventional quenching oil was maintained at 49 to 52 °C (120 to 125 °F) and circulation was 570 L/min (150 gal/min). Changing from the conventional oil to a fast oil resulted in consistent hardness values of 60 to 64 HRC.

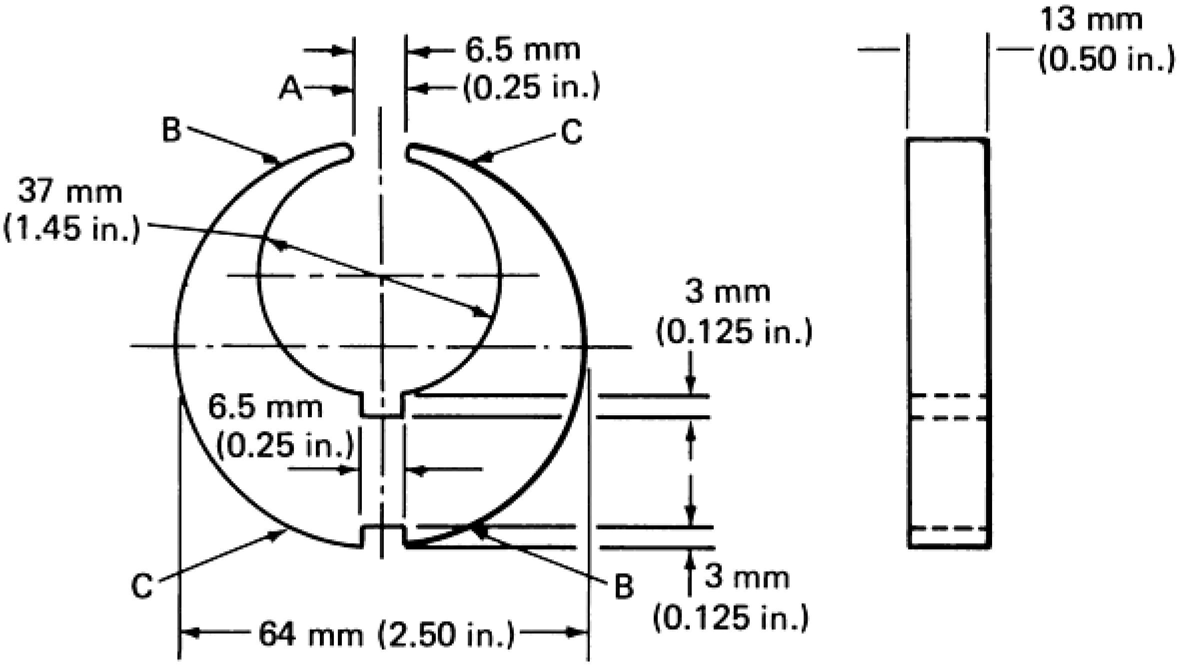
Example 3: Changing from Conventional to Fast Oil Results in 15 HRC Hardness Increase in 52100 Bearing Steel.

A minimum hardness of 62 HRC was needed on 100 mm (4 in.) diameter by 815 mm (32 in.) long steel-mill rolls, made of 52100 steel. Water quenching developed sufficient hardness, but resulted in cracking of the 50 mm (2 in.) diameter, 100 mm (4 in.) long bearing areas at the ends of the rolls. Quenching in a conventional oil resulted in hardness values of only 48 to 52 HRC. By using a fast oil, it was possible to develop hardness values of 64 to 65 HRC without cracking.

Effect of Fast Oils on Distortion. Greater distortion is sometimes associated with the use of fast oils, as indicated by these contrasting examples.

Example 4: Use of Fast Oil Minimizes Distortion in a 1085 Steel C-Section Component.

One laboratory used a modified Navy C test specimen made of 1085 steel to compare the distortion resulting from quenching it in water, conventional oil, and fast oil. The average distortion and hardness results tabulated in Fig. 61 indicate that the fast oil produced slightly less distortion than the conventional oil while providing hardness values comparable to those obtained in water quenching.



Quenching medium	Hardness, HRC		
	Maximum	Minimum	Variation
Water	67.0	63.0	4.0
Fast oil	66.0	63.0	3.0
Conventional oil	65.5	43.0	22.5

	Dimensional change					
	Gap A		Diameter B		Diameter C	
	mm	in.	mm	in.	mm	in.
Water	0.3404	0.0134	0.2591	0.0102	0.2946	0.0116
Fast oil	0.0533	0.0021	0.0813	0.0032	0.0610	0.0024
Conventional oil	0.0559	0.0022	0.0965	0.0038	0.0965	0.0038

Quenching medium	Hardness, HRC		
	Maximum	Minimum	Variation
Water	67.0	63.0	4.0
Fast oil	66.0	63.0	3.0
Conventional oil	65.5	43.0	22.5

	Gap A		Dimensional change			
			Diameter B		Diameter C	
	mm	in.	mm	in.	mm	in.
Water	0.3404	0.0134	0.2591	0.0102	0.2946	0.0116
Fast oil	00533	0.0021	0.0813	0.0032	0.0610	0.0024
Conventional oil	0.0559	0.0022	0.0965	0.0038	0.0965	0.0038

Fig. 61 Hardness values and changes in dimensions of a 1085 plain carbon steel test specimen after quenching in water, fast oil, and conventional oil

Example 5: Quenching Carburized 8620 Steel Transmission Gears in Straight Mineral Oil Yields Less Distortion than Quenching in Fast Oil.

Figure 62 shows that significantly greater distortion occurred in carburized 8620 steel transmission gears when quenched in a fast oil than when quenched in a straight mineral oil. The temperature of both oils was 65 °C (150 °F). The results represent 60 tests for each type of oil.

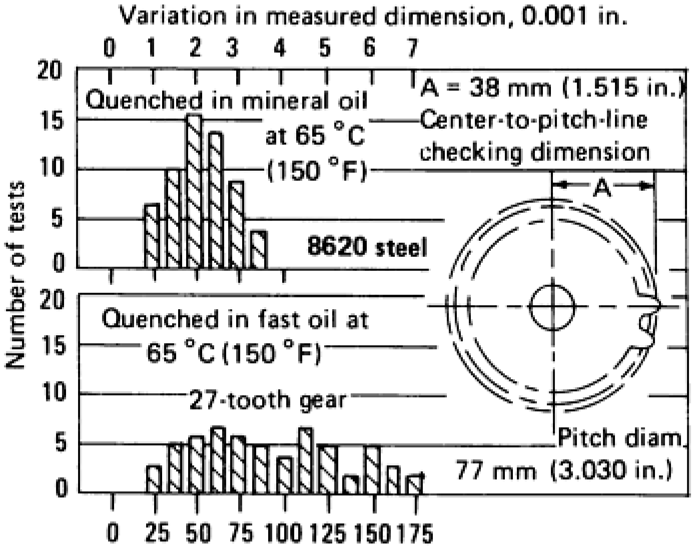


Fig. 62 Effect of type of quenching oil on variations in center-to-pitch-line dimension. For transmission counter gears of 8620 steel, paraffin-base mineral oil had viscosity at 40 °C (100 °F) of 86 to 110 SUS. Gears, carburized and direct quenched from 870 °C (1600 °F), were tempered at 155 °C 1310 °F) after quenching and had a hardness of 59 to 63 HRC.

Quenching Oil Selection Determines Steel Grade Used. In selecting a quenching oil, its contribution to the cost of the finished part must be considered. Aside from the initial cost (and the cost of replacing dragout), quenching oils can influence overall cost by:

- Limiting the type of steel from which parts can be made
- Determining the percentage of rejected parts that will require reworking
- Determining the extent of cleaning after quenching

Although it is more common to fit the oil to the steel being treated than to fit the steel to the oil, there have been instances in which fast quenching oils permitted changing to steels of lower hardenability, with accompanying reductions in cost. One such situation is described in the following example.

Example 6: Switching from Conventional Oil to Fast Oil Allows Use of Simple Steel Grade instead of Two Steels in Gear Drive Components.

Truck ring gears were being made from 3310 steel and pinion gears from 4815 steel. It was found that by using a fast quenching oil in place of conventional oil, 4718 steel could be used for both parts without sacrifice of properties. This resulted in a saving of about 15%, on a per-kilogram (per-pound) basis, in metal costs.

Fast Oil More Cost-Effective than Conventional Oil. In the following example, a fast oil proved to be cheaper, even though its initial cost was higher than a conventional oil.

Example 7: Changing from Conventional Oil to Fast Oil Reduced Long-Term Costs by 5.3%.

In a plant employing a 3000 L (800 gal) quenching tank, 1500 L (400 gal) of conventional oil was consumed in quenching 29,500 kg (65,100 lb) of steel. This amounted to 20 kg of steel per liter (163 lb of steel per gallon) of oil. For the same system and type of work, only 1135 L (300 gal) of fast oil was consumed in treating 45,600 kg (100,500 lb) of steel. Thus, despite the higher initial cost of the fast oil, the oil cost per kilogram or pound of steel treated was reduced about 5.3%.

The lower oil consumption was mainly the result of decreased dragout. In addition, the conventional oil formed more sludge which resulted in higher maintenance cost and increased the cost of cleaning the heat-treated parts.

Mechanical conditioning of quenching oils involves the removal of the following contaminants:

- Scale
- Carbonaceous materials, which may be products of oil oxidation (sludge) or carbon fallout, encountered in protective-atmosphere installations
- Other insoluble solids, such as sand
- Water
- Soluble compounds, such as carbon dioxide

These contaminants can be removed by filtering, evaporation, or draining. The solids can best be removed by appropriate bypass filters. The choice of filtering medium for removing solids is important. The most commonly used filtering media are the waste-pack, mineral-wool, and cellulose types that must be replaced after their filtering ability has been exhausted. Clay filtering media are more expensive than the above types but can be reused after exhaustion by suitable regeneration. However, the regeneration will not remove scale or sand. Clay media should be carefully selected when fast quenching oils are to be filtered, because it is possible to remove the additive along with the undesirable carbonaceous materials.

Magnetic filters, traps, and strainers are useful in removing scale and other foreign materials. These types of filters can be easily cleaned and returned to service. They are especially helpful for preventing premature filter clogging and for protecting pumps.

Water can be removed by filtering or centrifuging, but these methods are expensive and rarely used. Usually, bulk water is removed by draining, and suspended water is removed by heating. Carbon dioxide is removed by heating.

Polymer Solutions

The technology of polymer quenching has seen dramatic growth in the past 50 years. The principal quenchants were initially water, perhaps modified by additives such as inorganic salts and naturally occurring oils. With the discovery of petroleum, hydrocarbon products became a major medium for quenching. More recently, it has been established that some water-soluble organic polymers are useful in modifying the cooling characteristics of water.

The patent literature describes several polymers, however only three types are prominent commercially in the United States. These are: polyalkylene glycol (PAG), polyvinyl pyrrolidone (PVP), and polysodium acrylate. Although polyvinyl alcohol (PVA) has been used in the past, it has only limited use in the United States at the present time. However, polyvinyl alcohol is still used in some international heat-treating markets.

In general, it has been an objective of polymer quenchant suppliers to develop products that can be used to provide quench severities ranging from those equivalent to oil to those that may be greater than water.

Polyalkylene glycol, or polyalkylene glycol ethers, were first introduced as commercial products in the early 1940s. These materials are formulated by the random copolymerization of ethylene and propylene oxides although higher alkylene oxides and/or aryl oxides may also be used. The structure of PAG is schematically illustrated in Fig. 63(a).

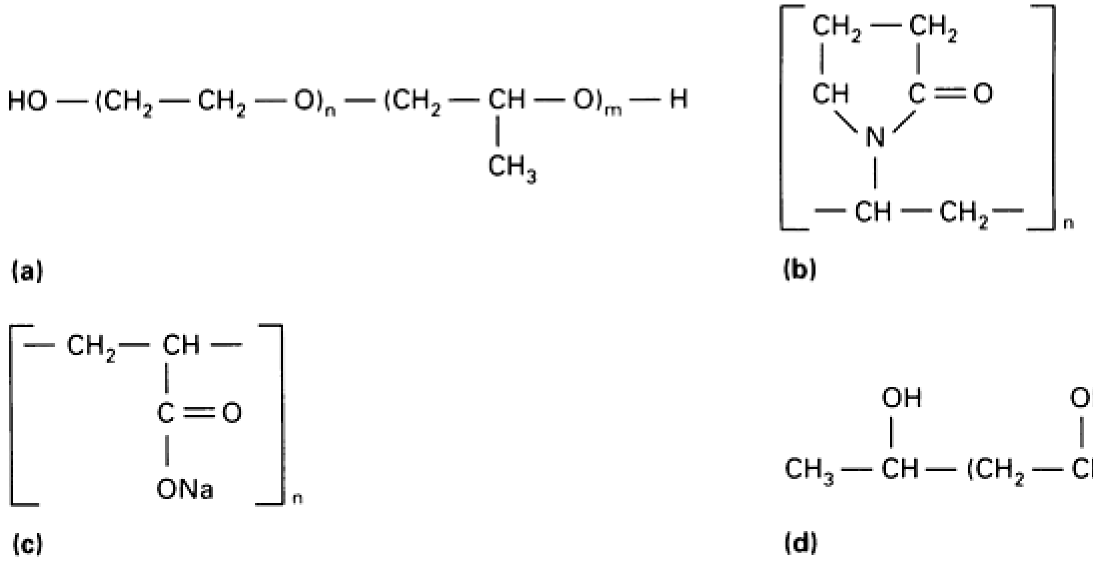


Fig. 63 Chemical structure of selected polymer quenchants. (a) Polyalkylene glycol (PAG). (b) Polyvinyl pyrrolidone (PVP). (c) Sodium polyacrylate (PA). (d) Polyvinyl alcohol (PVA)

By varying the molecular weights and the ratio of alkylene oxides used to manufacture the product, polymers having broad applicability may be produced. Some of the higher molecular weight PAG polymers have exhibited excellent metal quenchant properties when used in aqueous solutions (U.S. Patent 3,230,893).

The proper selection of the polymer and its molecular weight provides a PAG product that is soluble in water at room temperature. However, the PAG polymers typically exhibit inverse solubility--that is, they are soluble at room temperature but insoluble at elevated temperatures. This thermally reversible phenomenon provides a unique mechanism for controlling the heat transfer from hot metal by surrounding the metal piece with a polymer-rich coating.

Then, as the metal part approaches the temperature of the quenchant, the PAG polymer coating redissolves in the quenchant bath. The interfacial behavior of a representative PAG polymer at the hot metal interface at selected times during a typical quench cycle is shown in Fig. 4 (Ref 53). The application of water as a quenchant in many heat-treating processes is limited by its relatively high quench severity. The quench severity of water can be reduced by increasing the water temperature, as shown in Fig. 2, but this typically results in extended A-stage cooling times which may lead to low as-quenched hardness values.

Polyalkylene glycol quenchants have been particularly useful in view of the processing latitude they provide since quench severities from slow oil to brine may be possible by varying the bath temperature, agitation rate, and polymer concentration. Relatively dilute solutions will provide a quench severity similar to water but reduce cracking and distortion because of the slow cooling it provides at low temperatures.

The proper PAG quenchant can also provide accelerated wetting so that the cooling rates achieved are faster than water and approach those achieved by brines. Thus, brine quenching is possible without the hazards and corrosiveness attendant with the use of salts or caustic solutions.

U.S. Patent 3,475,232 teaches that the addition of water-soluble alcohols, glycols, or glycol ethers with 2 to 7 carbon atoms also can improve the wetting characteristics of PAG quenchants. However, control of a multicomponent system is considerably more complex.

Aqueous solution of PAG quenchants may be inhibited to provide corrosion protection of the quench-system components. Since corrosion inhibition of quenched parts may be of relatively short duration, specific protection should be provided following the tempering operation unless auxiliary corrosion inhibitors are used.

Cooling Characteristics. Three principal parameters are recognized as controlling the rate of cooling during polymer quenching:

- Quenchant concentration
- Quenchant temperature
- Quenchant agitation

The influence of PAG concentration on cooling rates in a 25 mm (1 in.) diameter stainless steel probe is illustrated in Fig. 64. The slower cooling rates achieved at the higher concentrations correspond to an increase in the thickness of the polymer layer that surrounds the part during quenching (see Fig. 4). PAG quenchants also are not sensitive to minor changes in polymer concentration. This problem is a recognized deficiency of polyvinyl alcohol and some other film-forming polymers used as quenchants.

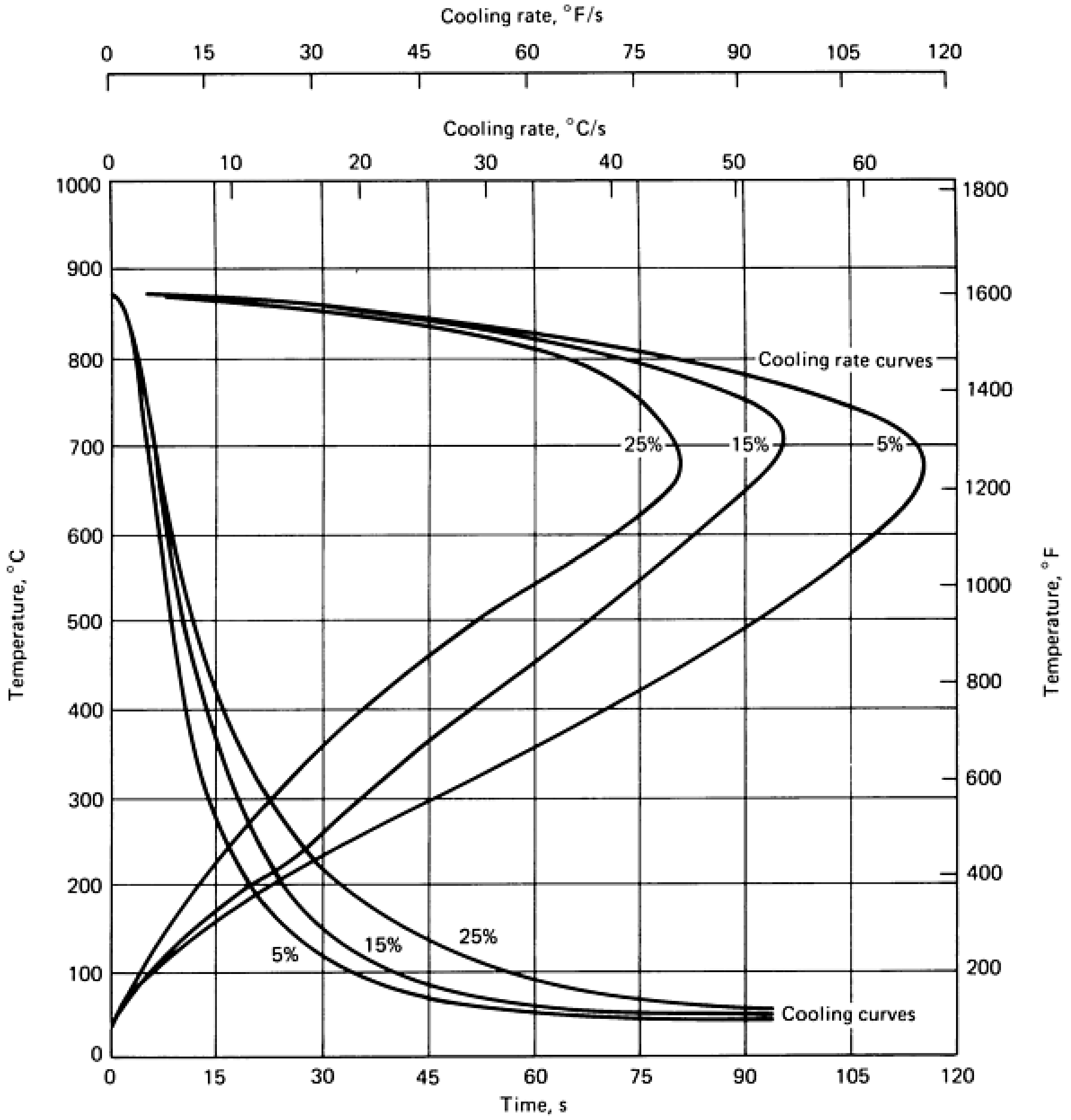


Fig. 64 Cooling curves and cooling rate curves for a 25 mm (1 in.) diameter stainless steel probe quenched in 5, 15, and 25% polyalkylene glycol at 45 °C (110 °F) that is flowing at 0.25 m/s (50 ft/min)

Additional effects of concentration on cooling rates produced by a PAG quenchant are shown in the contour plots of Fig. 65.

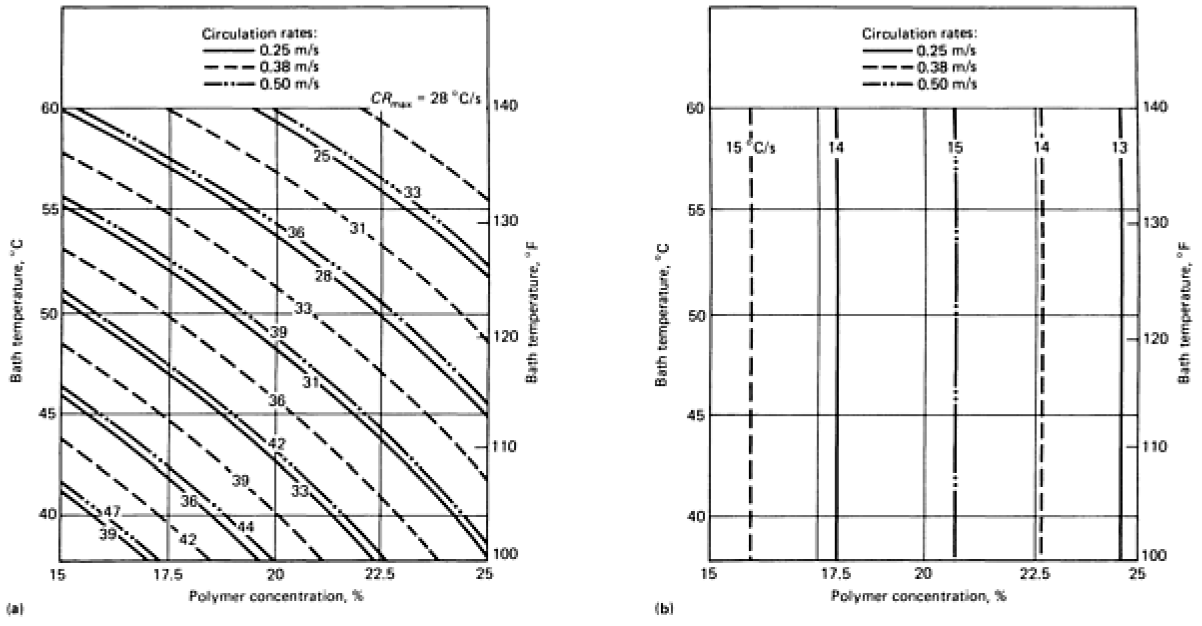


Fig. 65 Predicted properties of polyalkylene glycol quenchant at bath temperatures ranging from 38 to 60 °C (100 to 140 °F). (a) Maximum cooling rate, CR_{max}. (b) Cooling rate at 345 °C (650 °F). The plot in (b) indicates that quenching from a temperature of 345 °C (650 °F) at a predicted cooling rate of 15 °C/s (27 °F/s) will require a polymer concentration of ≈16% or ≈21%, corresponding to an agitation rate of 0.38 m/s (75 ft/min) or 0.50 m/s (100 ft/min), respectively. To determine the cooling rate at an agitation rate of 0.38 m/s (75 ft/min) between ≈16% to ≈22.5% polymer concentration, extrapolation will be required. The data show that cooling rates are independent of bath temperatures of 345 °C (650 °F) but are dependent on agitation rates.

Just as water exhibits a marked decrease in cooling capability as its temperature is elevated (see Fig. 42 and 44), this same loss is translated to the aqueous solutions of PAG quenchants. The curves shown in Fig. 66 are illustrative of the general trends that occur with changes in bath temperature. More detailed data would require specific identification of the particular PAG quenchant employed.

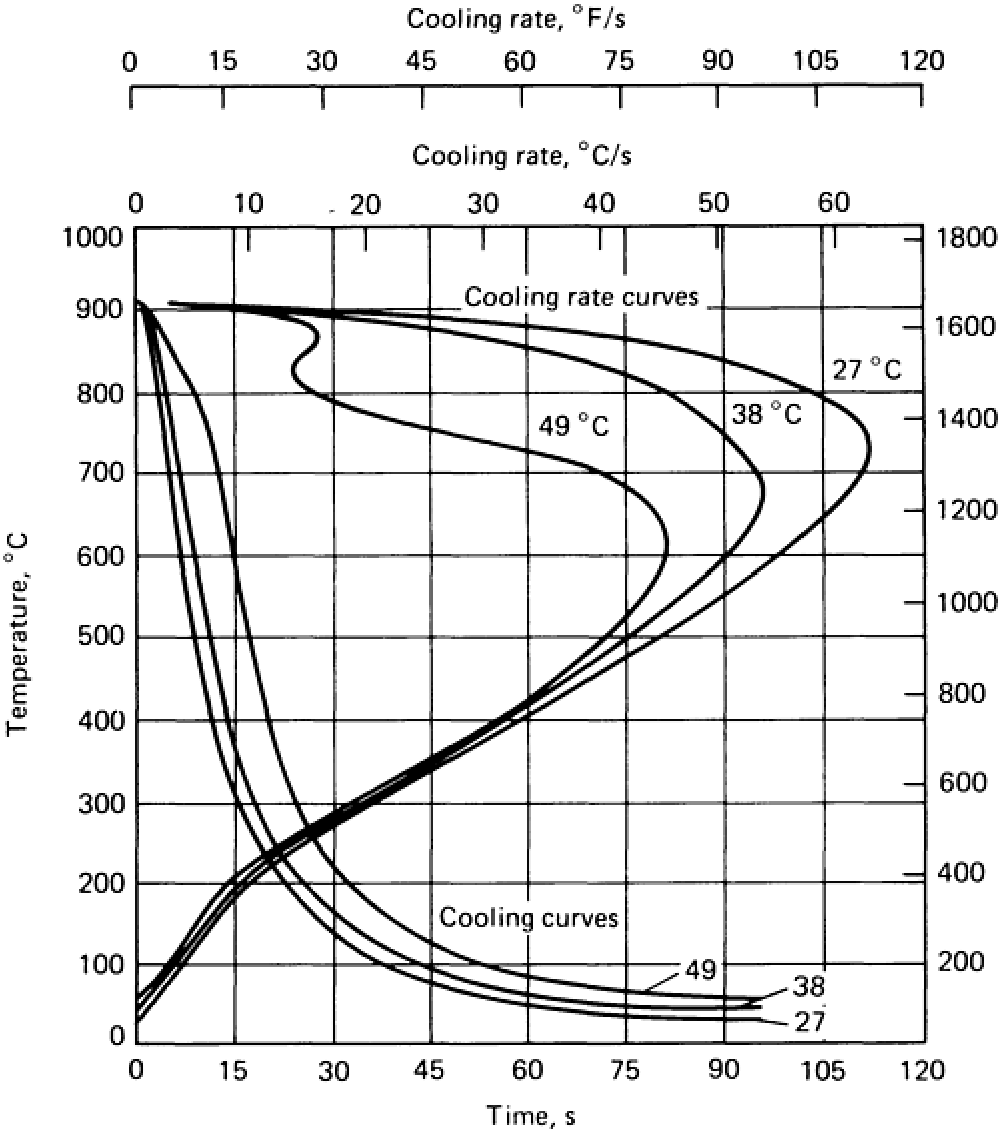


Fig. 66 Cooling curves and cooling rate curves for 25 mm (1 in.) diameter stainless steel probe quenched in 10% polyalkylene glycol at 27, 38, and 49 °C (80, 100, and 120 °F) that is flowing at 0.25 m/s (50 ft/min)

The use of polyglycol quenchants without agitation is not recommended. In general, low to moderate agitation is essential to ensure that adequate replenishment of polymer occurs at the hot metal surface and to provide uniform heat transfer from the hot part to the surrounding quenchant. Vigorous agitation may be essential to achieve a rapid rate of cooling (for example, with a low hardenability steel) to avoid undesirable transformation products. As agitation is increased, the cooling rates rapidly increase, as clearly illustrated in Fig. 67. A contour plot illustrating the variation in Grossmann *H* factor, with varying polymer concentration, bath temperature, and circulation rates of an illustrative PAG quenchant is shown in Fig. 68.

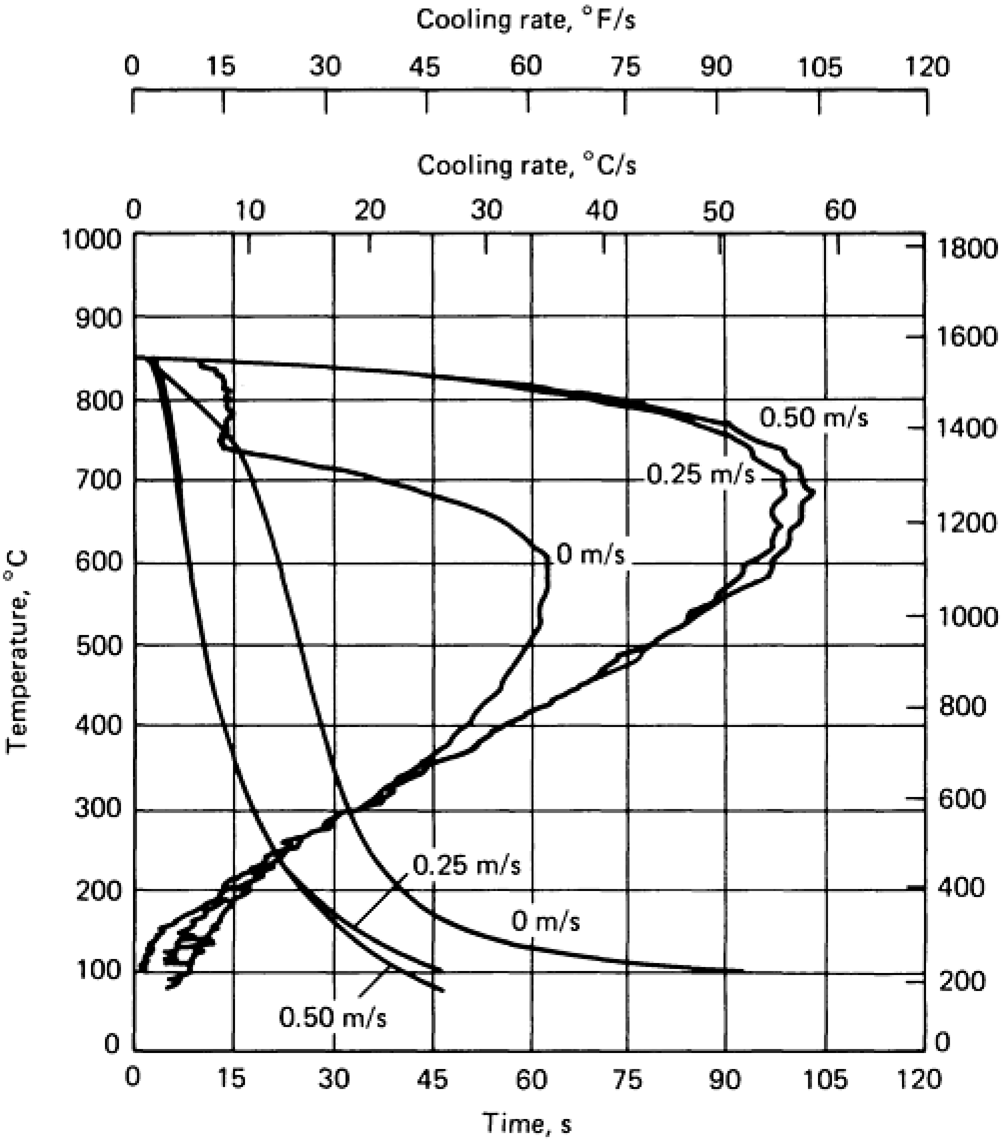


Fig. 67 Cooling curves and cooling rate curves for 25 mm (1 in.) diameter stainless steel probe quenched in 20% polyalkylene glycol at 45 °C (110 °F) that is flowing at 0, 0.25, and 0.50 m/s (0, 50, and 100 ft/min)

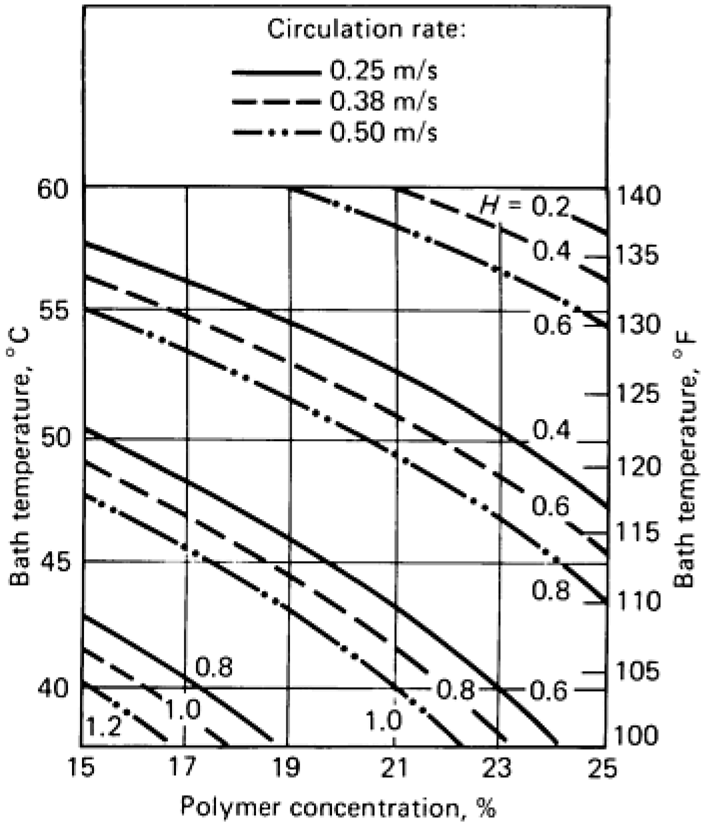


Fig. 68 Variation in the Grossmann hardenability factor, *H*, of a PAG quenchant as a function of polymer concentration, bath temperature, and circulation rate

The effect of varying polymer concentration, bath temperature, and circulation rate on a typical PAG-base polymer quenchant on the maximum cooling rate and cooling rate at 345 °C (650 °F) is illustrated by the contour plots shown in Fig. 65. The data are based on cooling curves obtained by the method described by Hines and Mueller (Ref 54).

Control Measures. The refractive index of polyalkylene glycol polymer solutions (in the range employed for quenching) is almost linear with concentration. Thus, the refractive index of a PAG quenchant solution can serve as a measure of product concentration. Refractive index versus quenchant concentration calibration plots are usually available from quenchant manufacturers. However, since this relationship is typically linear, a calibration plot can be easily constructed by the heat treater by obtaining refractive index values at 0, 10, and 20% concentrations. A best-fit line can be calculated by a linear regression analysis of the data. The resulting equation can then be used to calculate the quenchant concentration from a refractometer reading.

Industrial optical refractometers that employ an arbitrary scale may also be calibrated. Whereas such instruments prove valuable for day-to-day monitoring of the quenchant concentration, the refractometer also registers other water-soluble components such as salts in the quenchant. When the refractometer reading begins to provide erroneous numbers, another analytical test is required to define the effective quenchant concentration.

With PAG quenchants, kinematic viscosity measurements, which also correlate with concentration, have proved to be most useful as a cross-checking procedure. These plots also are available from quenchant manufacturers, and are similar to those for refractive index with one exception. The exception is that viscosity usually has a nonlinear relationship to polymer concentration. Therefore, first-order linear regression analysis should not be used as a line fitting procedure.

Additional tests for pH, inhibitor level, and conductance also are useful adjuncts to a monitoring program.

If the level of contaminants in the PAG quenchant becomes excessive, quenchant recovery can be effected thermally. The contaminants may be the same materials detrimental to water or oil quenchants. By heating the quenchant solution above the separation temperature, a more-dense polymer-rich layer is obtained (see Fig. 69). Generally, the polymer layer is the

lower layer. However, in cases where high salt contamination has been encountered, there may be a layer reversal. Where this condition is thought to exist, the quenchant manufacturer should be consulted. Much of the water-soluble contamination can be withdrawn with the supernatant water layer. Thermal separation is useful for water-soluble contaminants. The removal of solid contaminants, such as scale or carbon, requires separation by settling, filtration, or centrifugation. Membrane separators that allow water and soluble salts to escape from the PAG solution are also used to remove contaminants.

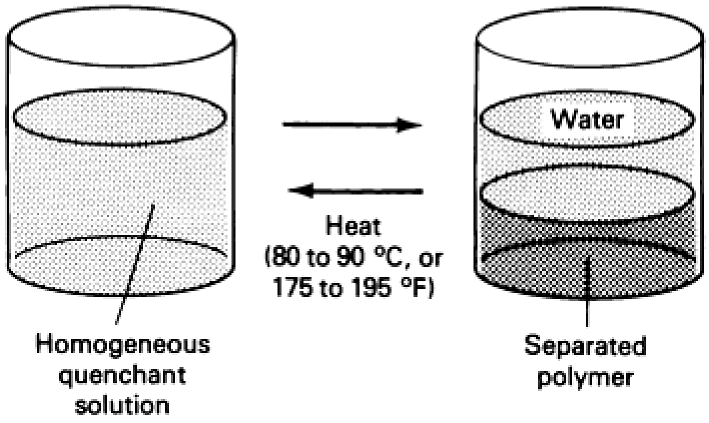


Fig. 69 Typical thermal separation procedure that utilizes inverse solubility. The water concentration in the bottom polymer layer at a separation temperature of 80 °C (175 °F) is 70%, while at 90 °C (195 °F) it is 46%. Source: Ref 55

Because PAG quenchants are bioresistant, the addition of a bactericide to the as-supplied quenchant is not generally required. Biochemical activity in use is traceable not to the PAG polymer itself, but to the introduction of nutrient contaminants. Microbiological treatment, such as is employed with other aqueous metal-working fluids, generally will keep this foreign biological activity under control.

Polyvinyl pyrrolidone is derived from the polymerization of N-vinyl-2-pyrrolidone. Polyvinyl pyrrolidone is a water-soluble polymer characterized by its complexing and colloidal properties and by its physiological inertness. Polyvinyl pyrrolidone is available in the United States as a white, free-flowing powder, manufactured in four molecular-weight grades. Its structure is shown in Fig. 63(b).

Solutions of polyvinyl pyrrolidone in water were first introduced as quenchants in 1975, coinciding with the issuance of U.S. Patent 3,902,929. The patent defines the molecular weight range for the pyrrolidone polymer, the quantity of polymer recommended for a solution concentrate (generally about 10% polymer solids) and the preferred use of a rust inhibitor and a bactericidal preservative.

Quenchant Variables. As with other polymer-type quenchants, concentration, bath temperature, and agitation play a role in establishing the cooling characteristics. The quenching rates tend to be faster with polyvinyl pyrrolidone quenchants during the stable film and nucleate and boiling stages, but slower during the convection stage. Contour plot relationships illustrating the effect of quenchant concentration, agitation, and bath temperature on Grossmann H factor, the maximum cooling rate (CR_{max}), and cooling rate at 365 °C (650 °F), under laboratory quenching conditions is shown in Fig. 70. Since polyvinyl pyrrolidone is soluble up to the boiling point of water, a broader working range of temperatures for quenching can be employed.

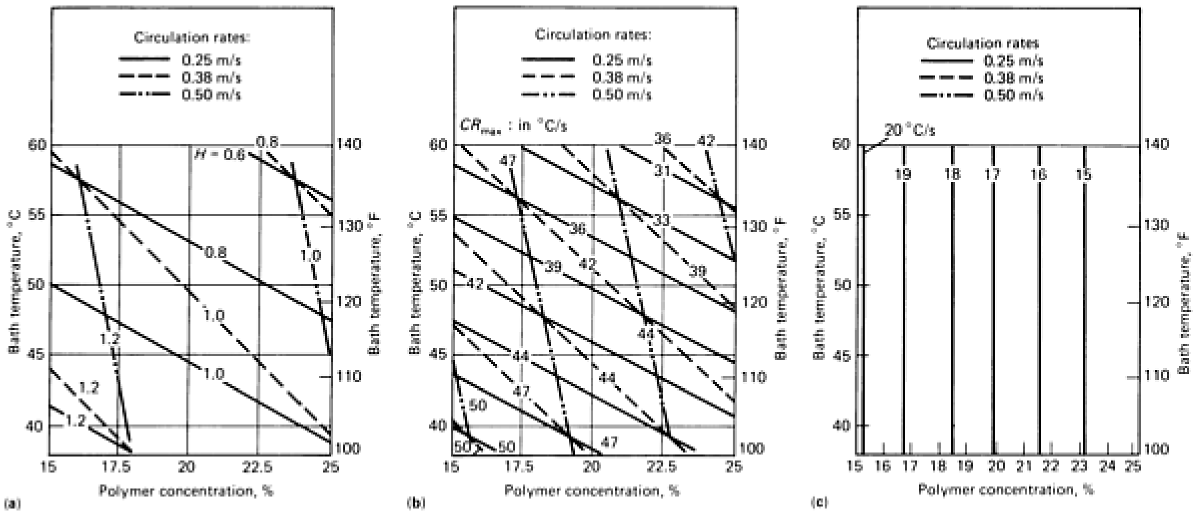


Fig. 70 Predicted quenching characteristics of polyvinyl pyrrolidone quenchant at bath temperatures ranging from 38 to 60 °C (100 to 140 °F) (a) *H* factor. (b) Maximum cooling rate (CR_{max}). (c) Cooling rates at 345 °C (650 °F) The data in (C) apply to all circulation rates.

Optical refractometer readings will provide initial control of concentration, but backup with viscosity measurements is strongly recommended. A means for removal of impurities by ultrafiltration was recently patented (U.S. Patent 4,251,292). This can be done without interrupting the quenching process.

Polyacrylates. Another class of polymers that is used to formulate aqueous polymer quenchants is the sodium polyacrylates (PA) class. The PA polymer can be produced by the homopolymerization of sodium acrylate, or the alkaline hydrolysis of a polyacrylate ester. The material has the structure illustrated in Fig. 63(c).

Like polyvinyl pyrrolidone, aqueous sodium polyacrylate solutions are soluble up to the boiling point of water. Their ability to reduce the rate of heat removal is proportional to the molecular weight of the polymer and its effect on solution viscosity. By varying the polymer molecular weights, a whole family of quenchants can be designed to cover applications ranging from water to oils.

The effect of polymer concentration and temperature for one of the commercially available sodium polyacrylate quenchants is shown in Fig. 71. The cooling curves obtained with polyacrylate solutions can be almost linear with time, which is a result of the extended A-stage cooling and reduced cooling rates during nucleate boiling. This property of the polyacrylate quenchants allows their use in hardening crack-prone parts made of high hardenability steels. A comparison of cooling curves of a sodium polyacrylate quenchant with those of water, conventional oil, and a few typical polymer quenchants is shown in Fig. 72. The cooling rates produced by the sodium polyacrylate solutions are distinctly slower than those of other polymer quenchants. This is an advantage in applications requiring slow quenching.

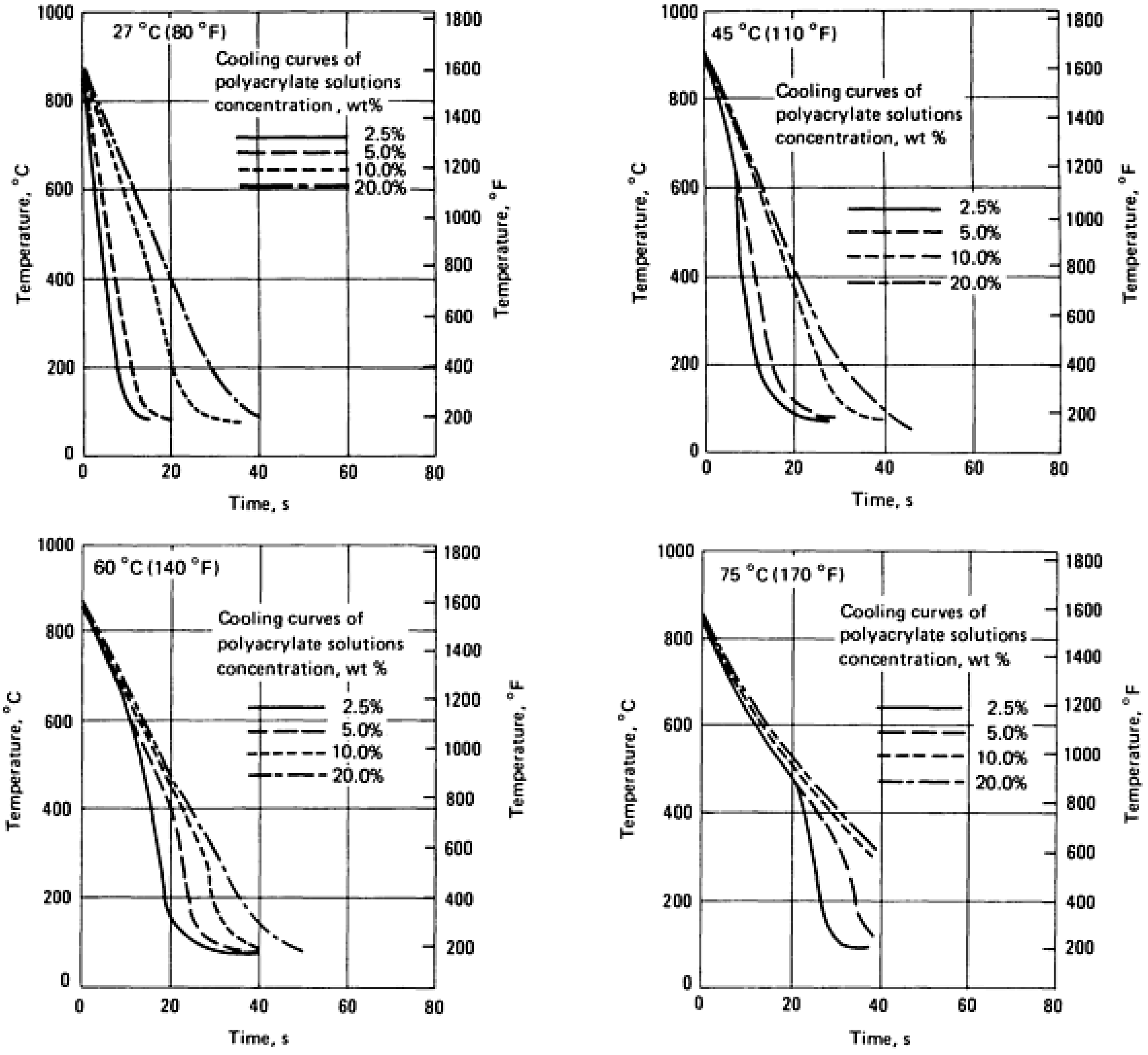


Fig. 71 Cooling rate of an agitated sodium polyacrylate quenchant as a function of concentration and temperature that was used to treat an austenitic steel. Test specimen dimensions were 10 mm (0.4 in.) diam by 60 mm (2.4 in.).

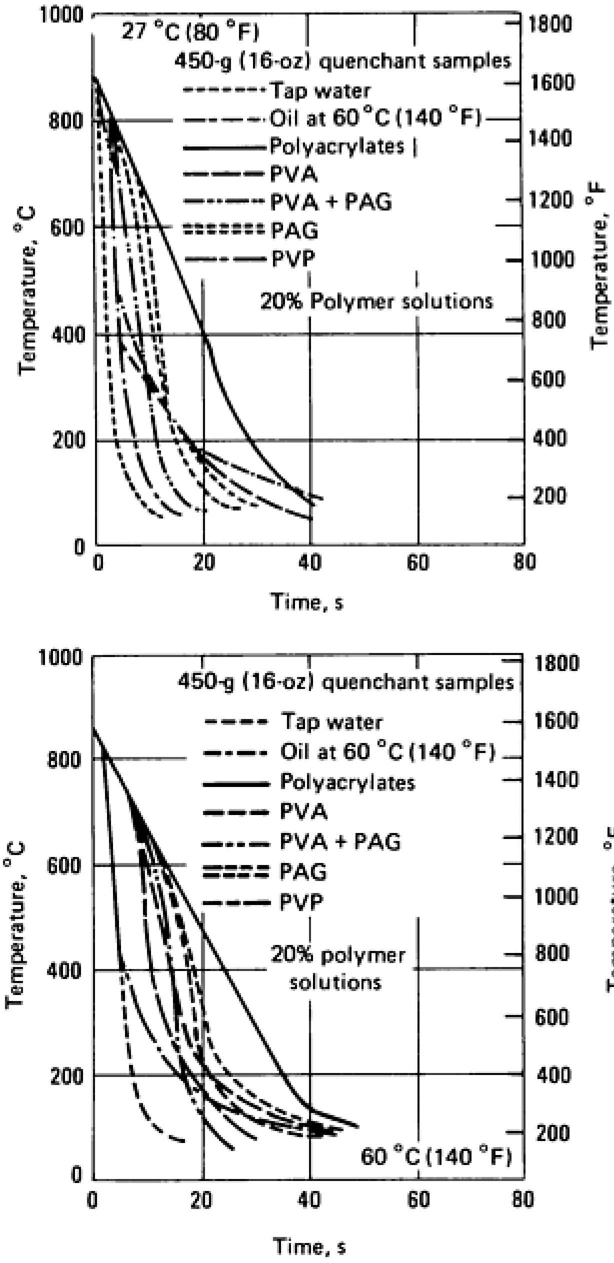


Fig. 72 Cooling rates of selected polymer quenchants at 20% concentration and bath temperatures of 25 and 60 °C (80 and 140 °F). Test specimen type and dimensions: 10 mm (0.4 in.) diam by 60 mm (2.4 in.) scaleproof austenitic steel, medium agitation

With increasing PA concentration and bath temperature, the cooling rate can be reduced to such an extent that many ferrous metals do not transform to martensite at all, but form bainite or fine pearlite. This nonmartensitic quenching can be utilized for achieving lower hardness values.

Some applications of the sodium polyacrylate solutions for nonmartensitic quenching are as follows:

- Deep carburized parts, such as bearing races, balls, and rollers, which are often double quenched in oil to obtain grain refinement. The first quenching can be done in a polyacrylate solution
- Direct quenching of plain carbon steel with a high carbon concentration to obtain similar mechanical properties as obtained by quench and temper or austempering, such as automotive sway bars or railroad rails made of SAF 1070 to 1090
- Rod or wire patenting in sodium polyacrylate solutions, instead of lead or salt baths at 510 to 565 °C

(950 to 1050 °F)

- Direct quenching of hot formed parts to obtain good machinability without having to temper after quenching of steels of low hardenability such as carburizing steels
- Cooling of hot formed parts in sodium polyacrylate solutions to prevent scaling and decarburization such as might occur during slow cooling in air, while achieving practically the same microstructure
- Large continuously cast steel slabs may be water quenched to shorten cooling duration, thus permitting inspection shortly after casting

This is possible only for slabs of plain carbon steel containing up to about 0.2% C. Alloy steels and steels with higher carbon concentrations cannot be water quenched because of their cracking tendency but may be quenched in polyacrylate solutions.

As with all polymer quenchants, sodium polyacrylate solutions require agitation, the degree of which depends on the specific application. As a general rule, a high degree of agitation is recommended for hardening operations.

The concentration control of the sodium polyacrylate quenchants is based on kinematic viscosity. To take into account the influence of contaminations, they also should be periodically checked with other laboratory methods including cooling curve analysis. This service is usually provided by a quenchant supplier.

Polyvinyl Alcohol. The use of aqueous solutions of polyvinyl alcohol (PVA) as quenching media was first described in U.S. Patent 2,600,290, issued in 1952. The chemical formula for polyvinyl alcohol is schematically illustrated in Fig. 63(d).

Although polyvinyl alcohol can be regarded as a polymer of vinyl alcohol, in reality all PVA resins are made by the hydrolysis of polyvinyl acetate. The extent of hydrolysis, which can govern commercial applications, may vary from partial (87 to 89%) through fully hydrolyzed (95%) to superhydrolyzed (99.7%). The water solubility and quenching characteristics of PVA resins vary with the molecular weight of the polymer.

Cooling Characteristics. Slight variations in solution concentration are needed to produce changes in cooling characteristics of PVA solutions, as illustrated in Fig. 73. Concentrations as low as 0.10% have significant effects. Since small concentration variations have substantial effects, close control of PVA solutions is necessary. Control is complicated by the fact that quenched parts can become coated with an insoluble layer of resin, thus reducing the bath concentration. Maintaining an effective concentration requires specific control measures. Very little polyvinyl alcohol is used in quenching at the present time, largely because of the difficulty of maintaining the correct bath concentration.

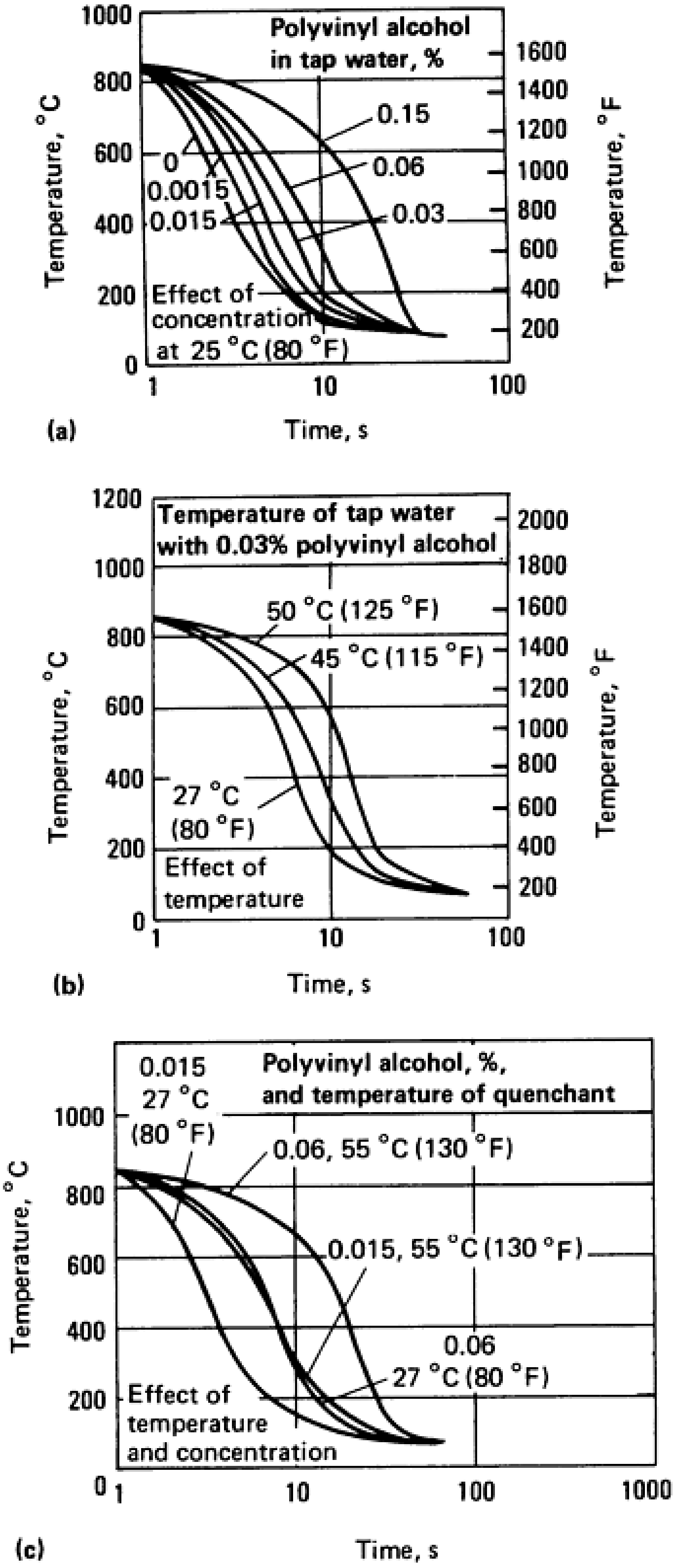


Fig. 73 Effect of temperature and concentration on polyvinyl alcohol solutions. Center cooling curves for type 304 stainless steel specimens 13 mm ($\frac{1}{2}$ in.) diam by 100 mm (4 in.) long quenched in still tap water at 25 °C (80 °F) (or at other temperatures shown) containing various concentrations of polyvinyl alcohol. Thermocouple was placed in geometric center of each specimen. Water hardness, 130 ppm

Molten Salts

The relation between molten salt flow and the cooling rates in bars quenched in a marquenching salt at 205 °C (400 °F) is shown in Fig. 57. Also shown in Fig. 57 are similar curves obtained from water and oil quenching, thus providing comparisons among three media that provide a wide range of cooling rates. The data are plotted to allow correlations between cooling times in quenched round bars and standard end-quench hardenability specimens. The bars were of medium-carbon 9400 steels, heated in an exothermic atmosphere.

The small-diameter bars (and the surface of all bar sizes shown) may be cooled faster in rapidly flowing salt at 205 °C (400 °F) than in still or mildly agitated oil at 50 °C (120 °F) However, as the bar size increases, subsurface regions of salt quenched parts cool more slowly than those quenched in still oil. This limits the section size or steel composition that can develop a fully martensitic structure by quenching in hot salt.

Gas Quenching

Gas quenching is used to provide a cooling rate that is faster than that obtained in still air and slower than that obtained in oil.

In gas quenching, the austenitized work-piece is placed directly in the quenching zone and heat is extracted by a fast-moving stream of gas. The cooling rate of the metal is related to the surface area and mass of the part and to the type, pressure, and velocity of the cooling gas. The cooling rate can be adjusted and controlled by altering the type, pressure, and velocity of the gas, thus providing a degree of flexibility that can be obtained with very few other quenching media.

Recirculation. During the quench period, large volumes of gas are directed through nozzles or vanes to achieve impingement on the surface of the work load. After absorbing heat from the material being processed, the gas is cooled by being passed through water-cooled or refrigerated coils. Recirculating fans return the gas to the nozzles, through which they are again directed at the work load.

Gas quenching units are designed for either batch or continuous processing, but batch processing is more common. Atmospheres containing some hydrogen or helium are commonly used, not only to produce bright work but also to increase the heat transfer rate between the gas and the work.

Applications. In some applications, quenching in a still gas is too slow and oil quenching is undesirable because of distortion, cost factors, handling problems, or the final hardness obtained. In these applications, gas quenching constitutes a useful compromise between two extremes.

Gas quenching is used to advantage in hardening aircraft tubing made of low-alloy steel. Tubing with up to 3.2 mm ($\frac{1}{8}$ in.) wall thickness can be satisfactorily quenched in a continuous process. A comparison of the cooling curves obtained in quenching 4130 steel tubing 31.8 mm (1.25 in.) OD by 1.7 mm (0.065 in.) wall in gas, oil, and still air (normalizing) is presented in Fig. 74.

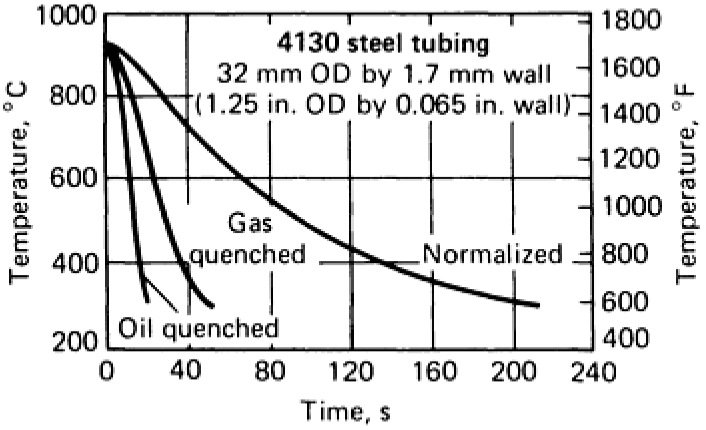


Fig. 74 Cooling curves obtained in quenching 4130 steel tubing in gas, oil, and still air (normalizing)

When a steel that is not air hardenable because of its chemical composition or section size, or both, is quenched in oil, gas, or still air, considerable differences in hardness are obtained. Brinell hardnesses, surface to center, obtained by quenching 100 mm (4 in.) thick disks forged from 1095 steel in each of the three different media, are shown in Fig. 75.

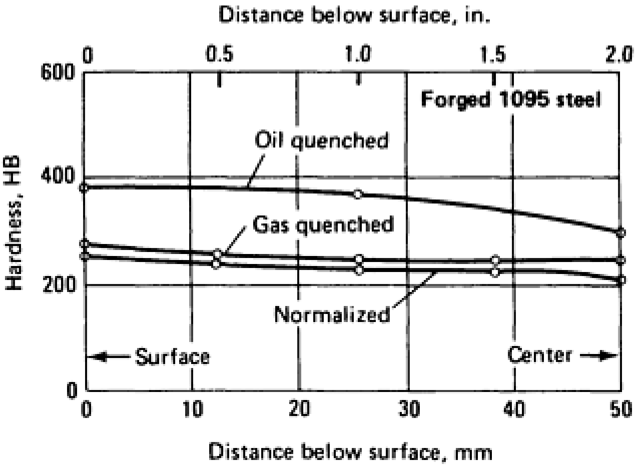


Fig. 75 Differences in Brinell hardness of forged 1095 steel disks, 100 mm (4 in.) thick, after oil quenching, gas quenching (forced air), and cooling in still air (normalizing)

Tool steels of types A2 and T1, in the form of solid blocks 50 by 100 by 100 mm (2 by 4 by 4 in.), were successfully austenitized and gas quenched with cylinder nitrogen in a vacuum furnace. A sealed fan in the roof of the furnace chamber chilled the nitrogen by forcing it over the water-cooled walls of the chamber; the cooled gas was then admitted to the chamber at 69 kPa (10 psig) and directed at the steel. As indicated in Fig. 76, the A2 steel cooled from 1010 to 345 °C (1850 to 650 °F) in 8 min, and the T1 steel from 1290 to 345 °C (2350 to 650 °F) in 13 min. These rates were sufficient for maximum hardness.

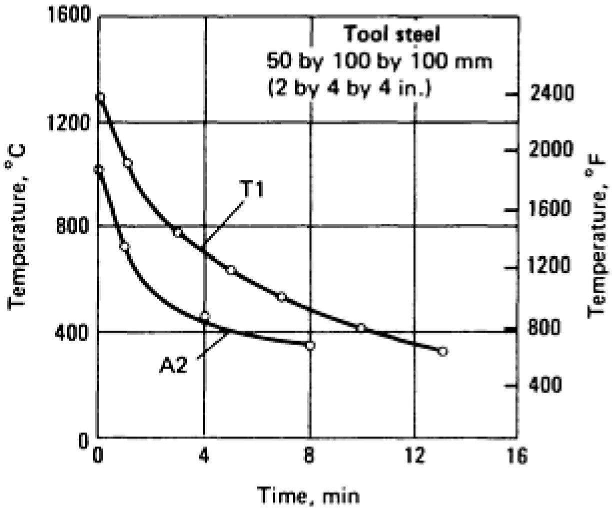


Fig. 76 Surface cooling curves for blocks made of types T1 and A2 tool steels quenched from austenitizing temperatures by cooled nitrogen in a vacuum furnace

Fluidized Bed Quenching

Quench severities intermediate between those for still air and slow oil quenchants are now possible with fluidized bed quenching (Ref 56, 57). Some of the variables that affect heat transfer in fluidized bed quenching include:

- Compaction, particle size, and distribution of the bed material
- Velocity, composition, and heat capacity of the gas or gas mixture flowing through the bed
- Dimensions of the fluidized bed relative to the size and mass of the parts being quenched
- Position of the part in the bed

Some of the advantages of fluidized bed quenching include its flexibility, improved process control, and cleanliness. One of the disadvantages of fluidized bed quenching that inhibits its use is the cost of the fluidizing gas. Fluidized bed quenching processes are being used increasingly as safer and more ecologically sound alternatives to molten metal and salt bath quenching (Ref 56, 57).

Cooling curves comparing fluidized bed quenching to quenching in selected aqueous solutions are shown in Fig. 77.

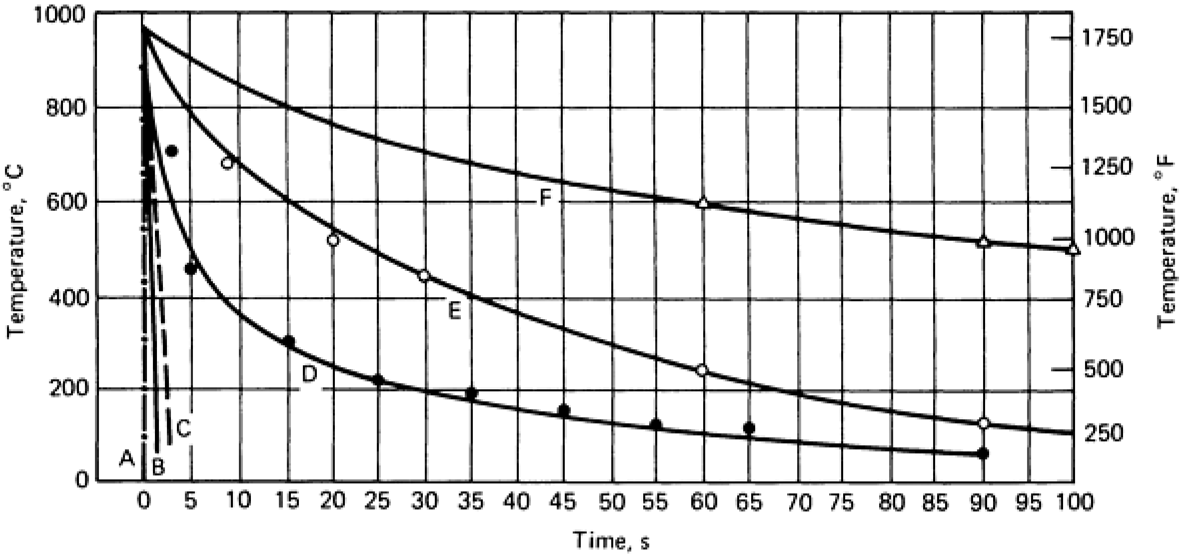


Fig. 77 Comparison of fluidized bed quenching to selected liquid quenchants and normalizing based on relative heat transfer (cooling) rates: A, salt solution; B, agitated water; C, still water; D, oil; E, fluidized bed; F, normalized. Test specimens were 12.6 mm (0.50 in.) diameter bars.

Fog Quenching

In fog quenching, heat is rapidly extracted from the metal by a fast-moving stream of gas that contains water droplets. The cooling capacity of the fog is derived from both the absorption of heat by the gas and the heat of vaporization of the water. The addition of water droplets (or fog) to an air stream can increase its cooling capacity by a factor of $4\frac{1}{2}$. Fog quenching is most effective in the lower temperature ranges.

An outgrowth of gas quenching, fog quenching normally is substituted for liquid quenching in an effort to minimize distortion. Although less severe than a liquid quench, fog quenching is more severe than a plain gas quench of equivalent velocity. In general, the types of parts that are fog quenched are similar to those that are considered suitable for gas quenching.

Cold Die Quenching

Thin disks, long slender rods, and other delicate parts that distort excessively when they are quenched in conventional liquid media can often be quenched between cold dies with virtually no distortion.

One means of solving such problems is to utilize various forms of cold, flat, or shaped dies, depending on the shape of the part being quenched. If only a few parts are involved, the dies will not require special cooling, provided they are allowed

to cool before another part is quenched. The dies usually are used in some sort of press located close to the austenitizing operation.

Large thin thrust washers that were blanked from cold rolled steel and contained machined oil grooves distorted as a result of blanking and machining stresses. A dimensional variation of 1.3 mm (0.050 in.) was common, and even larger variations sometimes occurred. Nevertheless, these washers had to be flat to within 0.13 mm (0.005 in.) after hardening. To ensure the required flatness, the washers were squeezed between a pair of water-cooled die blocks immediately after they left the hardening furnace. The die blocks provided the necessary quenching action while maintaining flatness. When water-cooled beryllium copper die blocks were used in this application, the rate of cooling approached that obtained in water quenching.

Cold die quenching is limited to parts with a large surface area and a relatively small mass, such as washers, rods of small diameter, and thin blades.

Press Quenching

Commercial quenching presses are designed for controlled quenching of ring gears and other round, flat, or cylindrical parts to permit heat treating with minimum distortion.

Probably the most widely used special technique is press quenching. To realize the maximum advantages of controlled quenching and to minimize distortion caused by the heating cycle, press quenching dies must be made to provide the proper oil flow and hold critical dimensions of the part being quenched. In press quenching, the die contacts the heated part, and the pressure of the press aligns the part mechanically. This occurs before quenching begins, while the part is hot and plastic. The machine and dies then force the quenching medium into contact with the part in a controlled manner (see Fig. 78).

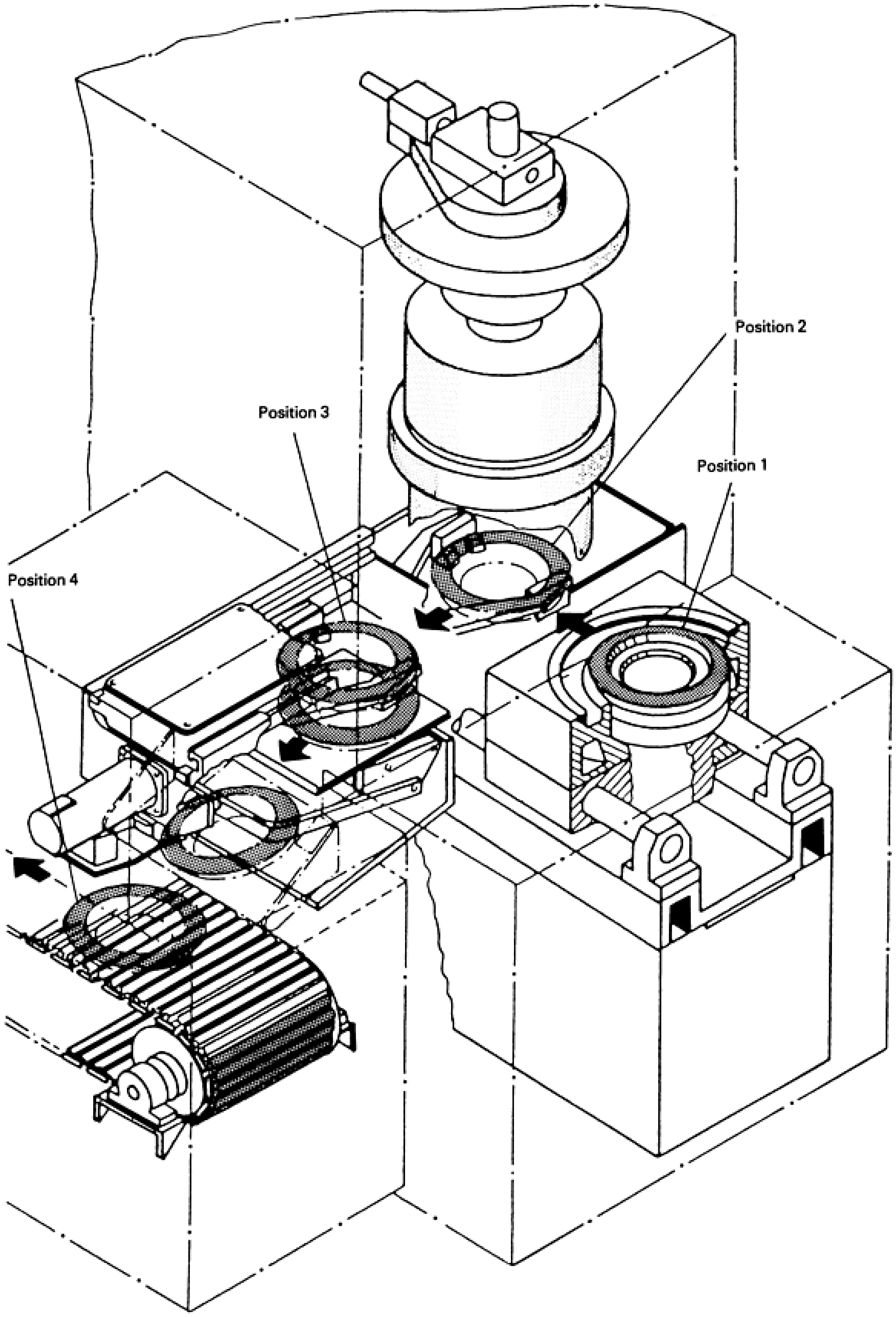


Fig. 78 Cutaway view of a four-position, automatic gear-quenching press using the pulsing principle. Hot gear placed in extended lower die (position 1) is transferred to the center of the quench chamber containing the upper die, the chamber is sealed, and the workpiece subjected to the intermittent pressure of flowing oil for 20 s (position 2). Quench chamber door opens as die is raised and workpiece is moved into an auxiliary quench chamber (position 3) that is subsequently also sealed to provide further cooling while submerged in oil.

Workpiece is then ejected into conveyor tank (position 4) for final cooling.

The quantity of quenchant and its rate of flow are controlled by the press. The distribution of the flow is controlled by the dies. The speed of the quench depends on the quenching medium and the rate of oil flow. The rate of cooling can be controlled by adjusting the rate of flow of oil through the die.

Although some basic types of dies are available for certain workpiece shapes, additional dies are usually required to accommodate specific parts.

Quenching to a tolerance of 0.025 to 0.050 mm (0.001 to 0.002 in.) for roundness and flatness is common practice for ring gears when the proper equipment and correctly designed dies are used.

Quenching of Flame and Induction Hardened Parts

A great many flame and induction hardening applications employ water as the quenching medium. Other media, such as oil, soluble oil, compressed air, aqueous polymer solutions, or brine are occasionally used. Because water provides the greatest ease in handling, and the greatest safety, it is used unless metallurgical considerations indicate the necessity for a less severe quenching media.

Although numerous agitation designs may be used in induction quenching applications, two of the most common are open and submerged spray. The spray orifice for water quenching is often relatively small to maximize cooling rates. However, the orifice diameter must be sized differently when aqueous polymers are used since high pressure and fine spray result in premature rupture of the polymer film that attenuates the cooling rate at the hot metal surface. Suggested types of sprays, pressures, and orifice sizes for quenchants from open and submerged spray systems are shown in Table 20.

Table 20 Recommended orifice size and fluid pressure for induction spray systems used to quench steels from an austenitizing temperature of 845 °C (1550 °F) with a PAG polymer quenchant

Type of spray[(a)]	Pressure[(b)]		Orifice diameter	
	kPa	psi	mm	in.
Open	<140	<20	3.2	$\frac{1}{8}$
Submerged	>275	>40	6.4	$\frac{1}{4}$

(a) All of the cooling curves for the quench factor correlation were determined using AISI type 304 stainless steel probes.

(b) Data for UCON (Union Carbide Chemicals and Plastics Company. Inc.) Quenchant B.

In order to minimize foaming, the quenchant reservoir volume should be at least five times the volume rate of flow. For example, if the flow rate is 25 L/min (6 gal/min), then the reservoir volume should be at least 110 L (30 gal).

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Testing and Evaluation of Quenching Media

The testing of quenching media can be classified into two broad categories:

- Tests of hardening power (metallurgical response)
- Tests of heat removal ability of the quenchant

The results of hardening tests are related to the size, microstructure, and composition of the steel being quenched as well as to the heat removal characteristics of the quenchant. Traditionally, steel hardening power tests have been determined experimentally by quenching test specimens and performing cross-sectional hardness (U-curves) and Jominy end-quench surveys (ASTM A 255).

Reproducibility problems are occasionally encountered due to procedural and lot-to-lot variations in the steel chemistry. Therefore, there has been a continuing interest in alternative tests that would relate metallurgical properties of steel, such as hardness, to the heat removal characteristics of the quenchant media.

Hardening-Power Tests

The final criterion for selecting a quenching medium is its hardening power, that is, its ability to develop a specified microstructure and hardness in a given material-section size combination under specified conditions of quenchant, agitation, and temperature. The major factors influencing the hardness obtained on quenching can be summarized as follows:

- Nature and concentration (if applicable) of the quenchant
- Quenchant temperature
- Quenchant agitation and mass flow
- Material composition, structure, and thermal history of the metal component
- Section size, geometry, and surface condition of the metal component

Jominy End-Quench Test (ASTM A 255). This test is widely used to determine hardenability of steels. It consists of heating a specimen 25 mm (1 in.) round by 100 mm (4 in.) long to the desired hardening temperature, and then withdrawing heat from one end of the bar by the use of a water jet quench. The bar is then ground along its length to 0.38 mm (0.015 in.) below the surface, and hardness readings of the specimen are taken 1.6 mm ($\frac{1}{16}$ in.) apart. Hardenability is expressed in terms of the distance from the quenched end to a given hardness. Detailed information is available in the article "Hardenability of Carbon and Low-Alloy Steels" in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.*

The standard end-quench procedure employs 25 °C (80 °F) water, but some investigators employ oils or polymers to perform the end quench and then compare the results obtained with the alternate quenchant with the results produced by water.

Immersion Quench Test. The standard Jominy end-quench test does not readily permit adequate modeling of agitation effects encountered in many commercial quench practices. Also, the Jominy end-quench test is not a generally acceptable method for use with aqueous polymer quenchants since the pressure of the flood quench at the end of the test specimen often disrupts film-forming properties of the polymer at the hot metal interface.

In view of limitations of the Jominy end-quench test, a cross sectional hardness survey, or U-curve, is often determined on a standard test piece under actual quenching conditions. The hardenability indicated by the U-curve may be related to the hardness of an end-quench test by use of the Lamont transformation as shown in Fig. 41 (Ref 59).

Cooling Power Tests

Because hardening power tests are time consuming and relatively difficult to perform, cooling power tests have been developed for the evaluation of quenching media. The three tests most commonly used today are:

- Cooling curve tests
- The magnetic test
- The hot wire test

Cooling Curve Tests. The most useful method to determine the cooling power of a quenchant is the cooling curve test, wherein cooling rates are established throughout the complete quenching process. The test is performed by quenching test specimens, containing one or more thermocouples, and following the cooling process by using a temperature measuring device. Test specimens can be made of stainless steel, silver, nickel, or carbon steel. Although cylindrical shapes are most common, other shapes may be used, including balls, plates, tubes, or production parts. A test specimen of relatively small mass may be desired for slow quenching fluids, whereas faster quenching fluids may require larger mass or a recorder having a very high response rate. Silver probes are used by some investigators because they are free from transformation effects and resistant to corrosion. The relatively high conductivity of silver averages out localized surface thermal variations while retaining high sensitivity to the quenchant properties.

The characteristic temperature (the lowest temperature at which a vapor envelope can be maintained) and the boiling point are unaffected by the temperature, the thermal conductivity, or the mass of the test piece when the cooling curve is taken at the surface of the test piece. This is not true when the curve is taken at any point below the surface. Overall, the cooling curve test is an excellent research and quality control tool and provides for a great degree of comparative accuracy. Standardization of the test would facilitate the comparison of results from different sources.

In conducting cooling curve analysis, it is critical that data acquisition rates be sufficient to provide enough data points to precisely determine cooling rates in the regions of highest heat transfer. Higher thermal conductivity or smaller probes require faster data acquisition rates.

A surface thermocouple is sometimes used to detect surface events that would be obscured in the center thermocouple output.

High data acquisition rates are usually required for surface thermocouples because of the high cooling rates encountered. For example, if a surface thermocouple is used with a 10 mm (0.4 in.) diameter silver test piece, the recorder must be capable of accurately registering rates of temperature change of at least 540 °C (1000 °F) in 0.1 s throughout the temperature range being explored.

It is generally recognized that surface temperature readings are important in calculating heat transfer coefficients and the surface heat flux during the quenching process. However, oxidation of the probe during the heating prior to quenching often makes it difficult to obtain reproducible surface cooling curves. However, surface temperatures during the quenching process can be calculated by finite-element method (FEM) or finite-difference method (FDM) analyses using commercially available computer programs (Ref 53).

As discussed earlier, Liščić has described the construction of a stainless steel probe that permits measuring cooling curves and temperature profiles across an instrumented specimen (see Fig. 10). This type of probe permits the calculation of heat transfer rates occurring during the quench process and may be related to the hardness properties of the steel being quenched (Ref 17).

Heat treaters are usually reluctant to measure the surface cooling behavior because they are more interested in the core hardness. Consequently, they have been more interested in centerline cooling curves in iron- or nickel-base alloys with thermal characteristics similar to the metals being heat treated.

When analyzing cooling curves obtained from probes of different construction, analysts should recognize that the ability of metals to diffuse heat from the core is reflected by the expression:

$$a = \frac{K}{rC_p} \quad \textbf{(Eq 19)}$$

where α is the thermal diffusivity; *k* is the conductivity; ρ is the density; and C_P is the specific heat of the metal.

The value of α is 0.25 cm^2/s for silver, 0.175 cm^2/s for nickel, and 0.11 cm^2/s for carbon steel. The temperature gradients in probes made of steel are higher than in nickel and both are higher than the temperature gradient in silver.

If cooling curves from different sources are to be compared, it is essential that they be obtained under the same conditions. This includes standardized test specimen (probe) alloys, probe size, thermocouple type and position, initial probe temperature, quenchant temperature, size and geometry of quenchant bath, volume of the quenchant, data acquisition rate, and so on. Currently, an International Organization for Standardization (ISO) specification is being developed for a standardized testing procedure. The procedure is based on work originally conducted by Wolfson Heat Treating Institute. A similar specification is being drafted by American Society for Testing and Materials in the United States.

Magnetic Quenchometer Test (ASTM D 3520). This test makes use of the properties of metals that lose their magnetism when heated above a Curie point, and regain their magnetism when cooled below this temperature. The quenchometer test was devised to provide a means of comparing the heat extraction rates of oil, molten salt, water, and other quenching media. The test method involves heating a 22 mm ($\frac{7}{8}$ in.) diameter nickel or chromized nickel sphere, weighing approximately 50 g (1.8 oz) to 885 °C (1625 °F) in either air or a controlled atmosphere. After temperature uniformity is attained, the sphere is quenched in a 200 mL (0.055 gal) sample of liquid located in a magnetic field. As the nickel sphere cools through its Curie temperature, it is attracted by the magnetic field to the side of the container. The time required for the nickel sphere to cool from 885 °C (1625 °F) to the Curie temperature 355 °C (670 °F) is a measure of the cooling power of the quenching medium. The higher the cooling power of the quenchant medium, the shorter the time required for the nickel to regain its magnetism.

Other alloys with different Curie points can be used to establish additional points on a cooling curve. A modification of the magnetic quench test can be used to study the influence of circulation and heat on the cooling power of quenching oils.

Magnetic quenchometer test results presented in Table 5 are reported in seconds. The time reflects the time required to cool a 48 to 52 g (1.7 to 1.8 oz), 22 mm ($\frac{7}{8}$ in.) diameter nickel ball from 885 °C (1625 °F) to 355 °C (670 °F) These results are listed for some commercially available conventional and fast quenching oils as well as for martempering oils with and without quench rate accelerators. Conventional and fast oils are usually tested at 25 °C (80 °F) Martempering oils, which are used at higher temperatures, are commonly tested at 120 °C (250 °F).

The test balls are made of either pure nickel or chromized pure nickel. The latter type was developed to approach the conditions and results obtained with pure nickel balls heated to 885 °C (1625 °F) under reducing atmospheres. This magnetic test, using the chromized nickel balls, is specified in ASTM D 3520, but it is so cumber-some that the much simpler plain nickel ball test usually is preferred.

The Hot Wire Test. This method of quenchant evaluation consists of heating a nichrome wire (of standard gage and electrical resistance) by means of an electrical current in 100 to 200 mL (0.025 to 0.055 gal) of quenchant. The wire is supported by two copper or brass electrodes and the quenchant is usually at its use temperature. The wire is heated by steadily increasing the current by means of a rheostat. The cooling power of the quenchant is indicated by the current flow at which the wire is melted or burned into. Quenchants capable of extracting heat more rapidly permit the passage of

higher currents through the wire. This test resembles the interval test in that it compares the heat removal capability of quenchants only in the higher temperature ranges.

Interval Test. This method, also known as the interval or 5-s test, is a method of comparing the cooling power of oil quenchants. In this test, a 2 L (0.5 gal) sample of an oil is placed in an insulated container and the oil temperature is determined. A bar of metal (usually, stainless steel) weighing about 250 g (8.8 oz) is heated to 815 °C (1500 °F), quenched for 5 s and then removed. The oil sample is then stirred to ensure temperature equalization throughout the bath, and the temperature rise is determined to the nearest tenth of a degree Celsius. This process may be repeated for several test bars.

Finally, a bar is fully quenched in a second sample of oil, and the rise in temperature is noted. The heat removal ability of the oil is computed using the following equation:

$$\%quench\ \text{speed}=100\frac{A}{B} \quad \textbf{(Eq 20)}$$

where *A* is the average rise in oil temperature for the 5-s quench bars; and *B* is the temperature rise in the oil sample after fully quenching. The interval test reflects the proportion of heat removed by the quenchant in a fixed 5-s interval compared to the total heat content of the specimen. A 5-s duration, however, only reflects heat removal in the higher temperature region of the quench and may be misleading because it encompasses only a portion of the cooling curve, namely, the vapor blanket and vapor transport stages.

References cited in this section

17. B. Liščić and T.J. Filetin, *Heat Treat.,* Vol 5, 1988, p 115-124

53. D.M. Trujillo and R.A. Wallis, *Ind. Heat.,* July 1989, p 22-24 (see 5)

59. J.L. Lamont, *Iron Age,* Oct 1943, p 64-70

Quenching Systems

Equipment requirements for quenching vary widely. A small plant making machine parts might require the hardening of only a few simple carbon steel parts each day. For such an application, the quenching system might be comprised of a container of water with a supply line and a drain. Handling equipment might consist of a pair of tongs. As the quantity of work and complexity of workpieces increase, however, various other items of equipment and equipment modifications must be added.

For a complete quenching system, the following functional parts are usually required and installed:

- Furnaces
- Quench tank
- Facilities for handling the quenched parts
- Quenching medium
- Equipment for agitation
- Coolers
- Heaters
- Pumps with strainers or filters
- Quenchant supply tank
- Equipment for ventilation and for protecting against hazards
- Equipment for removal of scale from tanks

Quenching Process Variables

The primary function of the quenchant is to mediate heat transfer rates from the hot metal to the cooler quenchant during the quenching process. At least three factors must be considered in understanding the cooling process:

- Nature and thermal properties of the metal
- Film forming characteristics of the quenchant at the hot metal interface
- Bulk properties quenchant itself

The heat transfer properties of the hot metal/quenchant interface can be described using Grossmann's relationship for quench severity (*H*), in Eq 2:

$$H = \frac{h}{2k}$$

where *h* is the film coefficient; and *k* is the thermal conductivity of the metal.

The Grossmann value is largely controlled by the quenchant medium. The conductivity, *k*, is a property of the metal and *h* defines the heat transfer rate from the metal to the quenchant solution. The thermal conductivity varies with the metal and is temperature dependent.

The heat transfer from the surface of a hot metal into a liquid quenchant solution is (Ref 12):

$$q = h \cdot \mathrm{A} \cdot (T_1 - T_2) \qquad \textbf{(Eq 21)}$$

where *q* is the amount of heat transferred; *h* is the heat transfer coefficient; *A* is the surface area; T_1 is the initial temperature of the hot metal; and T_2 is the bath temperature.

From Eq 21, it is evident that heat flow, *q*, increases as the (T_1 - T_2) value increases. Therefore, faster heat transfer rates are to be expected as the temperature of the quenchant bath decreases or as the initial temperature of the hot metal increases.

The amount of heat extracted, *Q*, from a part during quenching from the austenitizing temperature to the bath may be estimated from the equation:

$$Q = C_P \cdot W_m \cdot (T_1 - T_2) \qquad \textbf{(Eq 22)}$$

where C_P is the specific heat of the metal, for example, 0.166 Btu/lb · °F for steel; W_m is the metal weight (lb) being quenched including the quench trays; T_1 is the initial temperature of the load in °F; T_2 is the final temperature of the load in °F; and *Q* is the total amount of heat (Btu) given up by the load to the quenchant.

Although the specific heat of metal is actually a temperature dependent function, this simplified equation (Eq 22) permits a reasonable estimate of the amount of heat evolved from the metal being quenched. In making this calculation, it is assumed that no heat is lost to the environment during the process. A similar equation permits the temperature rise, T_r, in a quenchant bath during the quench cycle to be estimated:

$$T_r = (T_2 - T_1) = Q \cdot W_q \cdot C_{P(quench)} \qquad \textbf{(Eq 23)}$$

where T_r is the bath temperature rise; T_2 is the final bath temperature; T_1 is the initial bath temperature; W_q is the weight of the quenchant; $C_{P(quench)}$ is the heat capacity of the quenchant; and *Q* is the amount of heat given up by the metal as defined above.

From Eq 21, 22, 23, it is clear that the temperature rise, (T_2 - T_1), can be affected by the initial temperature of the metal, the mass of the load, volume, and temperature of the quenchant, and heat capacity of the metal.

It is important to remember that the heat transfer rate from the metal at the metal interface may be affected by oxidation. Typically, very small amounts of oxidation increase the heat transfer rate, but larger amounts reduce heat transfer rates.

Therefore, it is essential that surface oxidation be considered when attempting a detailed understanding of heat transfer behavior in a quenchant system.

Sometimes heat treaters closely pack trays of parts to be quenched. It is important to remember that this causes localized quenchant overheating which reduces the heat transfer rates. This may result in uneven quenching and low hardness values on interior parts in a tray in spite of the fact that the quenchant is satisfactory.

It is also important to remember that each quenchant has different film-forming properties during the three heat transfer regimes. Film thickness, stability, and strength are quite important. These properties can be significantly affected by agitation, bath temperature, and concentration.

Concentration, in this context, refers to several factors, including additive concentration in accelerated quench oils, polymer concentration in aqueous solutions, and the presence of oxides or contaminants in the bath. These factors, and others, can impact the quenchant performance.

Mass and Section Size Effects

The cooling curves in Fig. 79 and 80 illustrate the effect of mass and section size on the cooling curves of carbon steel in water and oil. Figure 81 summarizes data in Fig. 79 and 80, including data on still air at the center of bars of various diameters. The combined effects of mass and quenching medium for cooling small sections of selected steels are shown in Fig. 82, 83, and 84.

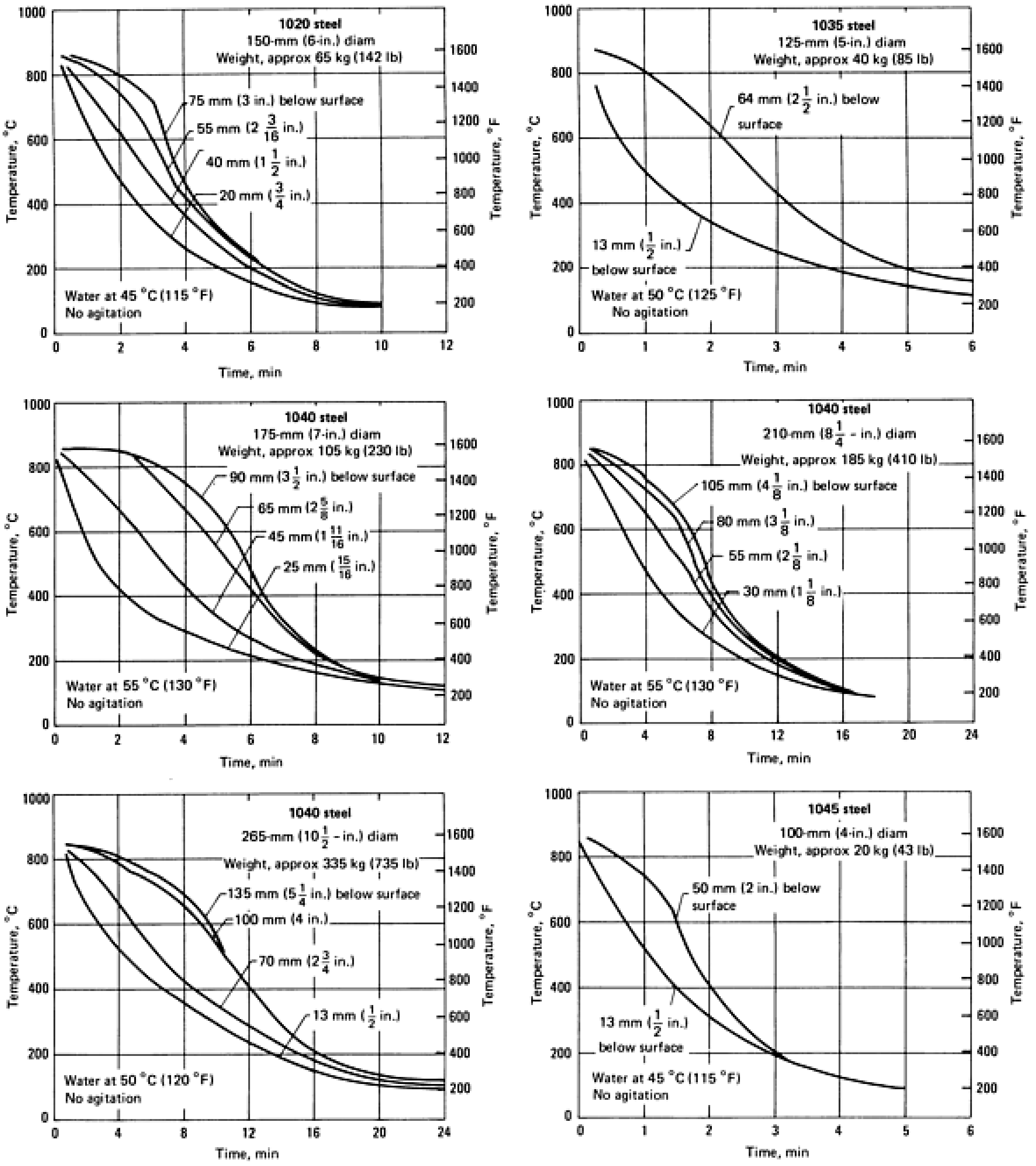


Fig. 79 Effect of mass and section size on cooling curves obtained for the water quenching of plain carbon steels

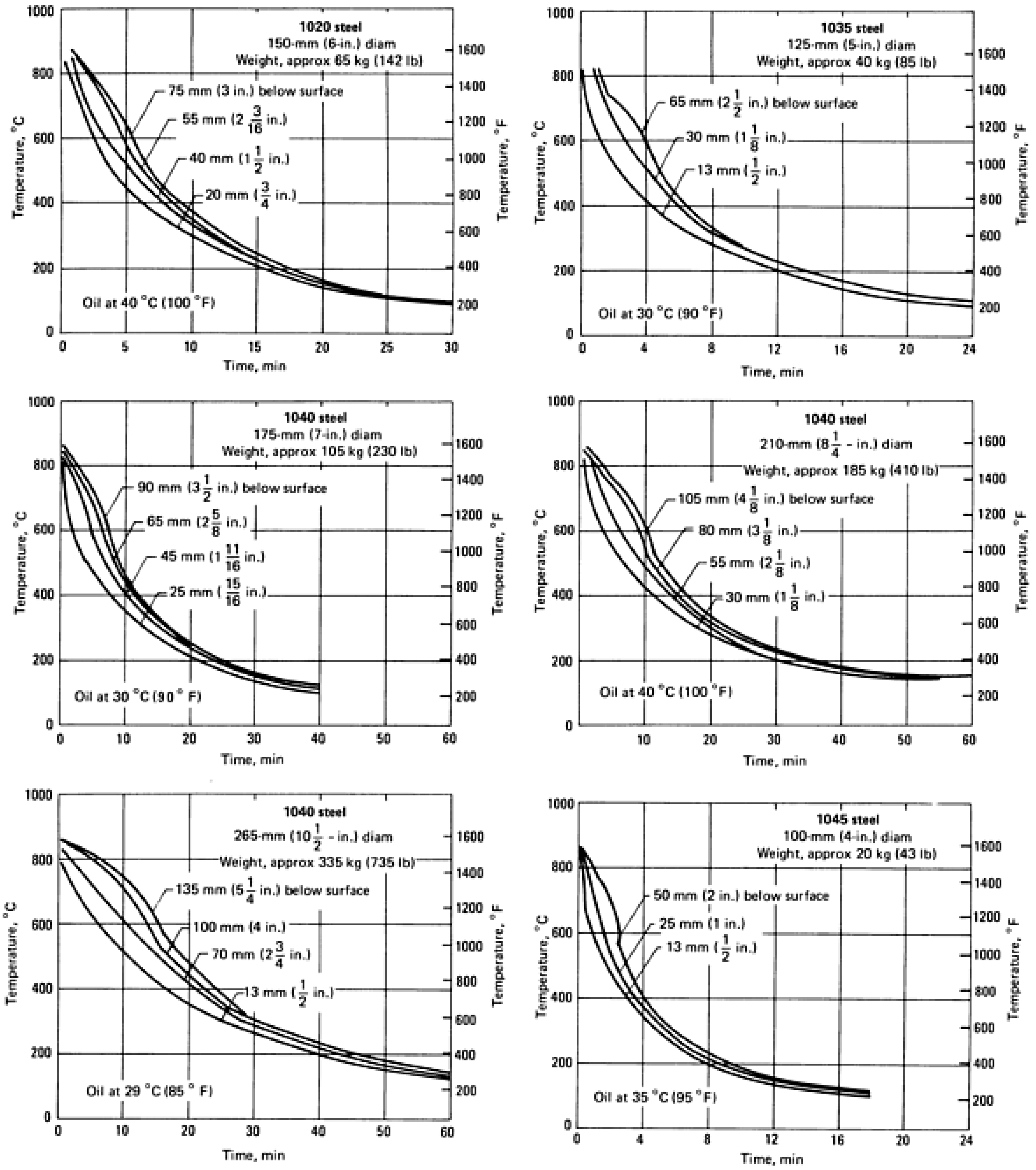
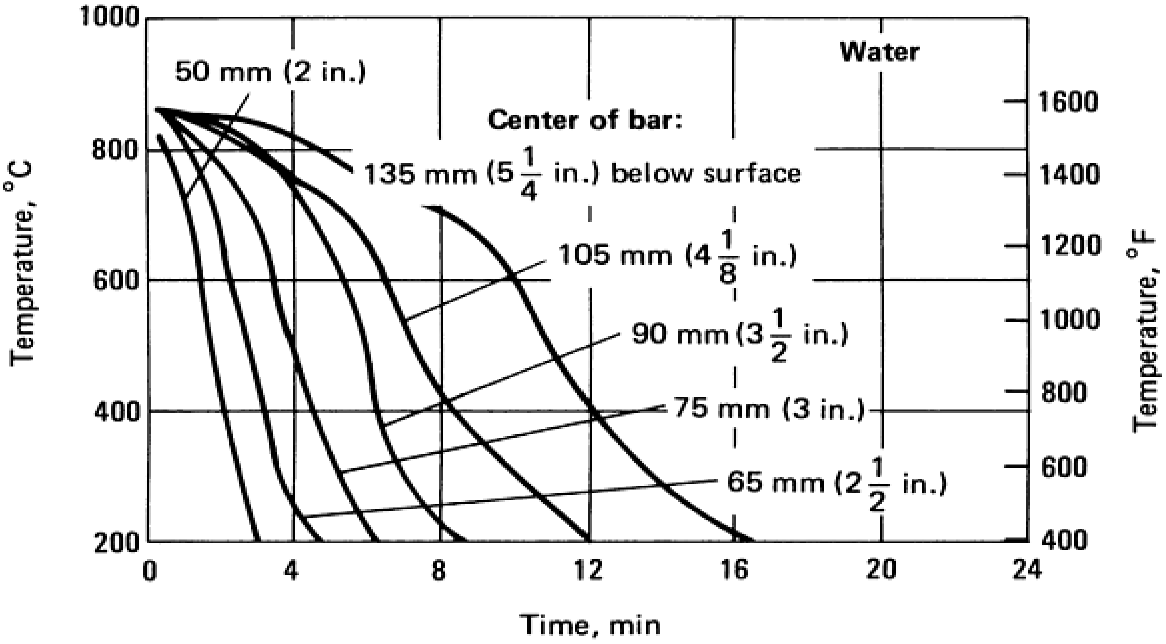
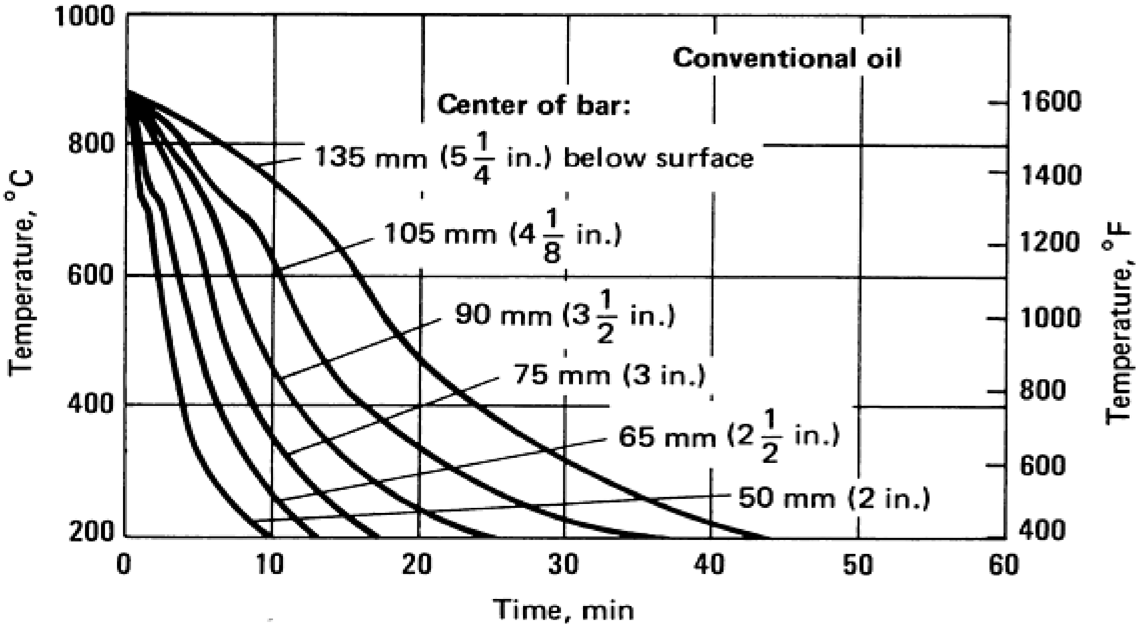


Fig. 80 Effect of mass and section size on cooling curves obtained for the oil quenching of plain carbon steels


Water
Center of bar:
50 mm (2 in.)
135 mm (5 1/4 in.) below surface
105 mm (4 1/8 in.)
90 mm (3 1/2 in.)
75 mm (3 in.)
65 mm (2 1/2 in.)
Temperature, °C
Temperature, °F
Time, min


Conventional oil
Center of bar:
135 mm (5 1/4 in.) below surface
105 mm (4 1/8 in.)
90 mm (3 1/2 in.)
75 mm (3 in.)
65 mm (2 1/2 in.)
50 mm (2 in.)
Temperature, °C
Temperature, °F
Time, min

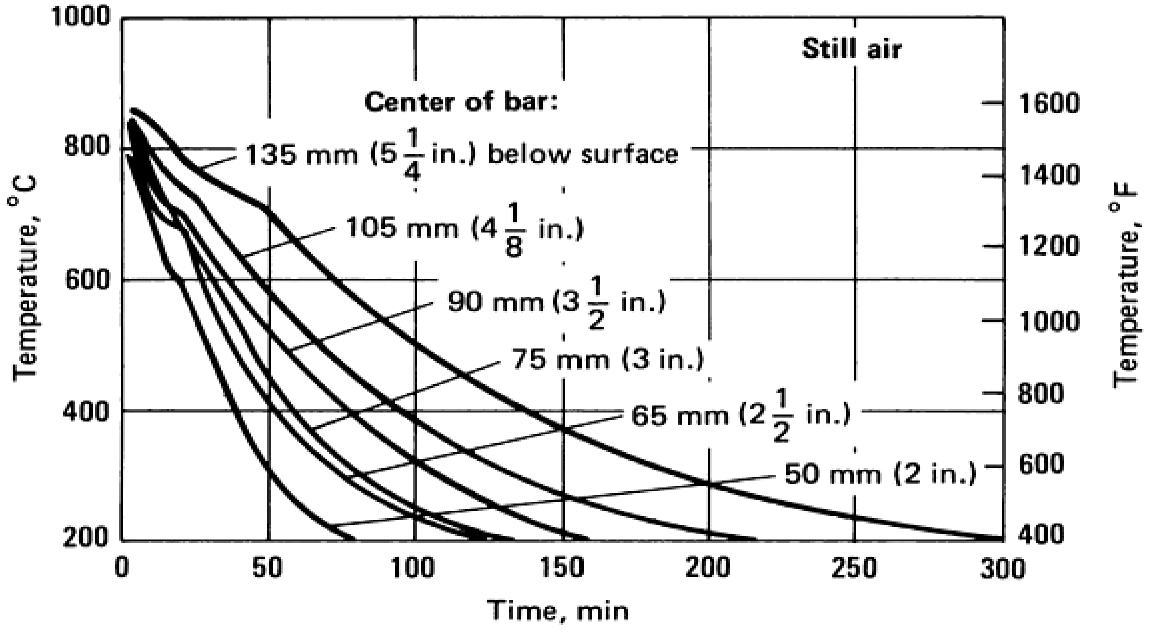

Still air
Center of bar:
135 mm (5 1/4 in.) below surface
105 mm (4 1/8 in.)
90 mm (3 1/2 in.)
75 mm (3 in.)
65 mm (2 1/2 in.)
50 mm (2 in.)
Temperature, °C
Temperature, °F
Time, min

Fig. 81 Summary of cooling curve data on water quenching (see Fig. 79) and conventional oil quenching (see Fig. 80) compared to still air quenching at the center of plain carbon steel bars

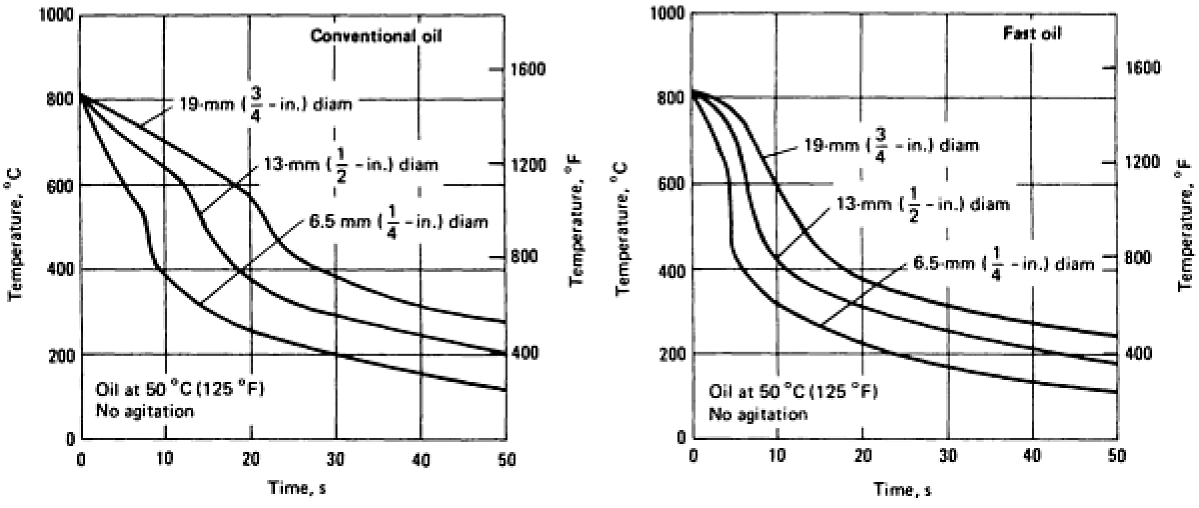


Fig. 82 Cooling curves for 64 mm ($2\frac{1}{2}$ in.) long austenitic stainless steel specimens of various diameters quenched in conventional oil and fast oil

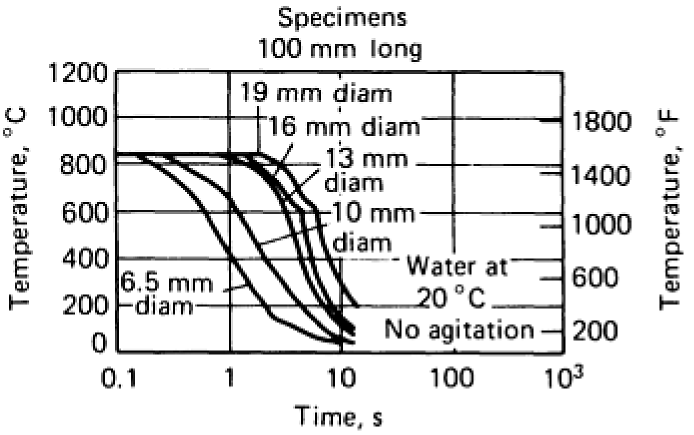


Fig. 83 Cooling curves for 100 mm (4 in.) long drill rod cylinders of various diameters quenched in water

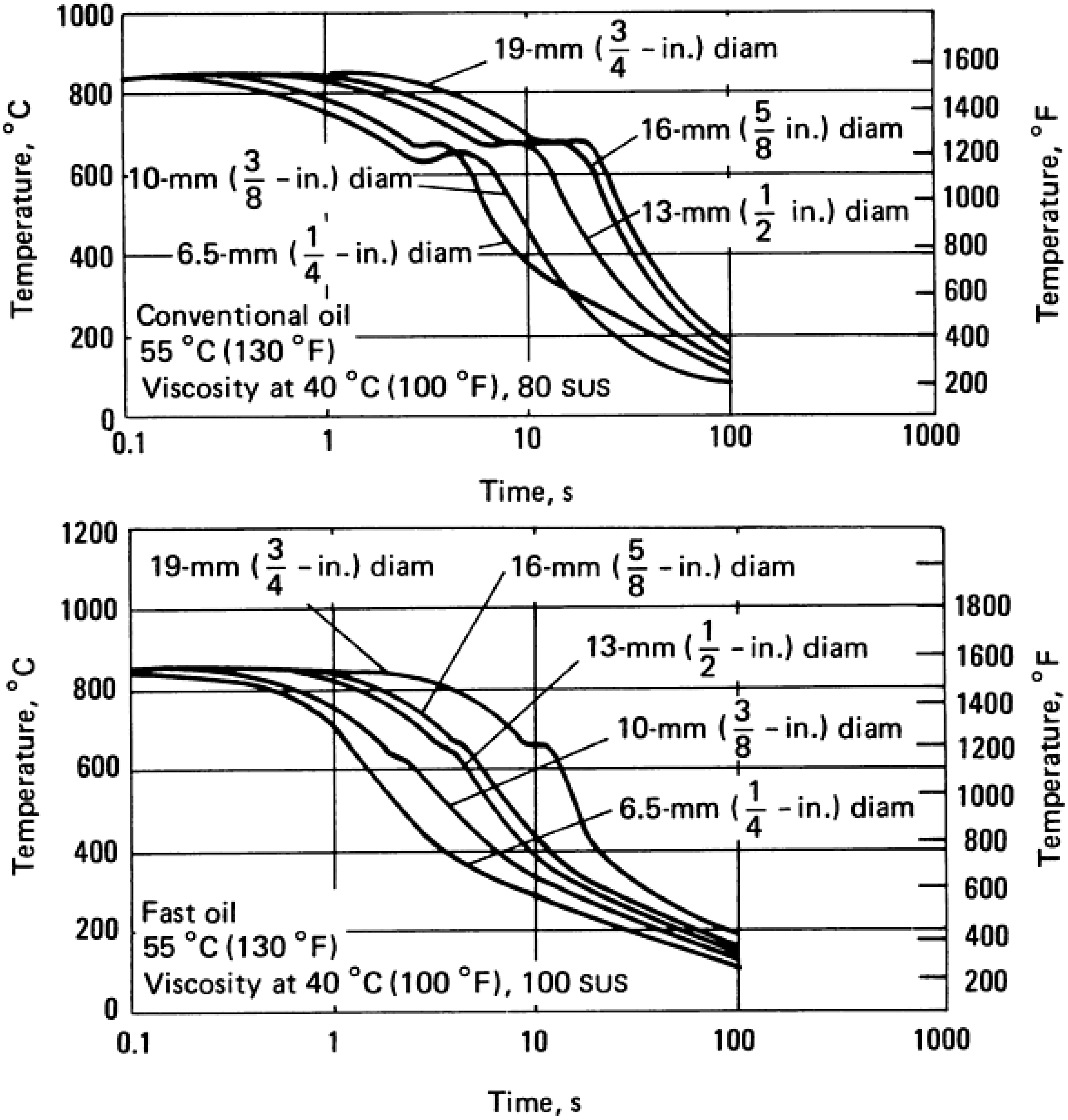


Fig. 84 Effect of mass and section size on center cooling curves in still quenching 100 mm (4 in.) long commercial drill rod cylinders of various diameters in a conventional oil and fast oil

Continuous Quenching

A tank, such as schematically illustrated in Fig. 85, is commonly used for continuous quenching of parts that can be dropped into the quenching liquid. The parts fall from the furnace belt through a chute into the quenching medium and onto a second belt that conveys them out of the quenchant. Agitation can be provided by an impeller directed at the lower end of the quench chute. If the mass of work entering the tank is large, a means of controlling the quenchant temperature is required. This type of quench system is usually limited to symmetric and simple shapes because free fall from the furnace belt can result in distortion and nonuniform quenching. Gravity fall of the hot workpiece through the quenchant usually is employed for quenching small parts that have a high ratio of area to weight.

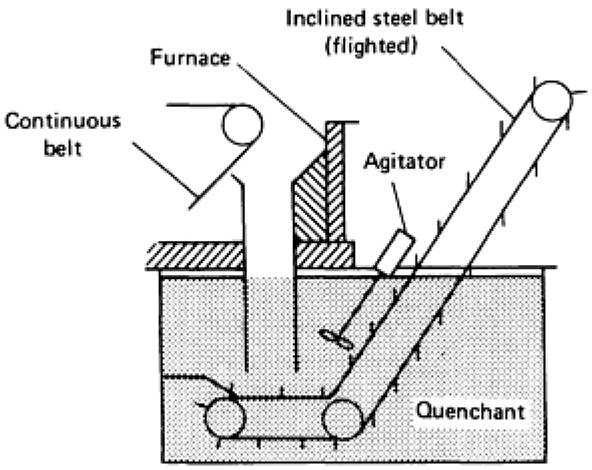


Fig. 85 Schematic of typical tank used for continuous quenching applications. The tank is designed for quenching parts of similar shape from a continuous hardening furnace. Parts fall from the furnace belt through the quenchant and onto a conveyor belt that transports them from the quenching tank. Quenchant may be water or oil.

Water Quenching System

A simple arrangement for water quenching, incorporating a method for controlling water temperature, is shown in Fig. 86. A supply of fresh water is continuously introduced and overflows to a drain. Temperature control of the water is provided by a regulator that opens and closes at predetermined temperatures.

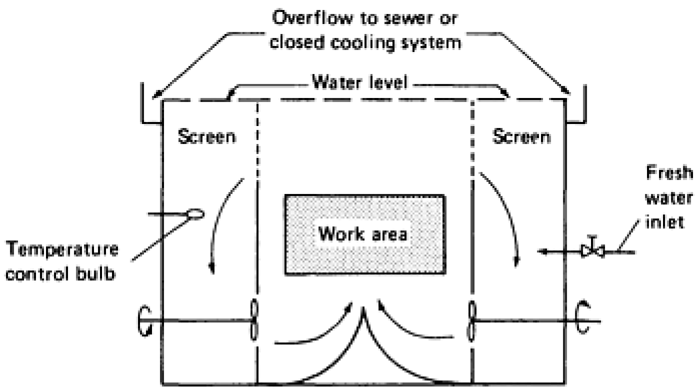


Fig. 86 Temperature-controlled overflow tank used for water quenching applications

This system can also be connected to a closed water-cooling system to minimize water consumption and control the bath temperature.

Oil Quenching Systems for Continuous Carburizers

Additional controls of the quenching operation are required for mass production of parts through a continuous carburizer. Plants involved in heat treating rear and front axle assemblies, gears, stem pinions, and differential side gears require loading fixtures for batch-quenched parts and quenching presses for ring gears. Because low unit cost must be maintained, quenching was integrated with heating and handling facilities were arranged accordingly. Machined gears were charged into a continuous pusher-type gas carburizer. Work-pieces were loaded on alloy trays with fixtures that permitted direct quenching.

Figure 87 shows a schematic arrangement of a system such as that described above. The principal elements are:

- Quenchant storage-supply tanks and pumps of sufficient capacity to maintain efficient quenchant transfer
- Coolers and heaters to maintain the quenchant temperature
- Filters to minimize free carbon and other foreign materials that may affect the rate of heat transfer or interfere with the operation of quenching presses
- Quenchant agitators
- Alloy fixtures and handling facilities to transfer workpieces
- Quenching oil
- Quenching presses

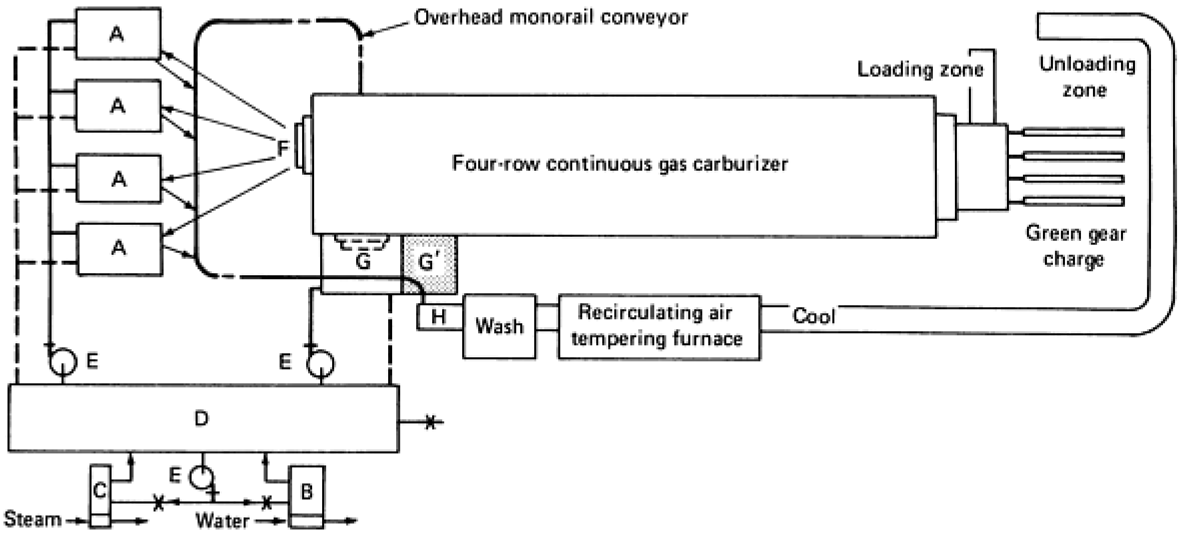


Fig. 87 Layout showing the elements of a quenching system used with a four-row continuous gas carburizing furnace. A, press quenches; B, cooler; C, heater; D, storage tank; E, pumps, strainers; F, slot door; G, atmosphere-hooded quench; G', open portion of G; and H, washer loading platform

A batch-quenching tank that can be used for high-volume production of work on trays is schematically illustrated in Fig. 88. Atmosphere protection, quenchant agitation, temperature control, and other features are included in this arrangement. The internal gas pressure must be greater than that of the outside air to prevent air entry into the chain-drive unit opposite the agitator motors. The revolving chain may otherwise carry air into the oil and cause oxidation.

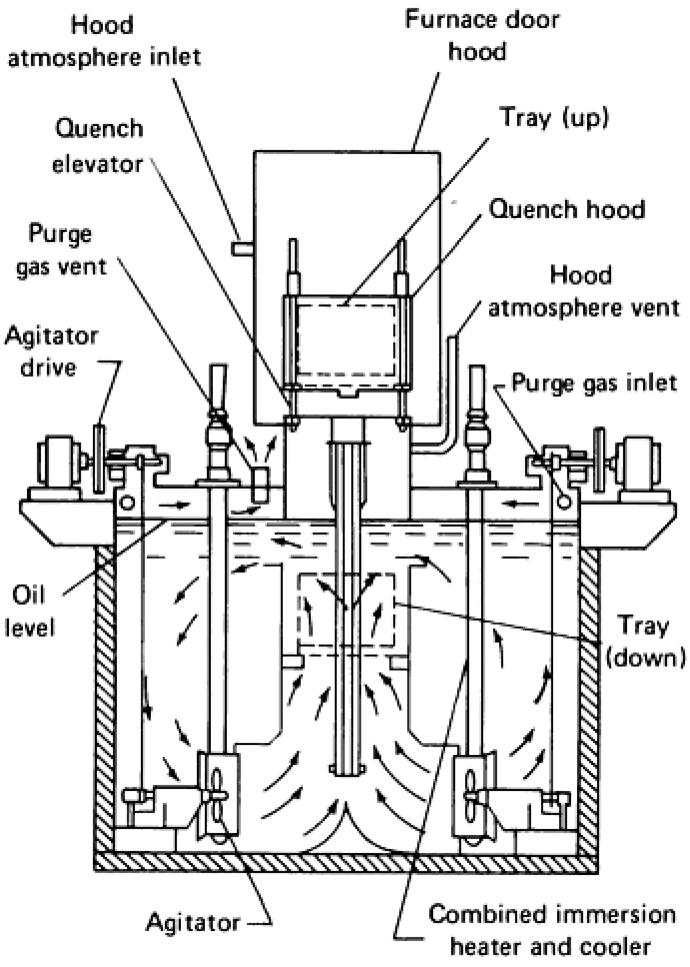


Fig. 88 Schematic of a typical installation for high-volume batch quenching of carburized or hardened parts on trays. Directional vanes in the oil stream distribute the oil flow uniformly. Unit contains combined heating and cooling elements and provision for blanketing the surface of the oil with an inert gas atmosphere. Radiant tube is used for heating and cooling.

Quenchant Agitation

The agitation of a quenchant can be obtained in several ways. In conventional quench tanks, circulation of the quenching medium is usually provided by:

- Pumps
- Passage of the workpiece through the quenching medium
- Manual or mechanical movement of the workpiece
- Mechanical propellers

The selection of the agitation method is dependent on the tank design, type of quenchant, volume of quenchant, the part design, and the severity of quench required.

Pumps are commonly employed because they provide a controllable means for directing the quenchant. The quenchant flow can be diverted to provide circulation to more than one location in the tank. When the quenching medium is oil and a cooling system is employed, the pump is used to recirculate oil to the cooling system and provide agitation. Recirculating pumps with directed outlets may be preferred for use in a floating fountain quench that is capable of removing heat quickly from an internal cavity of a workpiece.

Movement of the Workpiece. On small, low-production items, agitation can be accomplished by moving the part or a small basket or tray of parts through the quenchant by hand. Workpieces may also be driven mechanically with respect to the quenching medium. For example, shafts are sometimes rotated in the quenching medium to produce the effect of agitation. Propeller or pump agitation is more desirable, however, because it is more controllable and less dependent on the operator.

Propellers are compact, require no piping, and can be easily removed for maintenance. Propellers must, however, be properly located in the quench tank to function effectively.

Propellers are usually placed near the bottom of the tank. A liquid accelerated by a propeller flows in a helical motion in the same direction as the rotation of the propeller blades. This high-velocity stream moves across the bottom of the tank and spreads as it moves from the propeller. Upon striking the opposite wall, the stream is diverted in the direction of propeller rotation. This produces a general rotation of the liquid in the tank, which is partially disrupted by the return of the liquid to the propeller.

Propeller agitators may be either top-entry or side-entry units, as indicated in Fig. 89 and 90. Side-entry units are usually placed below the floor level to conserve floor space. Top-entry units require more floor space but less excavation for installation.

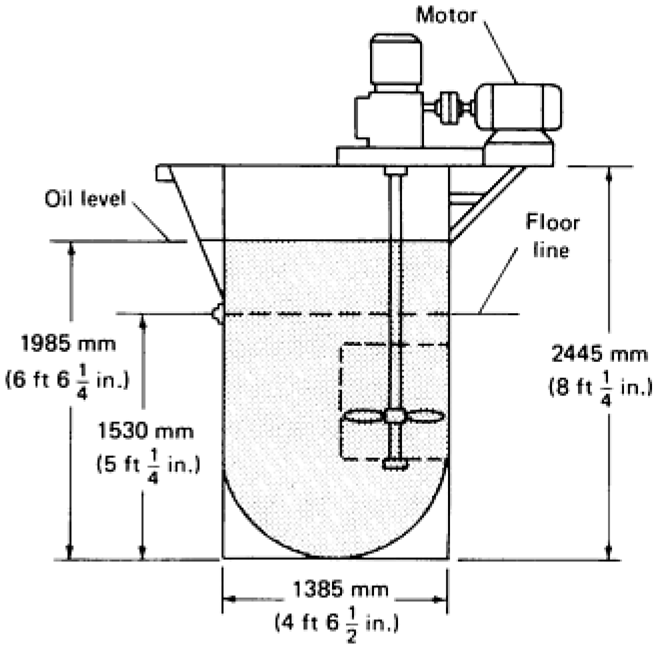


Fig. 89 Oil quenching tank with four top-entry propeller-type agitators used for quenching bar stock

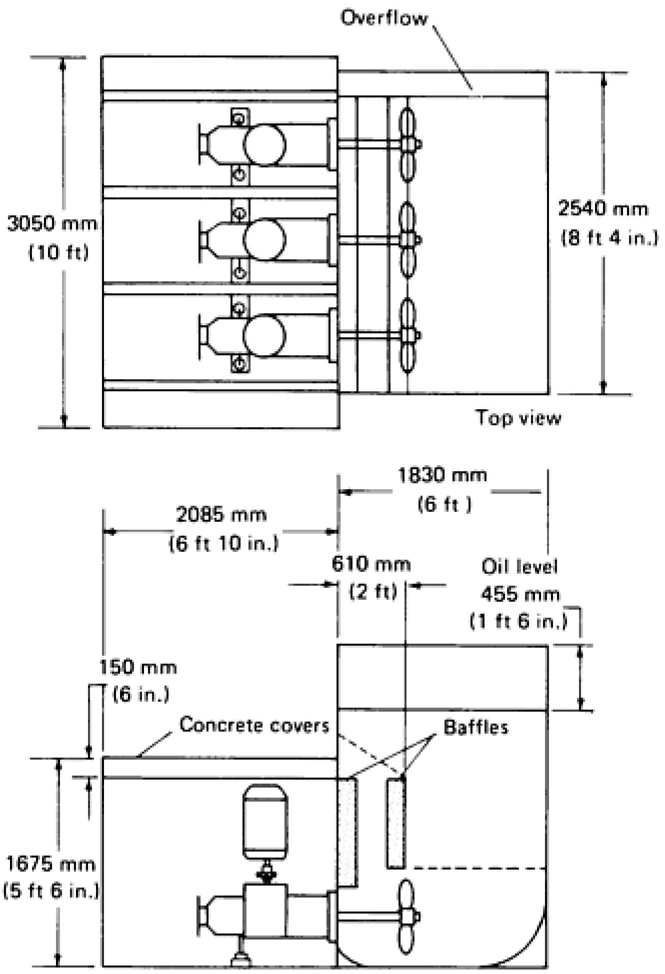


Fig. 90 Quench tank of 10 000-L (2600-gal) capacity with three propeller-type agitators entering from the side

The propeller horsepower is usually in the range of 0.6 to 1.0 kW/100 L (3 to 5 hp/100 gal) of quenchant. Horsepower estimates can be made from the data in Table 21. The volume of quenchant is typically about 8.3 L/kg (1 gal/lb) of steel. The power requirements in Table 21 are recommended minimums to produce a velocity of about 15 m/min (50 ft/min). Higher horsepower is required for higher quenchant flow velocities.

Table 21 Power requirements for propeller agitation of quenching liquids

		Power required for velocity of ≈15 m/min (≈50 ft/min)			
		Conventional oil		Water or brine	
L	gal	W/L	hp/gal	W/L	hp/gal
190-3000	50-800	0.985	0.005	0.788	0.004
3000-7600	800-2000	1.182	0.006	0.788	0.004

7600-11400	2000-3000	1.182	0.006	0.985	0.005
>11400	>3000	1.380	0.007	0.985	0.005

Once the horsepower of the motor used to drive the agitator is determined, the propeller diameter can then be determined from Table 22.

Table 22 Recommended propeller size as a function of motor power consumption

Power consumption[(a)]		**Minimum propeller diameter**[(b)]	
kW	**hp**	**mm**	**in.**
0.7	1	330	13
1.5	2	380	15
2.2	3	405	16
3.7	5	455	18
7.5	10	535	21
11	15	585	23
15	20	610	24
19	25	635	25

Source: Ref 59

(a) Motor speed, 1750 rev/min.

(b) Propeller speed, 420 rev/min.

Variables affecting agitation include oil velocity, agitator quantity, and relation of tank design to agitation sources.

Velocity. Tests have shown that quenching oil moving at a velocity of 23 m/min (75 ft/min) will increase the depth of hardening over that obtained at lesser velocities in sections up to 100 mm (4 in.) in diameter. In heavier sections, it is possible that no advantage can be gained by increasing agitation, because the rate of heat transfer from the core through the workpiece becomes the limiting factor. However, a practical upper limit on agitation is that which produces foaming on the surface of the quenchant. Foaming indicates that air is being entrapped and is undesirable.

Number of Agitators. The number of units required depends on the total horsepower required and the horsepower of available units. The sizing of the propellers for a system using multiple agitators is obtained by first determining the total horsepower required for the volume of the quenchant using Table 21. The horsepower per agitator is then (Ref 58):

$$hp_{agitator} = \frac{hp_{total}}{number \text{ of agotators}} \qquad \textbf{(Eq 24)}$$

The size of the propeller for each agitator is determined from Table 22.

Two or more smaller units provide more uniform agitation and more versatility than one large unit. The velocity of the quenchant can be varied by using two-speed motors or variable-pitch propellers or a combination of both devices.

Relation of Tank Design to Agitation. A properly designed tank and two or more propellers usually provide more uniform agitation throughout the working area. Sometimes baffles are required to direct the quenchant flow throughout the tank. On top-entry units, guide vanes are usually installed in the draft tube to prevent the quenchant from vortexing.

An oil quench tank used primarily for quenching bar stock is shown in Fig. 89. The four agitators develop a total of 75 kW (100 hp). Power consumption per unit volume of quenchant is 0.008 kW/L (0.04 hp/gal). The velocity is 60 m/min (200 ft/min), and the turnover is 113 500 L/min (30,000 gal/min). A similar tank holds 13 600 L (3600 gal) and has two 37 kW (50 hp) motors driving the propellers. The quenchant velocity is 110 m/min (360 ft/min) and the turnover of the quenchant is 196,000 L/min (51 800 gal/min); power consumption per unit volume of quenchant is 0.0055 kW/L (0.028 hp/gal).

A 10,100 L (2660 gal) oil quenching tank with three 19 kW (25 hp) side-entry agitators is shown in Fig. 90. This amounts to 0.00556 kW/L (0.0282 hp/gal) and produces a velocity of 20 m/min (66 ft/min), with a turnover of 51 100 L/min (13 500 gal/min).

The tanks illustrated in Fig. 89 and 90 are designed with baffles and curved bottoms to obtain uniform and smooth flow of oil. Baffles are used in the return path to direct the flow oil to the input side of the propeller with a minimum of turbulence.

With these design features, a higher-velocity flow or more general circulation can be obtained with a given input horsepower. Without these features, high agitation can spill the quenchant from the tank.

Factors Controlling Agitation. In all agitated quenching baths, the degree and character of the agitation varies from point to point within the bath. Although accurate measurements of velocity are difficult, the principal factors affecting velocity agitation are known. These include the shape of the bath, location of the work, direction of flow currents, type of agitator, flow rate, and power consumed. In spray or jet quenching, additional factors are encountered, such as the shape, arrangement, and placement of the spray head in relation to the work; the pressure, velocity, and size of the jets; and the total volume of quenching fluid used per unit of time.

Quenching velocities depend primarily on the mode of agitation. Very low velocities, not exceeding 0.9 m/s (3 ft/s), are encountered in immersion by gravity. Intermediate velocities, ranging from 1.1 to 1.8 m/s (3.5 to 6.0 ft/s), are achieved in hand quenching with an up-and-down, circular, or figure eight movement over 510 mm (20 in.) of travel. Spray quench rings are usually operated between 4.6 and 30 m/s (15 and 100 ft/s), but special applications sometimes use velocities as high as 150 m/s (500 ft/s).

Measurement of Quenchant Velocity

The Pitot tube is useful for measuring unidirectional velocity, such as that of a lamellar or jet stream, although it is not suitable for measuring turbulent (multi-directional) flow.

The tube can be constructed by drawing 6.4 mm ($\frac{1}{4}$ in.) glass tubing to an inside diameter of approximately 0.4 mm ($\frac{1}{64}$ in.) and grinding the drawn end flat and square with the tube axis. It may also be made of metal, provided the tube opening is knife-sharp and square with the axis of the tube. A suitable Bourdon gage or a manometer is connected by

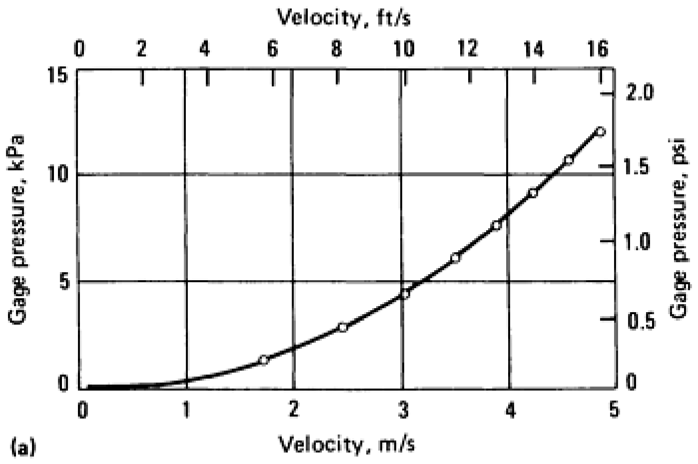
rubber or transparent plastic hose to the tube. If precise measurements are required, a correction must be made for the quenchant column height in excess of the level of the upper opening of the Pitot tube.

The axis of the Pitot tube must be accurately aligned parallel to, and in the center of, the stream being measured. Alignment is obtained by exploring the stream with the tube, and searching for the highest pressure reading. The velocity of the fluid as it strikes the tube is converted to a pressure head that is measured by the pressure gage. The pressure head, *h*, in feet of water, is converted into velocity, *v*, in feet per second, by the equation:

$$u = K.(2gh)^{\frac{1}{2}} \qquad \textbf{(Eq 25)}$$

where *K* is the Pitot tube constant (most often 1.0, or approximately unity); and *g* is the acceleration of gravity (980 cm/s^2 (32.2 ft/s^2).

The relationships are shown in the Pitot tube calibration charts in Fig. 91. Commercial instruments using immersible impellers with a magnetic pick up unit to provide direct readings of quenchant velocity are also available. These must also be rotated to find the maximum localized velocity similar to Pitot tubes.



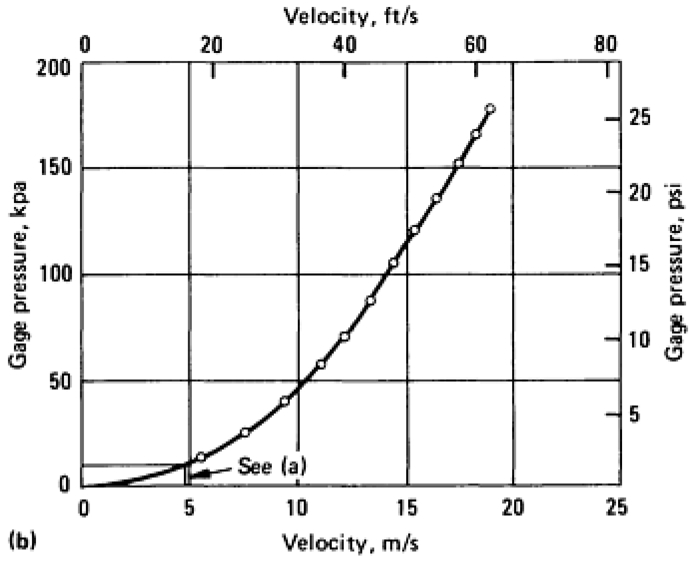


Fig. 91 Pitot tube calibration chart assuming a Pitot tube factor, *K*, of 1.0. Velocity equals *K* where *h* is the pressure head, in feet of water. (a) Low-velocity. (b) Full range

Turbulent agitation in a quenching bath takes the form of a multitude of swirling eddy currents. Turbulent agitation is desirable for uniform cooling of shapes that do not lend themselves to a complete washing of all surfaces with a lamellar or streamlined flow. A multitude of eddy currents will often cause sufficiently uniform average quenchant flow over irregular parts to produce adequate quenching.

Design of Quench Tanks

Quenching systems are integrated into heat-treating lines, and the automated lines are normally used to process many types of parts. It is seldom economically feasible to design a quench tank for only one type of part. One of the major goals of any design is to obtain as much flexibility in the quenching system as possible without appreciably affecting the cost of the unit.

The quench tank design is based primarily on such factors as the weight of steel to be quenched per hour, size of the part, part shape, weight, section thickness, grade of steel, and properties needed. A design based solely on the weight of metal treated per hour may produce unacceptable results.

Some practical suggestions for the design of quench tanks are as follows:

- The time required to quench out parts should be measured, and the desired part throughput per hour should be determined. From this information, the size of the quench tank and enclosure can be determined. The volume of quench medium and throughput is then used to select the size of the cooler and to determine whether a storage tank is necessary
- Adequate space should be provided around the workpiece to obtain quenchant circulation and maximum heat removal rate from quenched parts
- Hot and plastic workpieces should not be allowed to impact on a chute or conveyor until they have fallen through sufficient quenchant to produce a high-strength surface on the part
- The work tank should be accessible for maintenance and cleaning
- Provision for scale removal from the tank must be made for parts heated in air. The use of a controlled atmosphere furnace can be used to eliminate scaling
- Adequate ventilation should be provided to protect workmen from fumes
- Protection against fires should be provided when using oil quenchants
- Clean-out plates below the quenchant level in tank should be avoided because gaskets are prone to leakage and are difficult to maintain
- Special materials of construction are required for systems using brine or caustic solutions that usually result in a higher maintenance cost
- Alloy trays and fixtures of the 25Cr-12Ni or 35Ni-15Cr type can be quenched in oil quite satisfactorily, but not in water, caustic, or brine
- Wherever possible, the design of the work tank should provide for flexibility and control of such conditions as time cycle of quench, volume of circulation, and uniformity of bath conditions
- Excessive agitation can blow light parts off of conveyors
- A quenching bath should not be agitated so violently that foaming occurs on the bath surface. This entrained air reduces the heat transfer rate and the foaming of oils could lead to fires

Fixtures are widely used to minimize distortion during quenching. Fixtures vary in design from simple trays or racks to complex compartmented baskets and special holders. Distortion of shafts is minimized if they are hung or supported vertically during heating and quenching. Circular parts, such as rings, may be supported on flat surfaces during heating but quenching on the flat surface may result in nonuniform hardness, because quenchant flow may be restricted by the support surface. A preferred practice is to support such members on fixtures with ribs to permit flow of the quenchant around the part.

Distortion of thin-wall circular members is sometimes corrected by inserting pins inside the ring to force concentricity during tempering. The pins may be a part of an adjustable turnbuckle assembly.

Restraint fixtures are costly. Examples of parts requiring restraint during heating and quenching include rocket and missile casings and other large components with thin-wall sections. For such components, two or more external restraining bands may be used along with an articulated internal fixture. The internal fixture may be built up of cast or stamped pieces pinned to provide points of support and a free flow of quenchant to the inner surface of the workpiece. Articulated fixtures can accommodate workpieces of various diameters and lengths. The whole assembly is usually hung in the furnace and lowered into the quench tank.

Cooling Systems. As quenching proceeds, heat is removed from the workpieces and the temperature of the quenching medium rises. Uniform results in the hardening operation depend in part on the control of quenchant temperature. Accordingly, coolers (and sometimes heaters) are required to achieve temperature control. A typical oil-cooling system is shown schematically in Fig. 92.

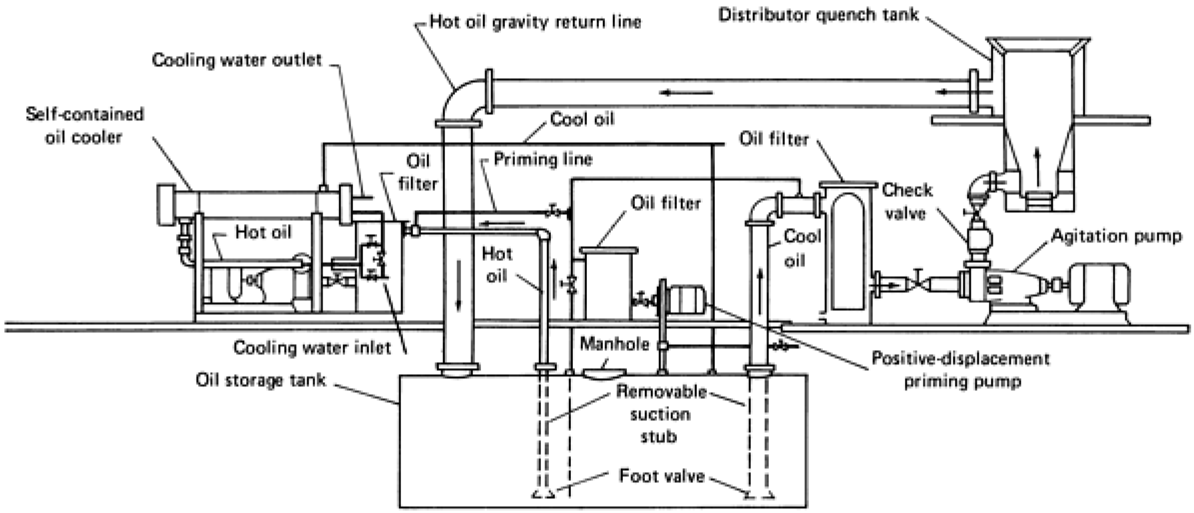


Fig. 92 Typical oil-cooling system employing an underground storage tank

Many types of heat exchangers are used for cooling quenching liquids, and each offers certain advantages. The rate of heat transfer through the cooling unit depends on the velocity of the cooling medium passing through it. As the velocity of the cooling medium increases, the rate of heat transfer increases up to the maximum flow rate capacity of the exchanger. Therefore, the efficiency of the cooling unit depends on an adequate pumping facility.

The maintenance of cooling equipment is also related to its design. If the cooling unit is capable of maintaining a uniform quenchant temperature, the possibility of fouling is minimized. To facilitate maintenance, cooling equipment should be designed for easy cleaning.

The shell-and-tube heat exchangers consist of a series of copper or steel tubes enclosed in a steel shell. The quenching liquid is circulated through either the tube section or the shell section, with the remaining section reserved for the coolant. Water is a commonly used coolant. With larger heat loads, an evaporative water-cooling unit may be employed to conserve water.

In general, disposable water is used when the total quenching load is less than about 910 kg/h (2000 lb/h). However, the use of disposable water depends on the water-consumption costs compared to the initial and operating costs of the evaporative unit. Usually, evaporative units do not provide water at as low a temperature as can be expected from well water or city water.

The shell-and-tube heat exchanger requires little maintenance, but when properly designed, the tubes can be removed for cleaning if necessary.

Maintenance costs are related to the number of mechanical units involved. Pumps are essential for quenchant circulation, and in some types of towers, motor-driven fans are required for air circulation.

Selection of Cooling System. To select a cooling system for the quenching circuit, the maximum heat load demand must be determined from the following data:

- Weight of steel quenched during a specified period
- Specific heat of steel and quench trays or fixtures
- Temperature of steel entering the quench
- Temperature of steel leaving the quench
- Temperature of quenching liquid entering the work tank
- Temperature of quenching liquid leaving the work tank
- Characteristics of the quenching medium such as specific heat, specific gravity, viscosity, flash point,

boiling point, and point of vaporization of toxic solutions

The proper cooling equipment can be selected for the quenching system from the above data and associated cost information.

Storage and Supply Tanks. Experience has indicated that the rise in temperature of the quenchant should be maintained within as narrow a range as possible--preferably within 5 °C (10 °F) during quenching. This requires a substantial volume of quenchant to limit the temperature rise in the quench tank. The volume can be supplied by an auxiliary storage tank. In addition to providing sufficient quenching liquid, the storage tank is an economical means of linking equipment such as pumps, coolers, heaters, and filters.

The storage tank design depends on individual requirements and conditions. The tank should be of the closed type and sufficiently large to supply the necessary quench capacity when about three-quarters full. The tank should be equipped with one or more manhole covers and appropriate openings for connections with quench tanks. The ends of the tank should have capped valve outlets, a sight gage, and a drain valve.

There are advantages in having tanks above the floor in a ventilated basement room with sufficient space to house pumps, coolers, filters, and other required equipment. This permits gravity feed of the quenchant to the pumps, eliminates the possibility of loss of pump prime, and allows insulation of the storage tank to minimize heat loss where temperature control is desirable. However, underground storage tanks require less space. The oil-cooling system illustrated in Fig. 92 employs an underground storage tank.

Heaters. Storage tanks containing water or brine may be heated economically by steam, hot water pipes, or radiant tubes in the tanks. The optimum storage temperature range for water or brine is 13 to 25 °C (55 to 75 °F). For oil storage tanks (or quenching tanks), the preferred temperature range is about 50 to 70 °C (120 to 160 °F), depending upon the type of quenching oil. When steam or hot water is used for heating quenching oils, there is some danger of contamination that can change the quenching characteristics of the oils, cause foaming, and create danger of explosion.

When fuel-fired radiant tubes are used they should burn deep in the tube well below the height of the quenching liquid. The products of combustion must be well vented.

Immersion-type electrical heating elements also are used for heating the oil in either quenching or storage tanks. A choice between immersion electric heaters and radiant-tube burners is a matter of economics and convenience.

Pumps are installed to maintain a quenchant flow through the quenchant bath and the heat exchanger. The flow is usually continuous and of sufficient mass to maintain the bath temperature in the desired range. Additional pumps or impellers may be installed in the quench tank to achieve agitation around the parts.

Centrifugal pumps are used wherever possible, because wear is minimized and the initial cost usually is lower. However, where a storage tank is employed, it may be necessary to raise the oil from the storage tank to the quenching tank.

Because a centrifugal pump is not self-priming, a small positive-displacement pump may be installed to ensure priming. The priming pump is often a positive-displacement pump that may be used both for continuous circulation and priming.

It is usually feasible to connect the pump such that it can be used for emptying or filling quenching tanks by opening and closing appropriate valves. Valves should also be installed to simplify pump repair.

Centrifugal pumps are not designed for great suction-lift operation and should be installed as near the quenchant supply as possible. Consideration should be given to the pipe flow resistance so the pump can be properly sized. If the pipe resistance is too high the pump motor may become overloaded.

Maintenance of Quenching Installations

Because quenching baths vary widely in design, shape, size, and method of operation, it is not feasible to establish universal procedures for maintenance. However, typical schedules for maintaining large oil, water, and brine quenching installations are outlined in Table 23.

Table 23 Recommended maintenance schedules for water, brine, and oil quenching systems

Quenchant	Maintenance schedule			
	Daily	Weekly	Monthly	Semiannually
Water	Check water temperature	Drain quench tanks and remove sludge	. . .	. . .
	Check water pressure	If water is recirculated, make necessary chemical addition(s) to prevent calcium compound buildup in tubes		
	Check water circulation			
Brine	Check brine temperature	Drain tanks and remove sludge	. . .	. . .
	Check brine concentration and adjust as required	Check pumps and tank condition		
		Check quenching fixtures for signs of deterioration		
Oil	Check oil level in quench tanks	Check quenching rate of oil in production system	Drain quench tanks and remove sludge	Check heat exchanger coils. pipes, and pumps Replace oil filters when necessary Check screens ahead of oil filter
	Check oil temperature			
	Check oil filter pressure	If oil filters are not included in oil system, check for solids in oil		
	Check operation of oil pumps and oil flow	Check oil temperature controller and control setting		Check oil storage tank for sludge, water leaks, and general condition Calibrate oil-temperature gage Check oil for

Safety Precautions

Fire hazards always attend the use of quenching oils. The causes of quenching-oil fires and the methods of extinguishing them should be thoroughly understood.

One of the most common causes of fire in open quench tanks--and one of which operating personnel should be made aware--is ignition of the oil surface from a partially submerged load. Some aids to the prevention of such fires are:

- Careful design of hoists or conveyors used to lower the work load into the quench
- Periodic inspection of chains, sprockets, and other components that may fail
- Having an alternate power supply in the event a power failure occurs during a quenching cycle
- The ignition of oil overflowing from a tank can produce a most damaging type of fire

When an oil quench tank is located adjacent to a furnace or other ignition source, special precautions are required, such as:

- Providing drains inside quench tanks to prevent overfilling and providing external drains to prevent the spread of burning oil
- Providing a system for detecting water in the oil (several detectors are commercially available)
- If the oil temperature approaches 120 °C (250 °F) with water present, foaming can result in an overflow of oil that exceeds the drain capacity

A third hazard arises when oil is heated by the work load to a temperature above its flash point. An oil bath temperature less than 30 °C (50 °F) below the flash point is considered dangerous. To minimize the temperature rise, several methods may be employed, including the use of:

- Cooling coils in the tanks
- External heat exchangers
- A larger tank
- Oil with a higher flash point

Extinguishing Oil Fires. A planned program for extinguishing quenching-oil fires should include:

- A quick method of extinguishing the fire without contaminating the oil, such as by smothering it with a cover or using carbon dioxide extinguishers
- Auxiliary methods, including foam or dry chemical extinguishers, or draining the tank
- Training of personnel in fire prevention and fire extinguishing

Tank covers or lids can be used effectively to smother a fire in a small tank. These covers can be actuated by heat or, from a safe distance, manually.

Carbon Dioxide Extinguishers. There are two general types of carbon dioxide systems: high-pressure systems, where the gas is stored at room temperature; and low-pressure systems, where the gas is refrigerated to -20 °C (0 °F).

The effectiveness of carbon dioxide is primarily a result of its ability to reduce the supply of oxygen at the surface of the oil to the point where combustion is not sustained. In some systems, carbon dioxide has a cooling effect as it sublimes from a solid snow to a gas.

The advantage of carbon dioxide is that it does not contaminate the quenching oil or require cleanup. Disadvantages are the short duration of the protection afforded and the storage costs for a large installation.

Fire-fighting foams are composed of fine, heat-resisting bubbles. The foam smothers the fire by floating on the oil and setting up into a protective blanket. There are two general types of foam: chemical and mechanical (or air). Both foam types are equally effective.

An advantage of foam is that it provides protection for an extended time. When a quench load has only been partially submerged, or when the fire has heated surrounding metal, the protection must last until these sources of reignition are eliminated. Some disadvantages of mechanical foams are the costs, and the possible oil contamination.

Dry chemical extinguishers use mainly sodium bicarbonate discharged through heads with high-pressure nitrogen. The extinguishing action, advantages, and disadvantages are similar to those of mechanical foams.

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Tempering of Steel

Revised by Michael Wisti and Mandar Hingwe, Atmosphere Annealing, Inc.

Introduction

TEMPERING OF STEEL is a process in which previously hardened or normalized steel is usually heated to a temperature below the lower critical temperature and cooled at a suitable rate, primarily to increase ductility and toughness, but also to increase the grain size of the matrix. Steels are tempered by reheating after hardening to obtain specific values of mechanical properties and also to relieve quenching stresses and to ensure dimensional stability. Tempering usually follows quenching from above the upper critical temperature; however, tempering is also used to relieve the stresses and reduce the hardness developed during welding and to relieve stresses induced by forming and machining.

Principal Variables

Variables associated with tempering that affect the microstructure and the mechanical properties of a tempered steel include:

- Tempering temperature
- Time at temperature
- Cooling rate from the tempering temperature
- Composition of the steel, including carbon content, alloy content, and residual elements

In a steel quenched to a microstructure consisting essentially of martensite, the iron lattice is strained by the carbon atoms, producing the high hardness of quenched steels. Upon heating, the carbon atoms diffuse and react in a series of distinct steps that eventually form Fe_3C or an alloy carbide in a ferrite matrix of gradually decreasing stress level. The properties of the tempered steel are primarily determined by the size, shape, composition, and distribution of the carbides that form, with a relatively minor contribution from solid-solution hardening of the ferrite. These changes in microstructure usually decrease hardness, tensile strength, and yield strength but increase ductility and toughness.

Under certain conditions, hardness may remain unaffected by tempering or may even be increased as a result of it. For example, tempering a hardened steel at very low tempering temperatures may cause no change in hardness but may achieve a desired increase in yield strength. Also, those alloy steels that contain one or more of the carbide-forming elements (chromium, molybdenum, vanadium, and tungsten) are capable of secondary hardening; that is, they may become somewhat harder as a result of tempering.

The tempered hardness values for several quenched steels are presented in Table 1. Temperature and time are interdependent variables in the tempering process. Within limits, lowering temperature and increasing time can usually produce the same result as raising temperature and decreasing time. However, minor temperature changes have a far greater effect than minor time changes in typical tempering operations. This is discussed in more detail in the section "Tempering Time." With few exceptions, tempering is done at temperatures between 175 and 705 °C (350 and 1300 °F) and for times from 30 min to 4 h.

Table 1 Typical hardnesses of various carbon and alloy steels after tempering

Grade	Carbon content, %	Hardness, HRC, after tempering for 2 h at									Heat treatment
		205	260	315	370	425	480	540	595	650	

		°C (400 °F)	**°C (500 °F)**	**°C (600 °F)**	**°C (700 °F)**	**°C (800 °F)**	**°C (900 °F)**	**°C (1000 °F)**	**°C (1100 °F)**	**°C (1200 °F)**	
Carbon steels, water hardening											
1030	0.30	50	45	43	39	31	28	25	22	95[a]	Normalized at 900 °C (1650 °F) water quenched from 830-845 °C (1525-1550 °F); average dew point, 16 °C (60 °F)
1040	0.40	51	48	46	42	37	30	27	22	94[a]	
1050	0.50	52	50	46	44	40	37	31	29	22	
1060	0.60	56	55	50	42	38	37	35	33	26	Normalized at 885 °C (1625 °F) water quenched from 800-815 °C (1475-1550 °F); average dew point, 7 °C (45 °F)
1080	0.80	57	55	50	43	41	40	39	38	32	
1095	0.95	58	57	52	47	43	42	41	40	33	
1137	0.40	44	42	40	37	33	30	27	21	91[a]	Normalized at 900 °C (1650 °F) water quenched from 830-855 °C (1525-1575 °F); average dew point, 13 °C (55 °F)
1141	0.40	49	46	43	41	38	34	28	23	94[a]	
1144	0.40	55	50	47	45	39	32	29	25	97[a]	
Alloy steels, water hardening											
1330	0.30	47	44	42	38	35	32	26	22	16	Normalized at 900 °C (1650 °F), water quenched from 800-815 °C (1475-1500 °F); average dew point, 16 °C (60 °F)
2330	0.30	47	44	42	38	35	32	26	22	16	
3130	0.30	47	44	42	38	35	32	26	22	16	
4130	0.30	47	45	43	42	38	34	32	26	22	Normalized at 885 °C (1625 °F), water quenched from 800-855 °C (1475-1575 °F); average dew point, 16 °C (60 °F)
5130	0.30	47	45	43	42	38	34	32	26	22	
8630	0.30	47	45	43	42	38	34	32	26	22	
Alloy steels, oil hardening											
1340	0.40	57	53	50	46	44	41	38	35	31	Normalized at 870 °C (1600 °F), oil quenched from 830-845 °C (1525-

3140	0.40	55	52	49	47	41	37	33	30	26	1550 °F); average dew point, 16 °C (60 °F)
4140	0.40	57	53	50	47	45	41	36	33	29	
4340	0.40	55	52	50	48	45	42	39	34	31	Normalized at 870 °C (1600 °F), oil quenched from 830-845 °C (1525-1575 °F); average dew point, 13 °C (55 °F)
4640	0.40	52	51	50	47	42	40	37	31	27	
8740	0.40	57	53	50	47	44	41	38	35	22	
4150	0.50	56	55	53	51	47	46	43	39	35	Normalized at 870 °C (1600 °F), oil quenched from 830-870 °C (1525-1600 °F); average dew point, 13 °C (55 °F)
5150	0.50	57	55	52	49	45	39	34	31	28	
6150	0.50	58	57	53	50	46	42	40	36	31	
8650	0.50	55	54	52	49	45	41	37	32	28	Normalized at 870 °C (1600 °F), oil quenched from 815-845 °C (1500-1550 °F); average dew point, 13 °C (55 °F)
8750	0.50	56	55	52	51	46	44	39	34	32	
9850	0.50	54	53	51	48	45	41	36	33	30	

Data were obtained on 25 mm (1 in.) bars adequately quenched to develop full hardness.

(a) Hardness. HRB

Structural Changes. Based on x-ray, dilatometric, and microstructural studies, there are three distinct stages of tempering, even though the temperature ranges overlap (Ref 1, 2, 3, 4):

- Stage I: The formation of transition carbides and lowering of the carbon content of the martensite to 0.25% (100 to 250 °C, or 210 to 480 °F)
- Stage II: The transformation of retained austenite to ferrite and cementite (200 to 300 °C, or 390 to 570 °F)
- Stage III: The replacement of transition carbides and low-temperature martensite by cementite and ferrite (250 to 350 °C, or 480 to 660 °F)

An additional stage of tempering (stage IV), precipitation of finely dispersed alloy carbides, exists for high-alloy steels. It has been found that stage I of tempering is often preceded by the redistribution of carbon atoms, called autotempering or quench tempering, during quenching and/or holding at room temperature (Ref 5). Other structural changes take place because of carbon atom rearrangement preceding the classical stage I of tempering (Ref 6, 7).

Dimensional Changes. Martensite transformation is associated with an increase in volume. During tempering, martensite decomposes into a mixture of ferrite and cementite with a resultant decrease in volume as tempering temperature increases. Because a 100% martensitic structure after quenching cannot always be assumed, volume may not continuously decrease with increasing tempering temperature.

The retained austenite in plain carbon steels and low-alloy steels transforms to bainite with an increase in volume, in stage II of tempering. When certain alloy steels are tempered, a precipitation of finely distributed alloy carbides occurs, along with an increase in hardness, called secondary hardness, and an increase in volume. With the precipitation of alloy carbides, the M_s temperature (temperature at which martensite starts to form from austenite upon cooling) of the retained austenite will increase and transform to martensite during cooling from the tempering temperature.

Example 1: Effect of Hardening and Tempering on the Dimensions of O1 Tool Steel Plates.

Steel plates made from O1 tool steel were hardened from two different hardening temperatures and two different soak times. The dimensional changes, after cooling to ambient temperature, are shown in Fig. 1 for tempering temperatures up to 400 °C (750 °F). The variation of 40 °C (70 °F) and 10 min has a negligible effect on dimensional changes. Tempering up to 200 °C (390 °F) is accompanied by a slight contraction in all directions of the plate. At a higher tempering temperature, there is an increase in the dimensions, with a maximum increase at 300 °C (570 °F), after which dimensions again decrease. The increased volume at 300 °C (570 °F) is attributed to the transformation of retained austenite to bainite. At 400 °C (750 °F), the dimensions revert to values closer to the original values, prior to quenching and tempering.

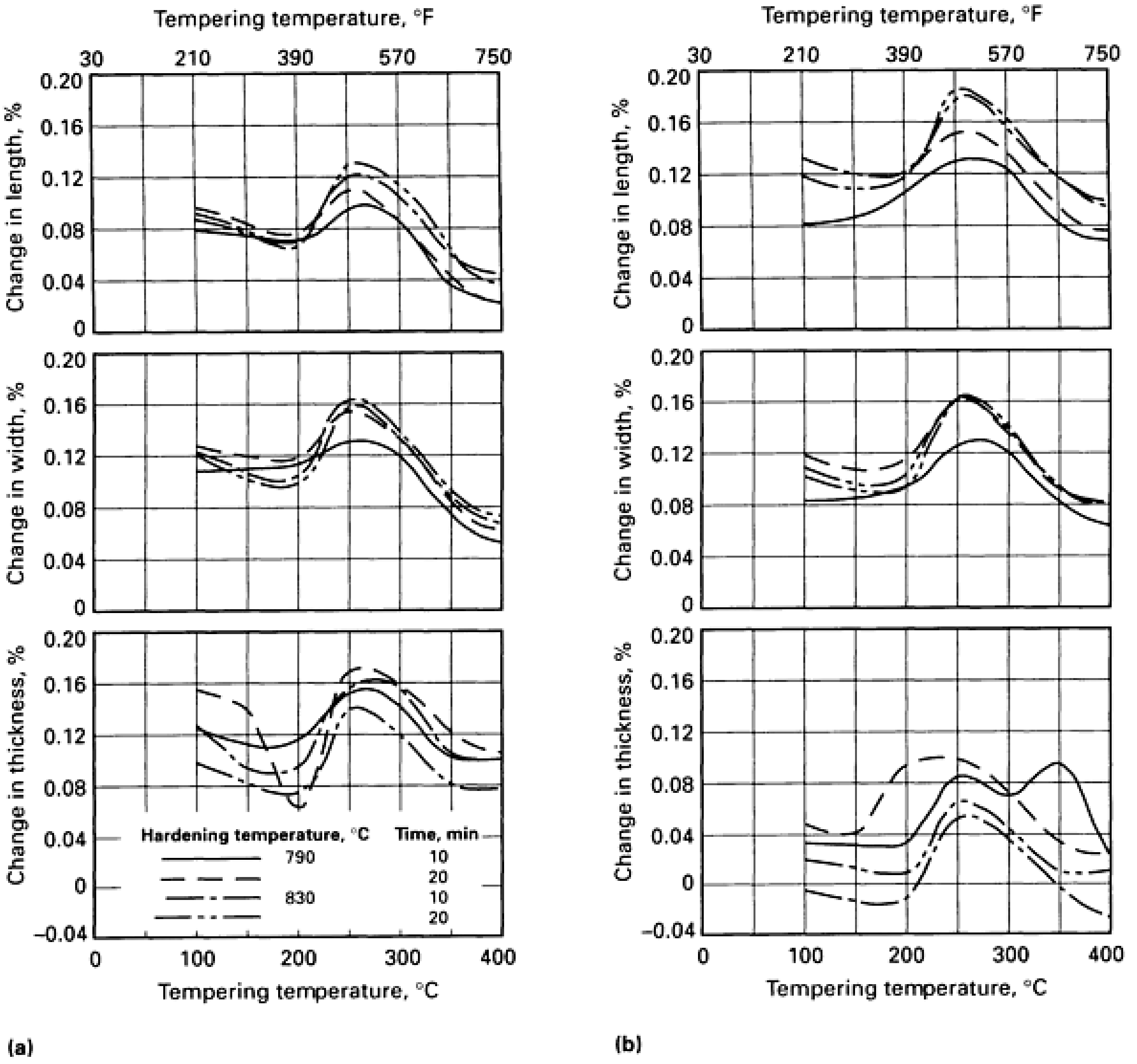

Fig. 1 Dimensional changes that occur in O1 tool steel (Bofors RT 1733) when heat treated at two hardening temperatures and two soak times using two tempering methods, (a) oil quenching, and (b) martempering. Specimen dimensions were 100 × 50 × 18 mm (4 × 2 × 0.7 in.). Steel was rolled in the longitudinal direction.

Source: Ref 8

Tempering Temperature. Several empirical relationships have been made between the tensile strength and hardness of tempered steels such that the measurement of hardness is commonly used to evaluate the response of a steel to tempering. Figure 2 shows the effect of tempering temperature on hardness, tensile and yield strengths, elongation, and reduction in area of a plain carbon steel (AISI 1050) held at temperature for 1 h. It can be seen that both room-temperature hardness and strength decrease as the tempering temperature is increased. Ductility at ambient temperatures, measured by either elongation or reduction in area, increases with tempering temperature.

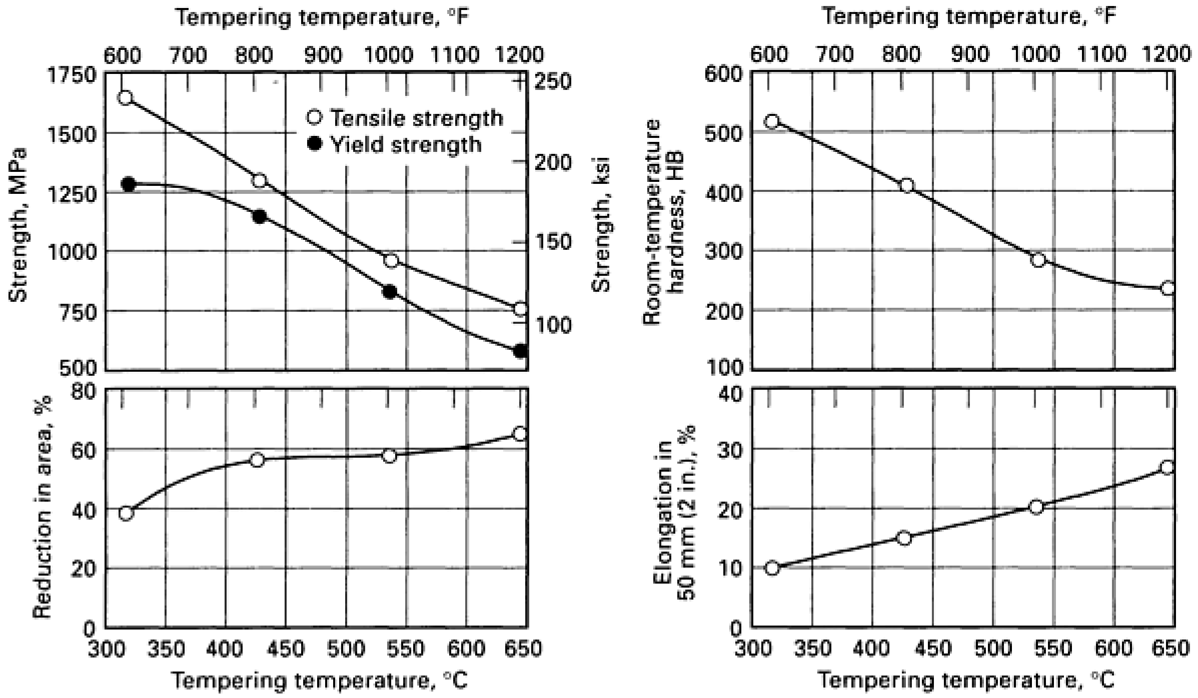

Fig. 2 Effect of tempering temperature on room-temperature mechanical properties of 1050 steel. Properties summarized are for one heat of 1050 steel that was forged to 38 mm (1.50 in.) in diameter, then water quenched and tempered at various temperatures. Composition of heat: 0.52% C, 0.93% Mn

Most medium-alloy steels exhibit a response to tempering similar to that of carbon steels. The change in mechanical properties with tempering temperature for 4340 steel is shown in Fig. 3.

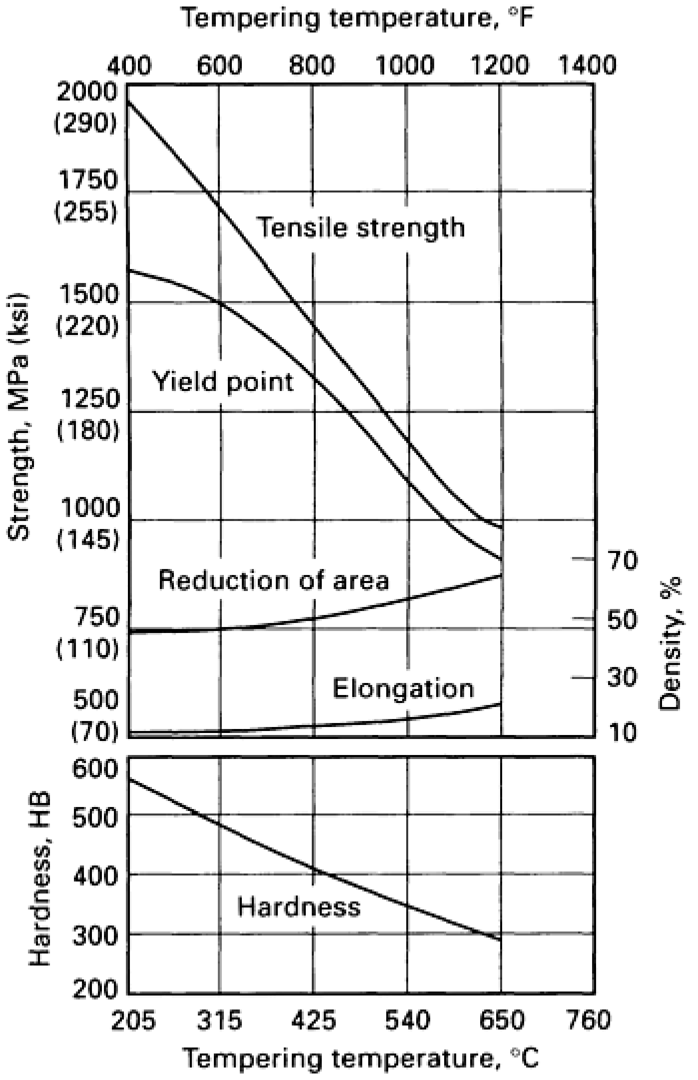

Fig. 3 Effect of tempering temperature on the mechanical properties of oil-quenched 4340 steel bar. Single-heat results: ladle composition, 0.41% C, 0.67% Mn, 0.023% P, 0.018% S, 0.26% Si, 1.77% Ni, 0.78% Cr, 0.26% Mo; grain size, ASTM 6 to 8; critical points, Ac_1, 730 °C (1350 °F); Ac_3, 770 °C (1415 °F); Ar_3, 475 °C (890 °F); Ar_1, 380 °C (720 °F); treatment, normalized at 870 °C (1600 °F), reheated to 800 °C (1475 °F), quenched in agitated oil; cross section, 13.46 mm (0.530 in.) diam; round treated, 12.83 mm (505 in.) diam; round tested; as-quenched hardness, 601 HB. Source: Ref 9

There is no decrease in ductility in the temperature range of tempered martensite embrittlement, or TME (also known as 500 °F embrittlement or one-step temper embrittlement) because the tensile tests are performed on smooth, round specimens at relatively low strain rates. However, in impact loading, catastrophic failure may result when alloy steel is tempered in the tempered martensite embrittlement range (260 to 370 °C, or 500 to 700 °F). Additional information is available in the article "Embrittlement of Steels" in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.*

Whereas elongation and reduction in area increase continuously with tempering temperature, toughness, as measured by a notched-bar impact test, varies with tempering temperature for most steels, as shown in Fig. 4. Tempering at temperatures from 260 to 320 °C (500 to 610 °F) decreases impact energy to a value below that obtained at about 150 °C (300 °F). Above 320 °C (610 °F), impact energy again increases with increasing tempering temperature. Both plain carbon and alloy steels respond to tempering in this manner. The phenomenon of impact energy minima centered around 300 °C (570 °F) is called tempered martensite embrittlement (TME) or 500 °F embrittlement.

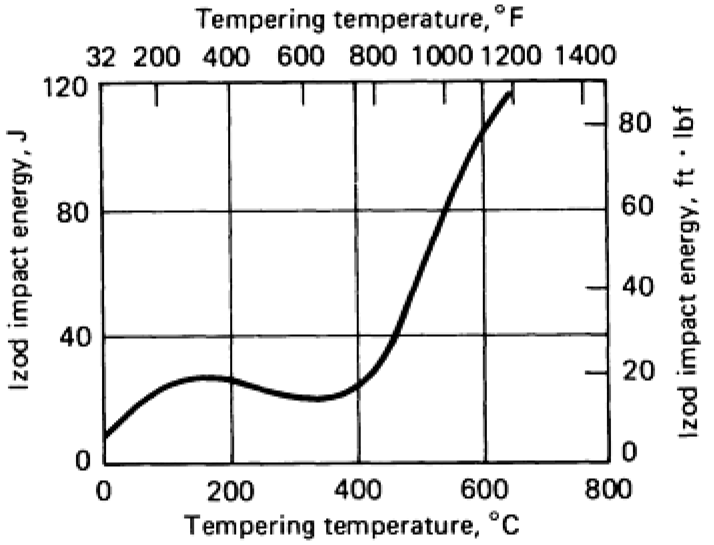

Fig. 4 Notch toughness as a function of tempering temperature for 4140 (UNS G41400) ultrahigh-strength steel tempered 1 h

Tempering Time. The diffusion of carbon and alloying elements necessary for the formation of carbides is temperature and time dependent. The effect of tempering time on the hardness of a 0.82% C steel tempered at various temperatures is shown in Fig. 5. The changes in hardness are approximately linear over a large portion of the time range when the time is presented on a logarithmic scale. Rapid changes in room-temperature hardness occur at the start of tempering in times less than 10 s. Less rapid, but still large, changes in hardness occur in times from 1 to 10 min, and smaller changes occur in times from 1 to 2 h. For consistency and less dependency on variations in time, components generally are tempered for 1 to 2 h. The levels of hardness produced by very short tempering cycles, such as in induction tempering, would be quite sensitive to both the temperature achieved and the time at temperature.

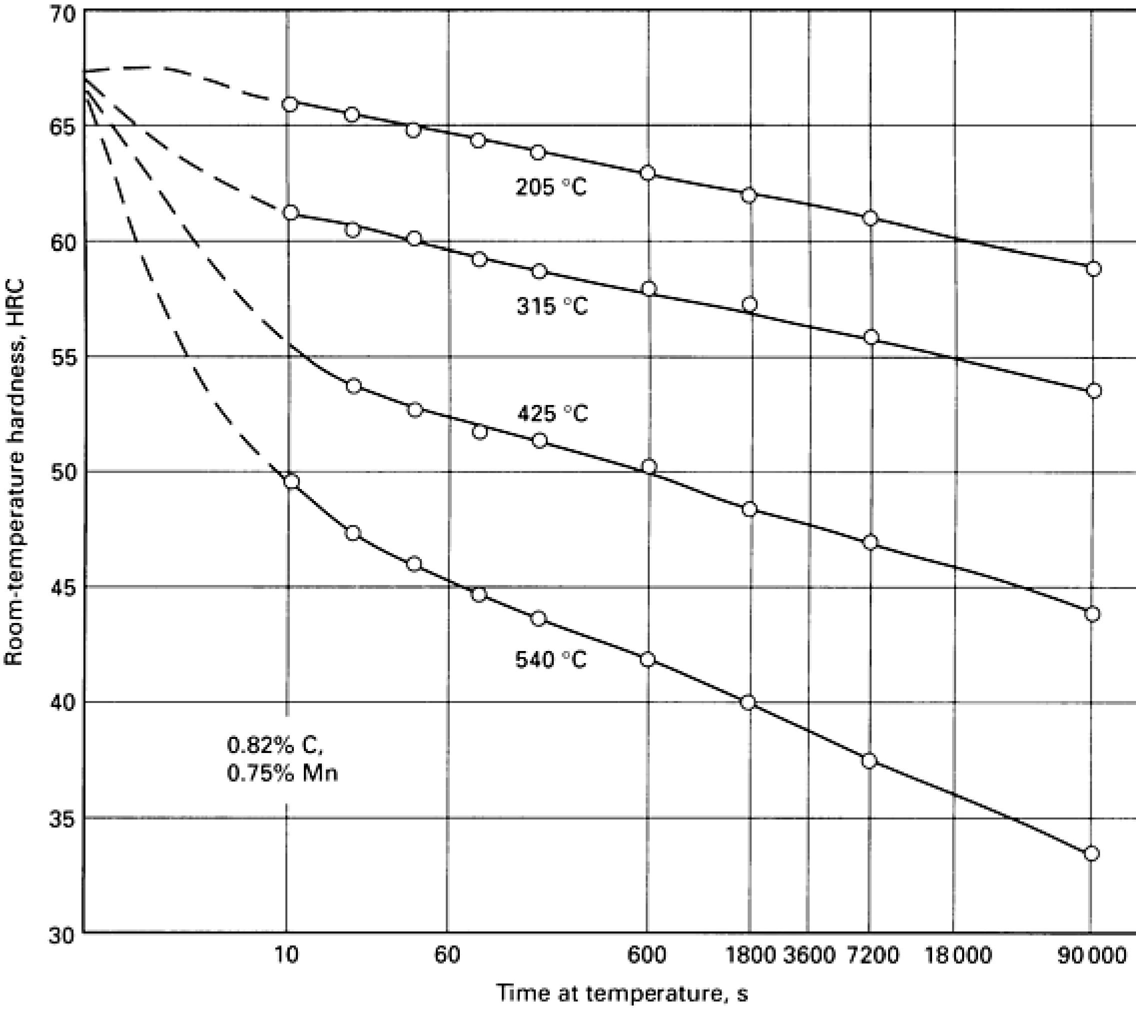

Fig. 5 Effect of time at four tempering temperatures on room-temperature hardness of quenched 0.82% C steel. Note nearly straight lines on logarithmic time scale. Source: Ref 10

By the use of an empirical tempering parameter developed by Holloman and Jaffe (Ref 11), the approximate hardnesses of quenched and tempered low- and medium-alloy steels can be predicted. The parameter is T (c + log t), where T is temperature in degrees Kelvin, t is time in seconds, and c is a constant that depends on the carbon content of the steel. Reasonably good correlations are obtained except when significant amounts of retained austenite are present.

Cooling Rate. Another factor that can affect the properties of a steel is the cooling rate from the tempering temperature. Although tensile properties are not affected by cooling rate, toughness (as measured by notched-bar impact testing) can be decreased if the steel is cooled slowly through the temperature range from 375 to 575 °C (705 to 1065 °F), especially in steels that contain carbide-forming elements. Elongation and reduction in area may be affected also. This phenomenon is called temper embrittlement and is discussed in the section "Temper Embrittlement" in this article. Additional information is available in the article "Embrittlement of Steels" in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.*

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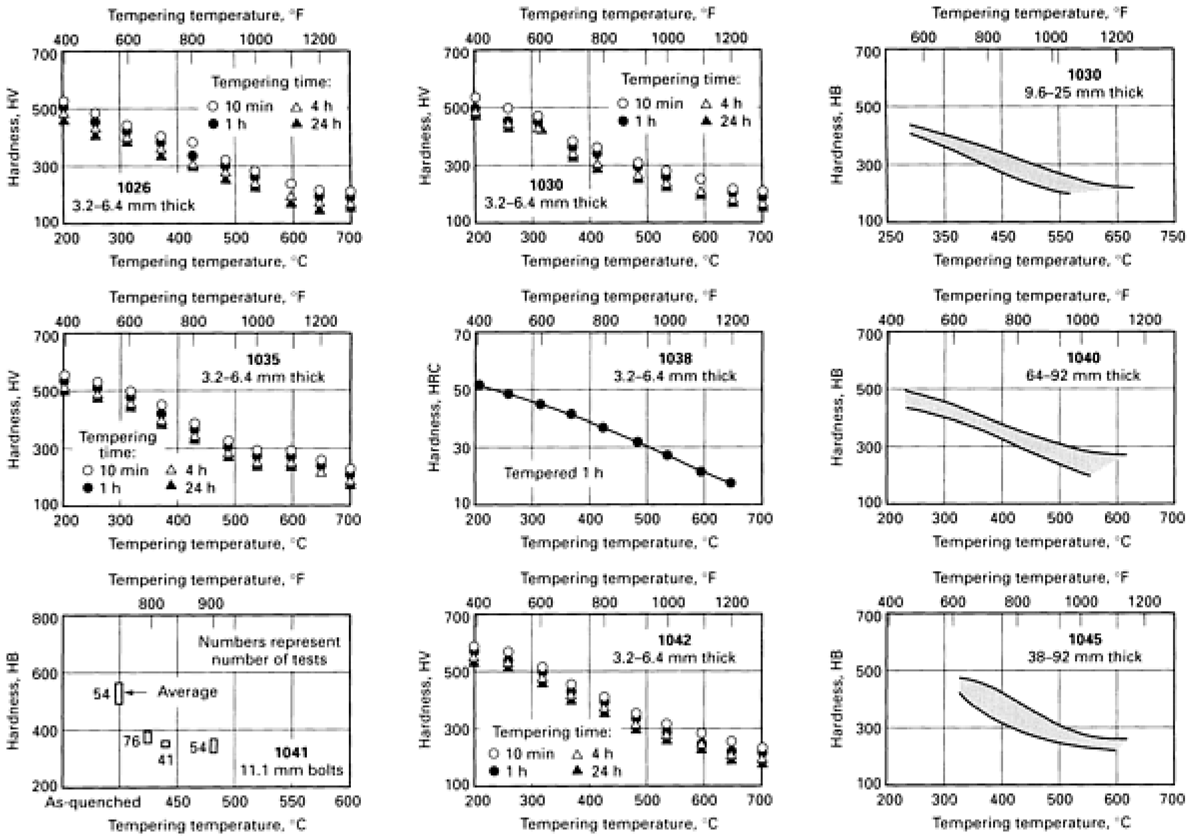
Carbon Content

The effect of carbon content on the properties of tempered steels is shown in Fig. 6, which presents hardness data for 14 carbon steels that were tempered at temperatures ranging from 205 to 705 °C (400 to 1300 °F) and for times from 10 min to 24 h. The principal effect of carbon content is on as-quenched hardness. Figure 7 shows the relationship between carbon content and the maximum hardness that can be obtained upon quenching. The relative difference in hardness compared with as-quenched hardness is retained after tempering. Figure 8 shows the combined effect of time, temperature, and carbon content on the hardness of three carbon-molybdenum steels of different carbon contents. Figure 9 shows the hardness of these steels after tempering for 1 h, as a function of tempering temperature. The effect of carbon content is evident.



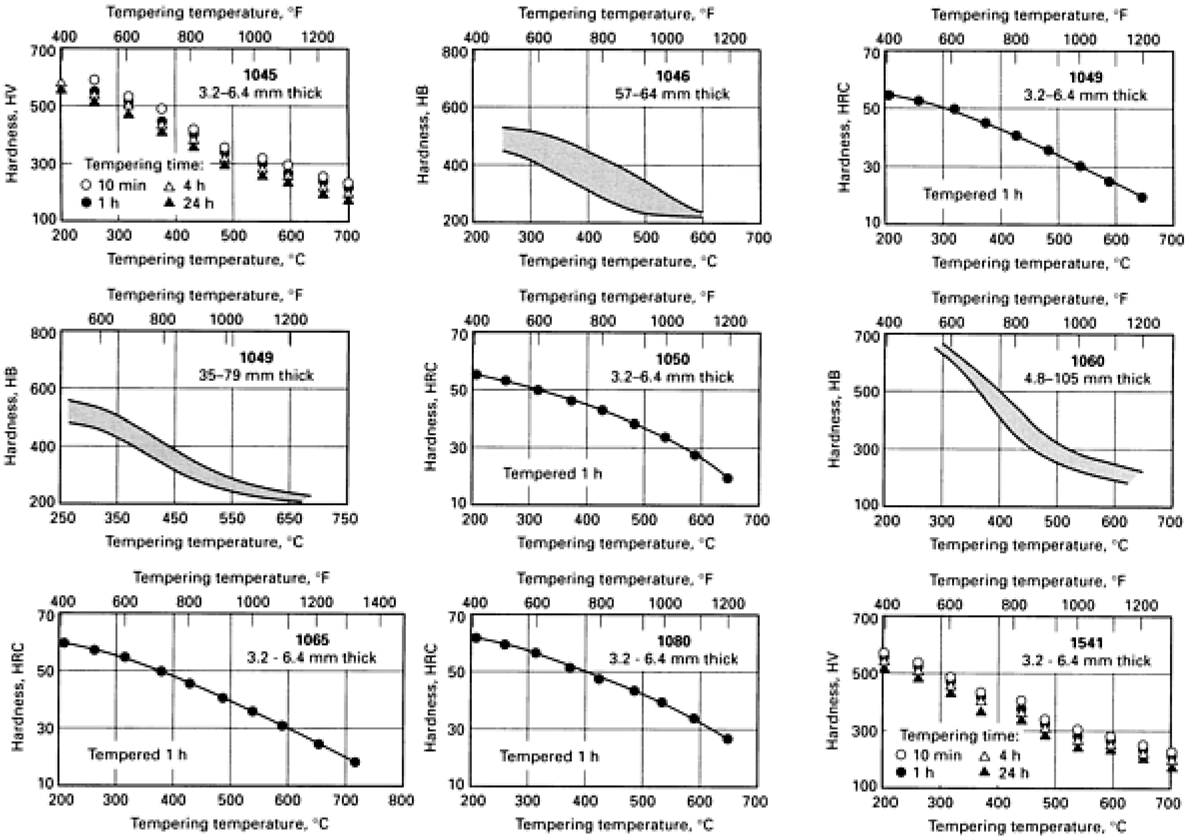


Fig. 6 Influence of tempering temperature on room-temperature hardness of quenched carbon steels. Source: Ref 12

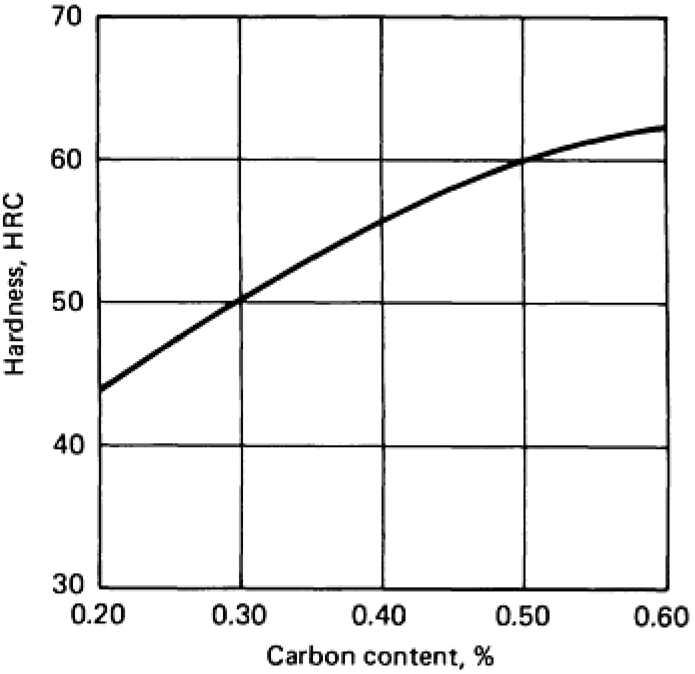
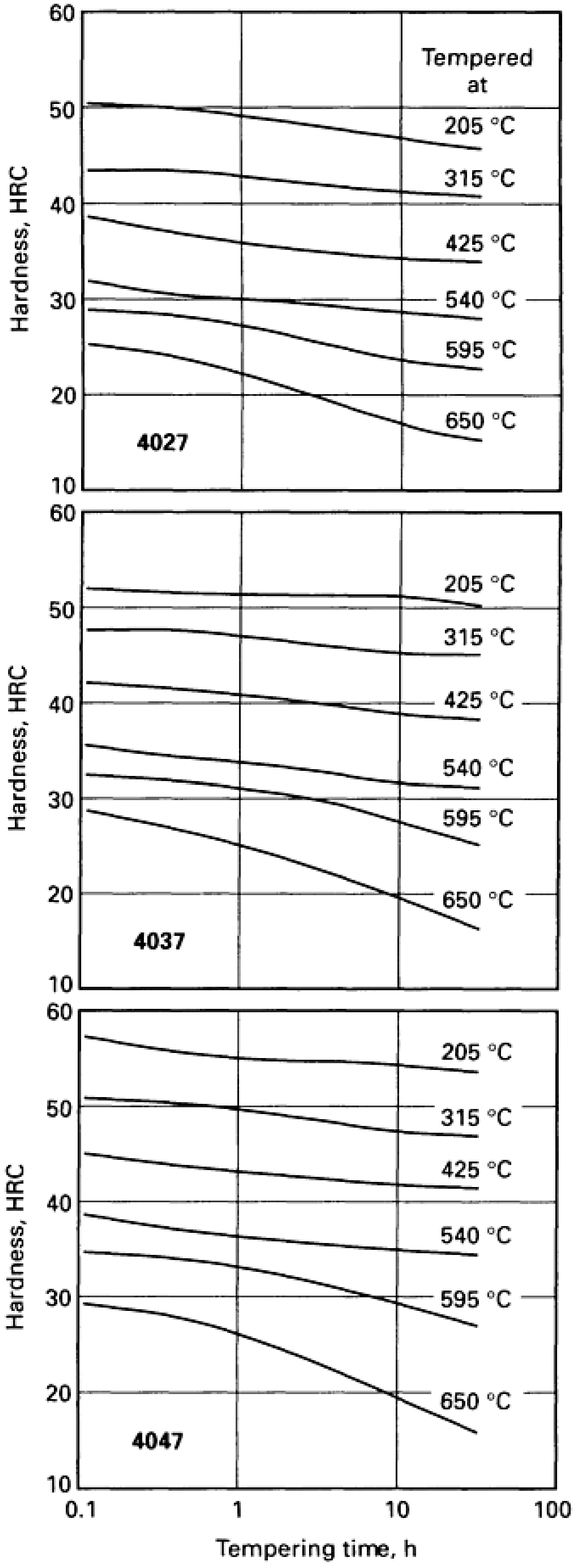


Fig. 7 Relationship between carbon content and room temperature hardness for steels comprising 99.9% untempered martensite



Tempered at
205 °C
315 °C
425 °C
540 °C
595 °C
650 °C
4027
4037
4047
Hardness, HRC
60
50
40
30
20
10
0.1
1
10
100
Tempering time, h

Fig. 8 Effect of tempering time at six temperatures on room-temperature hardness of carbon-molybdenum steels with different carbon contents but with prior martensitic structures

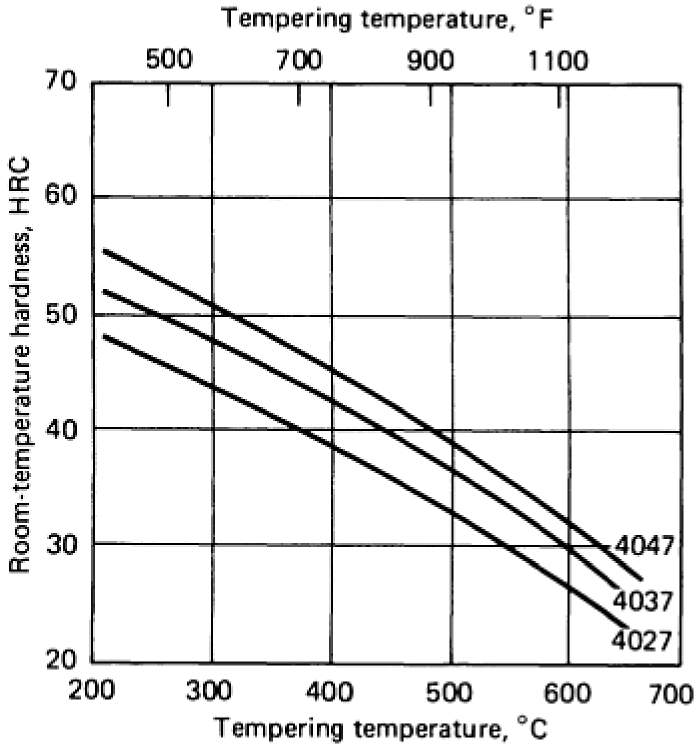


Fig. 9 Effect of carbon content and tempering temperature on room-temperature hardness of three molybdenum steels. Tempering time: 1 h at temperature

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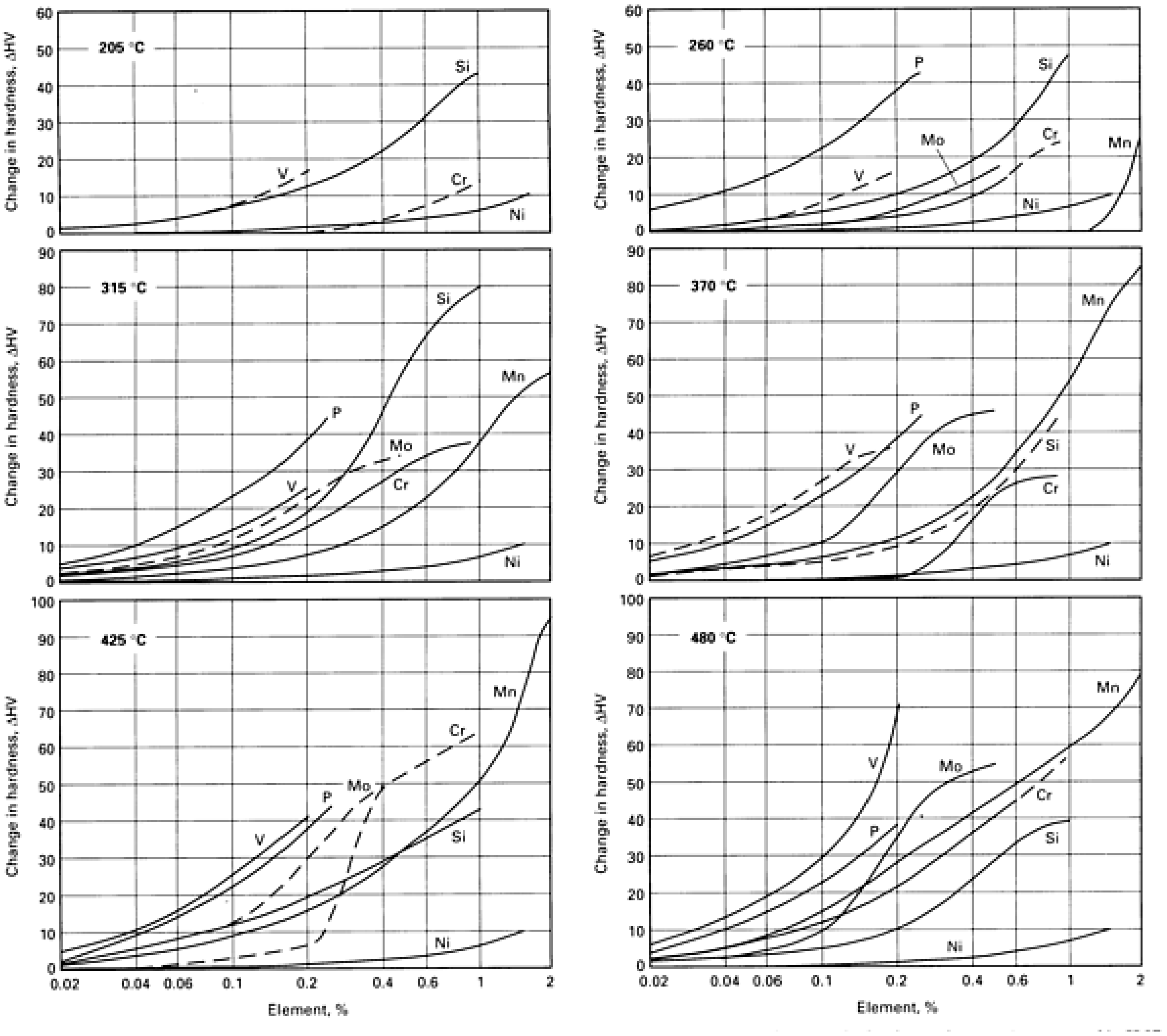
Alloy Content

The main purpose of adding alloying elements to steel is to increase the hardenability, that is, the capability of the steel to form martensite upon quenching from above its critical temperature. The general effect of alloying elements on tempering is a retardation of the rate of softening, especially at the higher tempering temperatures. Thus, to reach a given hardness in a given period of time, alloy steels require higher tempering temperatures than do carbon steels. Alloying elements can be characterized as carbide forming or non-carbide forming. Elements such as nickel, silicon, aluminum, and manganese, which have little or no tendency to occur in the carbide phase, remain essentially in solution in the ferrite and have only a minor effect on tempered hardness. Hardening due to the presence of these elements occurs mainly through solid-solution hardening of the ferrite or matrix grain size control. The carbide forming elements (chromium, molybdenum, tungsten, vanadium, tantalum, niobium, and titanium) retard the softening process by the formation of alloy carbides. The effect of the carbide-forming elements is minimal at low tempering temperatures where Fe_3C forms; however, at higher temperatures, alloy carbides are formed, and hardness decreases slowly with tempering temperature.

The increase in hardness due to the addition of alloying elements was plotted as a percent alloying element for various tempering temperatures from 205 to 705 °C (400 to 1300 °F). These graphs are shown in Fig. 10.



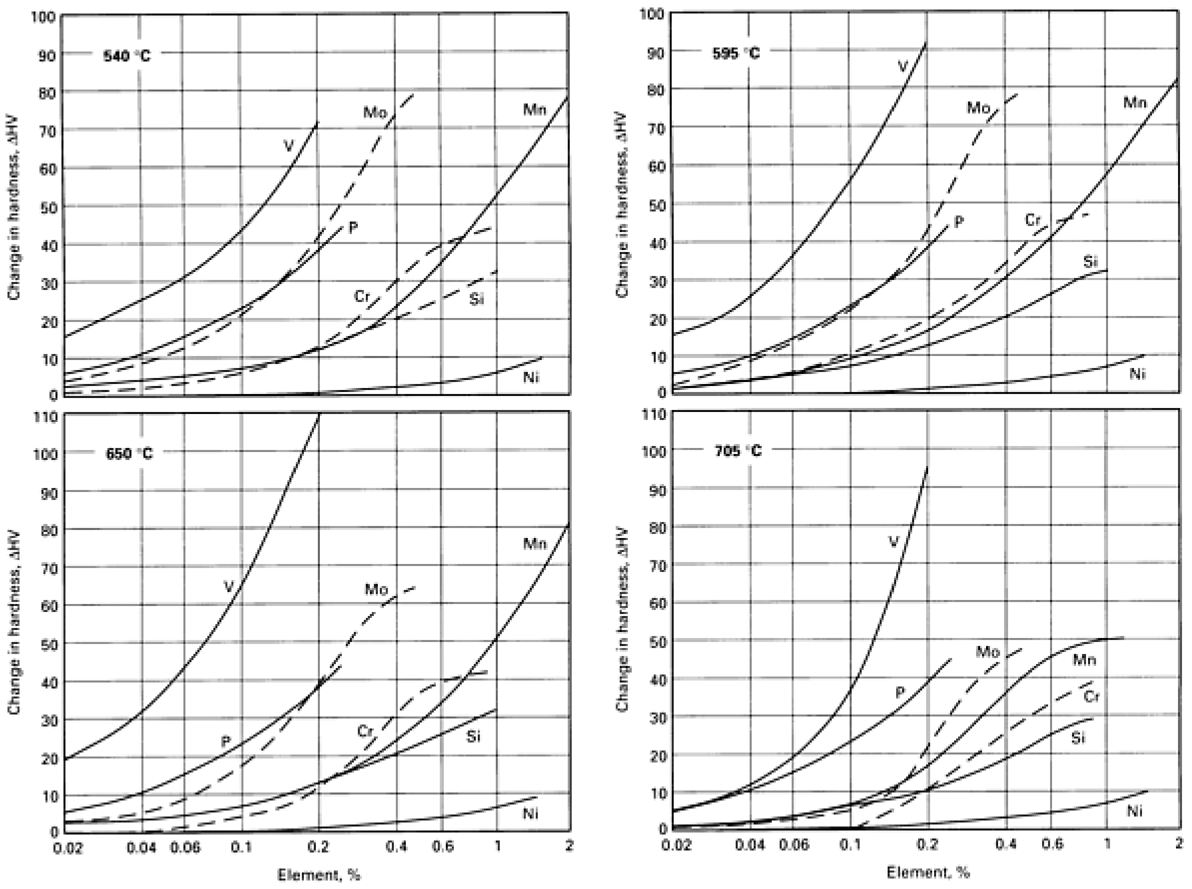


Fig. 10 Effect of seven elements (chromium, manganese, molybdenum, nickel, phosphorus, silicon, and vanadium) on the hardness of martensite tempered in 55 °C (100 °F) increments ranging from 205 to 705 °C (400 to 1300 °F), each for a 1-h duration. Note that manganese, molybdenum, and phosphorus have no effect on hardness at 205 °C (400 °F). Source: Ref 13

Strong carbide-forming elements such as chromium, molybdenum, and vanadium are most effective in increasing hardness at higher temperatures above 205 °C (400 °F). Silicon was found to be most effective in increasing hardness at 315 °C (600 °F). The increase in hardness caused by phosphorus, nickel, and silicon can be attributed to solid-solution strengthening. Manganese is more effective in increasing hardness at higher tempering temperatures. The carbide-forming elements retard coalescence of cementite during tempering and form numerous small carbide particles. Under certain conditions, such as with highly alloyed steels, hardness may actually increase. This effect, mentioned previously, is known as secondary hardening.

The effect of molybdenum content on the tempering behavior of a 0.35% C steel is shown in Fig. 11. As the alloy content increases, the magnitude of the secondary-hardening effect increases. Synergistic effects of various combinations of alloying elements can occur: Chromium tends to produce secondary hardening at a lower temperature than does molybdenum, and the combination of chromium and molybdenum produces a rather flat tempering curve, with the peak hardness occurring at a somewhat lower temperature than when only molybdenum is present. H11 steel is a widely used hot-working die steel that contains nominally 0.35% C, 5% Cr, 1.5% Mo, and 0.4% V. Figure 12 shows the room-temperature hardness of H11 as a function of tempering temperature. A very flat tempering curve results because of the specific combination of the three carbide-forming elements.

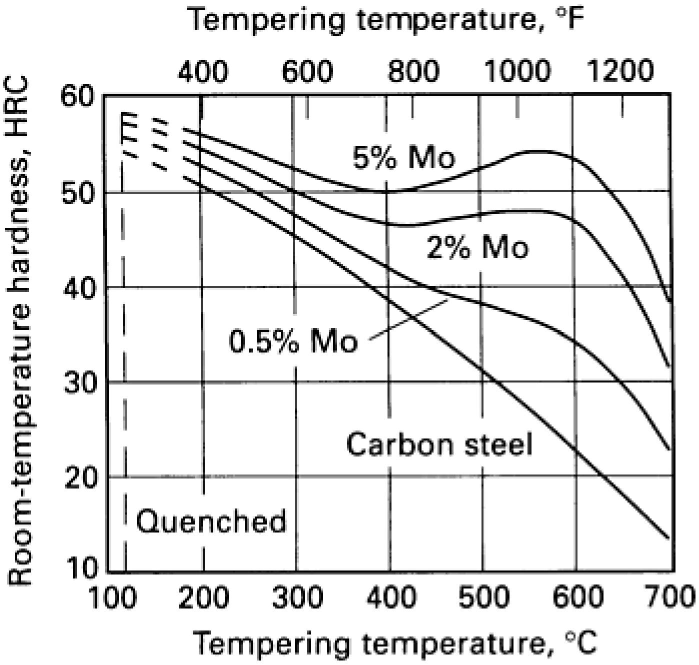


Fig. 11 Influence of molybdenum content on the softening of quenched 0.35% C steels with increasing tempering temperature. Source: Ref 10

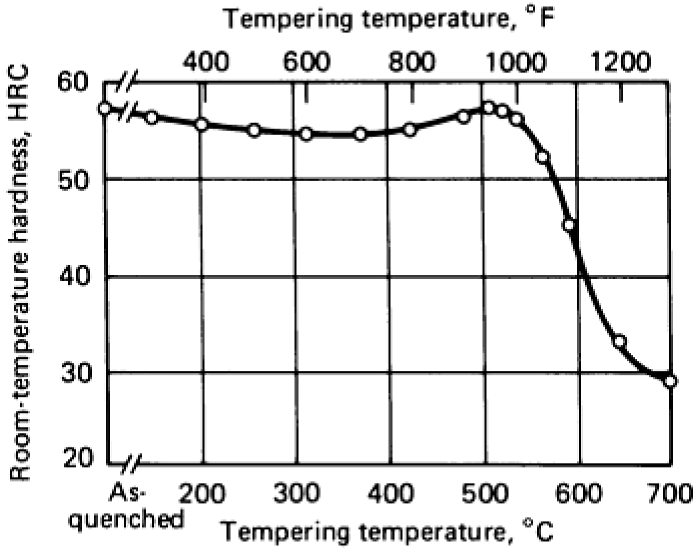


Fig. 12 Variation of room-temperature hardness with tempering temperature for H11 steel. All specimens air cooled from 1010 °C (1850 °F) and double tempered 2 h plus 2 h at temperature

Tool Steels and Stainless Steels. Extensive data on the tempering of tool steels (including H11) and martensitic stainless steels are given in the articles "Introduction to Heat Treating of Tool Steels", "Heat Treating of Specific Classes of Tool Steels", "Heat Treating of Stainless Steels", and "Heat Treating of Superalloys" in this Volume. Additional information is available in the Section "Specialty Steels and Heat-Resistant Alloys" in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.*

Other Alloying Effects. In addition to ease of hardening and secondary hardening, alloying elements produce a number of other effects. The higher tempering temperatures used for alloy steels presumably permit greater relaxation of residual stresses and improve properties. Furthermore, the hardenability of alloy steels requires use of a less drastic

quench so that quench cracking is minimized. However, higher hardenability steels are prone to quench cracking if the quenching rate is too severe. The higher hardenability of alloy steels may also permit the use of lower carbon content to achieve a given strength level but with improved ductility and toughness.

Residual Elements. Residual elements, that is, elements not intentionally added to a steel, can cause embrittlement. The elements that are known to cause embrittlement are tin, phosphorus, antimony, and arsenic. A discussion of the specific effects of these elements can be found in the section "Temper Embrittlement" in this article.

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Tempering Procedures

Tempering can be accomplished by soaking entire parts in the furnace for enough time to bring the tempering mechanism to the desired point of completion or by selective heating of certain portions of the part to achieve toughness or plasticity in those areas.

Bulk processing may be done in convection furnaces or in molten salt, hot oil, or molten metal baths. The selection of furnace type depends primarily on number and size of parts and on desired temperature. Table 2 gives temperature ranges, most likely reasons for use, and fundamental problems of these four types of equipment.

Table 2 Temperature ranges and general conditions of use for four types of tempering equipment

Type or equipment	Temperature range		Service conditions
	°C	°F	
Convection furnace	50-750	120-1380	For large volumes of nearly common parts; variable loads make control of temperature more difficult
Salt bath	160-750	320-1380	Rapid, uniform heating; low to medium volume; should not be used for parts whose configurations make them hard to clean
Oil bath	≤ 250	≤ 480	Good if long exposure is desired; special ventilation and fire control are required
Molten metal	>390	>735	Very rapid heating; special fixturing is required (high density)

Selective tempering techniques are used to soften specific areas of fully hardened parts or to temper areas that were selectively hardened previously. The purpose of this treatment is to improve the machinability, the toughness, or the resistance to quench cracking in the selected zone.

Induction and flame tempering are the most commonly used selective techniques because of their controllable local heating capabilities. The immersion of selected areas in molten salt or molten metal can be accomplished, but with somewhat less control.

Special processes are employed occasionally to achieve specific properties such as those derived from steam treating or the use of protective atmospheres.

The tempering mechanism in certain steels is enhanced by cyclic heating and cooling. A particularly important procedure employs cycles between subzero temperatures and the tempering temperature to increase the transformation of retained austenite. The term used for this procedure, multiple tempering, is also applied to procedures that use intermediate thermal cycles to soften parts for straightening prior to the actual tempering operation designed to achieve the desired degree of toughness and plasticity.

Equipment for Tempering

Steel is usually tempered in either an air (convection) furnace or a salt bath (Fig. 13). Molten metal baths, oil baths, and flame or induction heating units are also used.

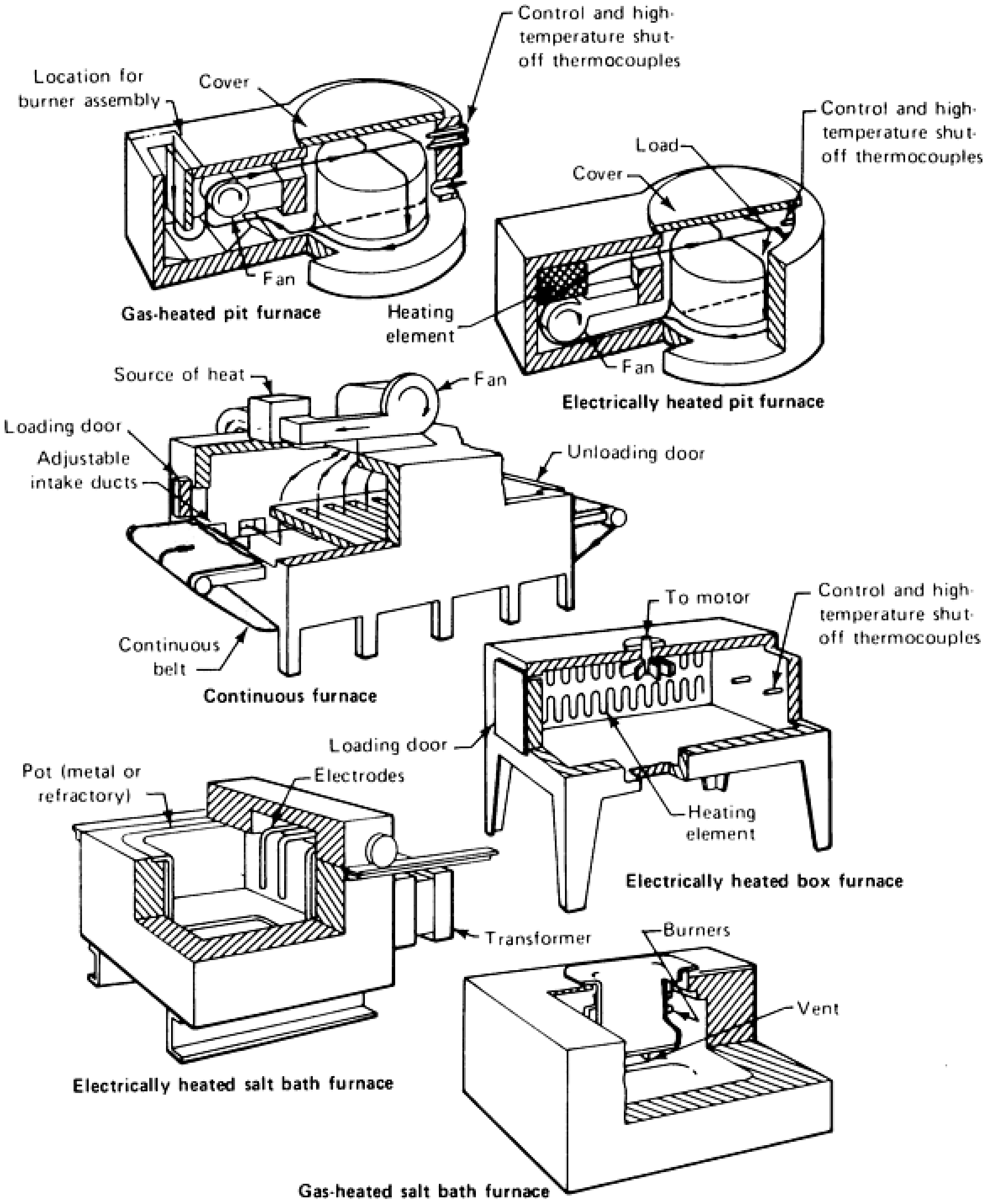

Fig. 13 Types of furnaces used for tempering of steel

Convection Furnaces. The most commonly employed tempering method utilizes the recirculating or forced-air convection furnace, and the equipment most commonly used in conjunction with convection furnaces includes continuous belt conveyor, roller rail, or dog beam pusher systems. Batch equipment such as box or pit types are also used.

Forced recirculating air is the most common and efficient method of tempering because it lends itself to a wide selection of furnace designs to accommodate a variety of products and capacities. Moreover, the metallurgical results are very good in terms of price per unit weight of yield.

Generally, convection furnaces are designed for tempering temperatures of 150 to 750 °C (300 to 1380 °F). For temperatures up to 550 °C (1020 °F), recirculated hot air is supplied to the product from a chamber separate from the work-holding area to avoid uneven heating by radiation. For temperatures of 550 to 750 °C (1020 to 1380 °F), either forced convection or radiant heating is used, depending on the metallurgical requirements of the product. To obtain closer control of metallurgical properties, recirculated forced hot air is employed; but for greater efficiency, radiant heating is used because the transfer of radiant heat is greater as the temperature approaches 750 °C (1380 °F).

The most important phase of convection furnace design is determining the proper amount of forced air. The objective of the blower is to furnish enough hot air to the complete work area so that it is efficiently used to heat the product in the shortest time thermophysically allowed. The type of product and the material being processed dictate the required forced-air supply, which is measured at the operating temperature. Consultation with fan manufacturers can help achieve maximum efficiency of heat transfer.

Heat for the furnace can be supplied by electricity, gas, or oil. In most furnace designs, a dual heat source capability can be built in, such as gas and electricity. This allows for more than one choice of utility when there is a shortage or a cost advantage of one over the other.

Temperature control is accomplished by positioning a thermocouple at the hot-air side of the recirculating system close to the product. When this technique is used, there is minimal danger of overheating, and loads of various sizes can be handled. This method also allows the duration of processing (holding time) to be varied by moving the thermocouple location, but only within the limits of the furnace size (and/or conveyor speed, for continuous-type furnaces). Temperatures generally are held within ±5 °C (±9 °F). If modern temperature controllers are used, baffle plates are positioned properly and furnace curtains are installed.

The efficient use of a continuous furnace cannot be attained when production quantities are small or when parts vary in size, shape, and mechanical requirements. A batch furnace is better suited for work of this type. When a continuous furnace is used for such applications, production time is lost when the furnace temperature is raised or lowered. Sometimes, when the process variables must be changed, a dummy load must be placed in the furnace to accelerate a desired reduction of temperature, or production must be stopped until the temperature is stabilized.

Salt bath furnaces may be used for tempering at 160 °C (320 °F) and above. Good heat transfer and natural convection in the bath promote the uniformity of workpiece temperature.

All moisture must be removed from parts before they are immersed in the molten salt because hot salt reacts violently with moisture. If dirty or oily parts are immersed in the bath, the salt will become contaminated and will require more frequent rectification. Rectification with chemical or gaseous compounds controls the soluble oxides within proper limits. A carbon rod rectification procedure is used to remove the insoluble metallics.

All parts tempered in salt must be cleaned soon after being removed from the bath because the salt that clings to them is hygroscopic and may cause severe corrosion. Parts with small or blind holes from which salt is difficult to clean should not be tempered in salt. Additional information is available in the article "Salt Bath Equipment" in this Volume.

Salt bath compositions and operating temperature ranges presented in Table 3 pertain to baths in common use for tempering and are classified according to Military Specification MIL-S-10699A (Ordnance).

Table 3 Compositions and operating temperatures for salt baths used in tempering

Class	Composition of bath, %								Operating temperature		Fuming temperature	
	$NaNO_2$	$NaNO_3$	KNO_3	Na_2CO_3	NaCl	KCl	$BaCl_2$	$CaCl_2$	°C	°F	°C	°F
1	37-50	0-10	50-60	. . .	. . .	. . .	. . .	. . .	165-595	325-1100	635	1175
2	. . .	45-57	45-57	. . .	. . .	. . .	. . .	. . .	290-595	550-1100	650	1200
3	. . .	. . .	. . .	45-55	. . .	45-55	. . .	. . .	620-925	1150-1700	935	1720
4	. . .	. . .	. . .	. . .	15-25	20-32	50-60	. . .	595-900	1100-1650	940	1725
4A	. . .	. . .	. . .	. . .	10-15	25-30	40-45	15-20	550-760	1025-1400	790	1450

Class 1 and class 2 salts are reasonably stable and seldom require rectification. If chlorides are added by carryover from a higher-temperature bath, they will cause an increase in the viscosity of the bath. Chlorides can be removed by filtering through fine screens or by cooling and settling out the insoluble chlorides as a sludge. Occasionally, carbonates become excessive. These can be removed by reaction with dilute nitric acid-base rectifiers. Upper temperature limits must not be exceeded or salt will become highly oxidizing, even toward alloy steels.

Class 3 salts seldom require rectification. However, their high melting points (about 560 °C, or 1040 °F) severely restrict their useful temperature range. Also, they are decarburizing to steels at temperatures above about 705 °C (1300 °F).

Class 4 salts, which are all-chloride neutral salts, are quite stable. They seldom require rectification but are restricted to temperatures above 595 °C (1100 °F).

Class 4A salts are close relatives of class 4 salts but contain calcium chloride, which lowers the minimum working temperature to 550 °C (1025 °F). The upper limit for these salts is more restricted than that for class 4 salts.

Commercial Availability. All of the salts for these baths are commercially available. The reader is referred to the military specification cited above for the chemical and other control procedures applicable to the various bath composition. For additional information, see the articles"Martempering of Steel", "Austempering of Steel" , "Introduction to Heat Treating of Tool Steels", and "Heat Treating of Specific Classes of Tool Steels" in this Volume.

Caution: The introduction of cyanide salts or other reducing agents into nitrite tempering baths will cause violent explosions.

Oil bath equipment for tempering may be similar in design to that used for salt baths, or a steel tank over hot plate burners will serve satisfactorily. Submerged electric heating elements may also be employed. Stirring is essential for temperature uniformity and satisfactory oil life. Simple, oven-type temperature controls may be employed but localized overheating must be avoided to prevent fire and the rapid decomposition of the oil. A standard thermometer of the proper range may be used to check the temperature of the oil.

Low-temperature tempering in a hot oil bath is a simple and inexpensive method that is especially useful for holding work at temperature for long periods of time. The practical temperature limit is about 120 °C (250 °F) without special ventilation or fire protection equipment and about 250 °C (480 °F) with such precautions, which may include extremely efficient ventilators or inert-gas blanketing systems. When a tempering temperature above 205 °C (400 °F) is required, a salt bath is usually preferable to an oil bath.

Oils for tempering must resist oxidation and have a flash point well above the operating temperature. The most commonly used oils are high-flash-point paraffinic oils with antioxidant additives. Oils used for martempering (see the article "Martempering of Steel" in this Volume) are also satisfactory for tempering.

Molten metal baths for tempering have largely been replaced by salt baths. When employed, commercially pure lead, which melts at about 327 °C (620 °F), has proved to be the most generally suitable of all metals and alloys. For special applications, however, lead-base alloys having lower melting points are used.

Lead oxidizes readily. Although lead itself will not adhere to clean steel, the adherence of lead oxide to steel surfaces is a problem, especially at higher temperatures. Within the range of temperatures usually employed, a film of molten salt will protect the surface of the lead bath, and the work will be easily cleaned. Above 480 °C (900 °F), granulated carbonaceous material, such as charcoal, may be used as a protective cover.

Because of its high thermal conductivity relative to the gaseous atmosphere, lead is useful for rapid local heating and selective tempering. A typical application is the tempering of a ball joint. The part is carburized and quenched to a minimum case hardness of 59 HRC and a core hardness of 30 to 40 HRC. The thread and taper are then tempered in lead to produce a maximum case hardness of 40 HRC.

Because of the high specific gravity of lead, parts tempered in molten lead will float unless held down by fixtures. All parts and fixtures must be dry when immersed in the bath to prevent the formation of steam in, and resultant violent expulsion of, the molten lead. Precautions also must be taken to protect personnel from industrial lead poisoning; hoods and ventilating equipment are required.

Temperature Control. For either gas or electric heat, properly adjusted potentiometers of the on-off type will control the tempering temperature within ±6 °C (±10 °F) at the thermocouple location. With proportioning controls, these instruments can maintain temperatures within ±1 °C (±2 °F) at the thermocouple location.

Selection of Tempering Equipment

The selection of equipment for tempering is based principally on the temperature requirements and the quantity and similarity of the work to be treated. Temperature requirements are dictated by prior heat treatment and by the properties to be developed by tempering.

Process Control

Variations in hardness after tempering are most frequently the result of differences in prior microstructure, as discussed previously. When prior microstructure is the same, the control of temperature is the most important factor in the control of the tempering process.

In general, the control of tempering temperature to within ±13 °C (15 °F) is adequate and is within the practical limits of most furnace and molten-bath equipment. Temperature variations are seldom permitted to exceed ±6 °C (±10 °F) unless mechanical property requirements are correspondingly broad. Examples of the range of variation in hardness obtained after tempering for a variety of wrought and cast steel parts are presented in Fig. 14, 15, and 16.

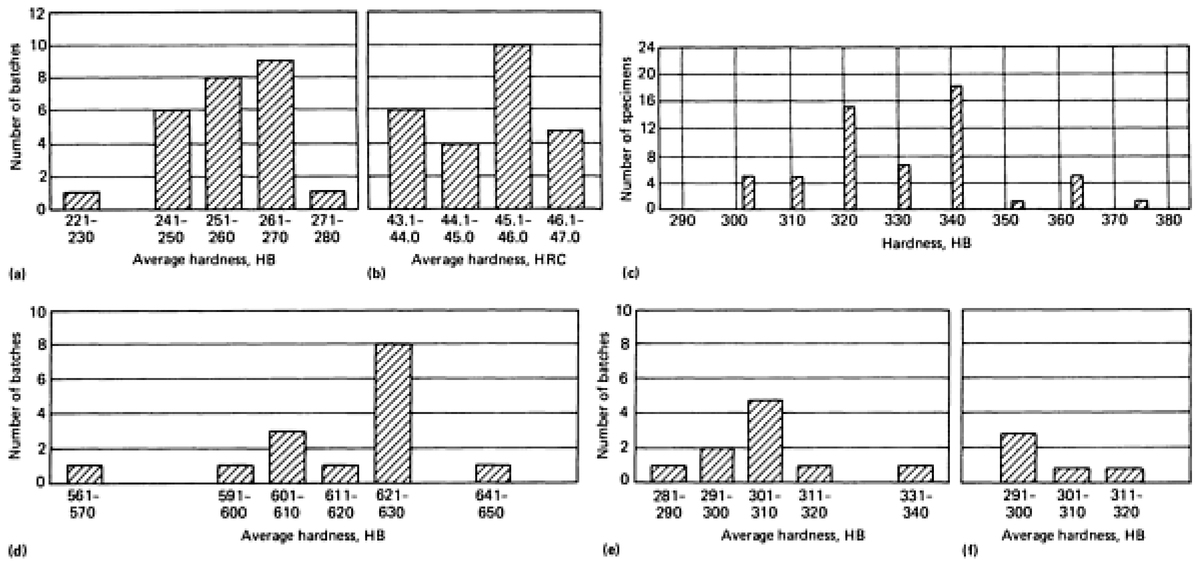

Fig. 14 Variations in room-temperature hardness of three carbon steels after production tempering. (a) Automotive steering-arm forgings made of fine-grain 1035 steel. Section thickness varied from 16 to 29 mm ($\frac{5}{8}$ to $1\frac{1}{8}$ in.). Forgings were austenitized at 825 °C (1520 °F) in oil-fired pusher conveyor furnace, held 45 min, quenched in water at 21 °C (70 °F), and tempered 45 min at 580 to 625 °C (1080 to 1160 °F) in oil-fired link-belt furnace to required hardness range of 217 to 285 HB. Hardness was checked hourly with a 5% sample; readings were taken on polished flash line of 29 mm ($1\frac{1}{8}$ in.) section. Survey of furnace revealed temperature variation at 605 °C (1120 °F) of 8, -4 °C (15, -7 °F). Data represent forgings from four mill heats of steel and cover a 6-week period. (b)Woodworking cutting tools forged from 1045 steel. Section of cutting lip was hardened locally by gas burners that heated the steel to 815 °C (1500 °F). Tools were oil quenched and tempered at 305 to 325 °C (585 to 615 °F) for 10 min in electrically heated recirculating-air furnace to a desired hardness range of 42 to 48 HRC. Data were recorded during a 6-month period and represent forgings from 12 mill heats. (c) Plate sections, 19 to 22 mm ($\frac{3}{4}$ to $\frac{7}{8}$ in.) thick, of 1045 steel were water quenched to a hardness range of 534 to 653 HRB and tempered 1 h at 475 °C (890 °F) in continuous roller-hearth furnaces. Data represent a 2-month production period. (d) Forged 1046 steel heated to 830 °C (1525 °F), and quenched in caustic. Forgings were heated in a continuous belt-type furnace and individually dump quenched in agitated caustic. Forgings weighed 9 toll kg (20 to 24 lb) each; maximum section, 38 mm ($1\frac{1}{2}$ in.). (e) As-quenched forged 1046 steel shown in (d), tempered at 510 °C (950 °F) for 1 h. (f) As-quenched forged 1046 steel shown in (d), tempered at 525 °C (975 °F) for 1 h. Average hardness data for all but (C) obtained by calculating average of high and low extremes of hardness specification range for each batch.

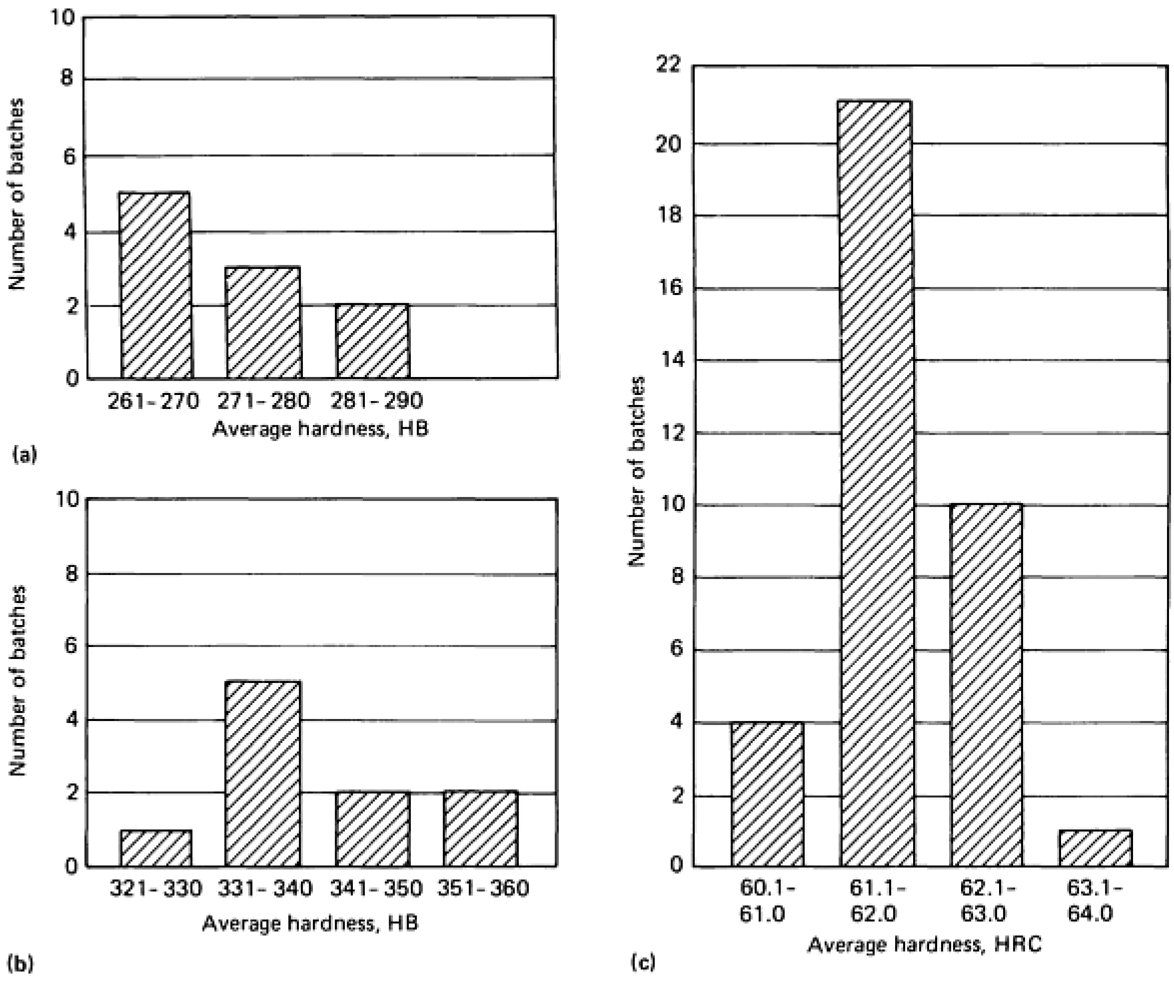

Fig. 15 Variations in room-temperature hardness of two alloy steels after production tempering. (a) Valve bonnets, 75 mm (3 in.) in diameter, made of 4140 steel from one mill heat. Parts were heated at 870 °C (1600 °F), oil quenched and tempered for 2 h at 605 °C (1125 °F) to a hardness specification of 255 to 302 HB. (b) Valve segments made of 4140 steel from one mill heat. Section thickness varied from 13 to 25 mm ($\frac{1}{2}$ to 1 in.). Parts were heated at 870 °C (1600 °F), oil quenched and tempered for 2 h at 580 °C (1075 °F) to a hardness specification of 321 to 363 HB. (c) Needle rollers made of E50100 steel wire varying in diameter from 2.2 to 2.6 mm (0.086 to 0.103 in.). Data represent 36 batches of parts (nine mill heats of steel) tempered to a hardness specification of 60 to 64 HRC. Each batch represents a minimum furnace load of 270 kg (600 lb). Average hardness data obtained by calculating average of high and low extremes of hardness specification range for each batch

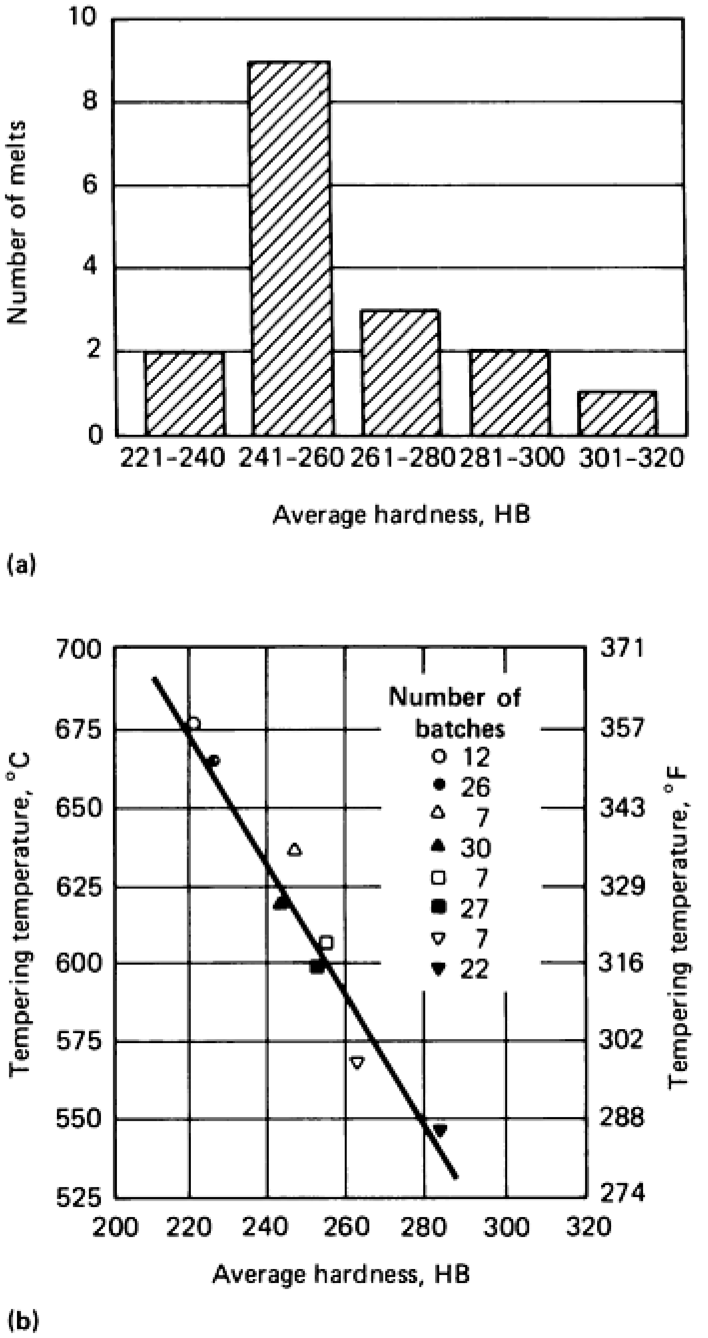

Fig. 16 Variations in room-temperature hardness of two cast steels after production tempering. (a) Cast C-V steel containing 0.25 to 0.30% C, 0.70 to 0.80% Mn, 0.08 to 0.12% V, and 0.40 to 0.60% Si, 25 mm (1 in.) thick, water quenched from 870 °C (1600 °F) and then tempered at 605 °C (1125 °F). Sample size was 17 batches. (b) Cast nickel-chromium-molybdenum steel containing 0.28 to 0.33% C, 0.70 to 0.90% Mn, 0.40 to 0.70% Ni, 0.40 to 0.60% Cr, 0.15 to 0.25% Mo, and 0.40 to 0.60% Si. Spread of hardness readings for various tempering temperatures

Tempering of Special Microstructures

Carburized Components. The tempering of carburized parts represents a special instance in that the combination of toughness, strength, hardness, residual stress, and retained austenite must be considered when selecting tempering time and temperature. Core properties cannot always be controlled by tempering when trying to achieve maximum case properties, and a favorable compressive residual stress pattern may be retained only at the expense of overall toughness.

The effect of tempering on the hardness of carburized cases is shown in Fig. 17, and the influence of tempering on residual stress is shown in Fig. 18. The transformation of retained austenite and the resultant change in the relative

volume of case and core are primarily responsible for the change in residual stress as a function of temperature. The effect of retained austenite on the performance of components is still a controversial issue. The reduction of retained austenite is apparently desirable for resistance to grinding abuse and to provide dimensional stability, but some retained austenite appears to be beneficial for contact-fatigue durability.

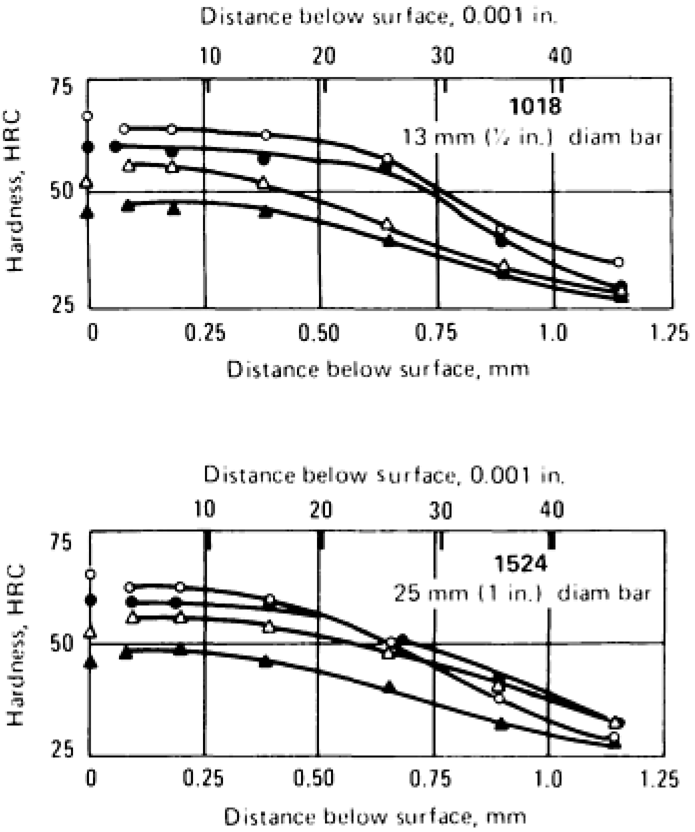

Fig. 17 Effect of tempering on room-temperature hardness of carburized cases. Carburized for 4.5 h at 925 °C (1700 °F), oil quenched and tempered. Data points: open circles, as quenched; closed circles, tempered at 205 °C (400 °F); open triangles, tempered at 315 °C (600 °F); closed triangles, tempered at 425 °C (800 °F)

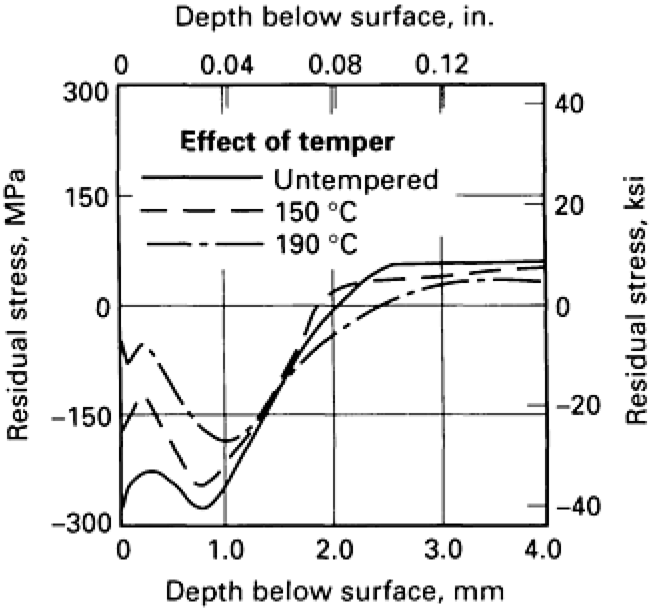

Fig. 18 Effect of tempering on residual stress in carburized steel. Bars of 8617 steel, 19 mm (0.75 in.) in

diameter, were carburized, direct oil quenched, and tempered for 1 h at the indicated temperature.

Nonmartensitic Structures. The tempering of microstructures other than martensite and retained austenite also represents special applications of tempering. Reactions of structures containing substantial amounts of lower bainite are relatively similar to that of martensite in terms of the phenomena associated with carbide growth and coalescence.

Upper bainite and fine pearlite formed by controlled or relatively slow cooling simply respond by carbide growth and eventual ferrite recrystallization. The softening associated with tempering in such instances is shown in Fig. 19. Impact properties of normalized and tempered and hardened and tempered structures at nearly equal hardnesses are shown in Fig. 20.

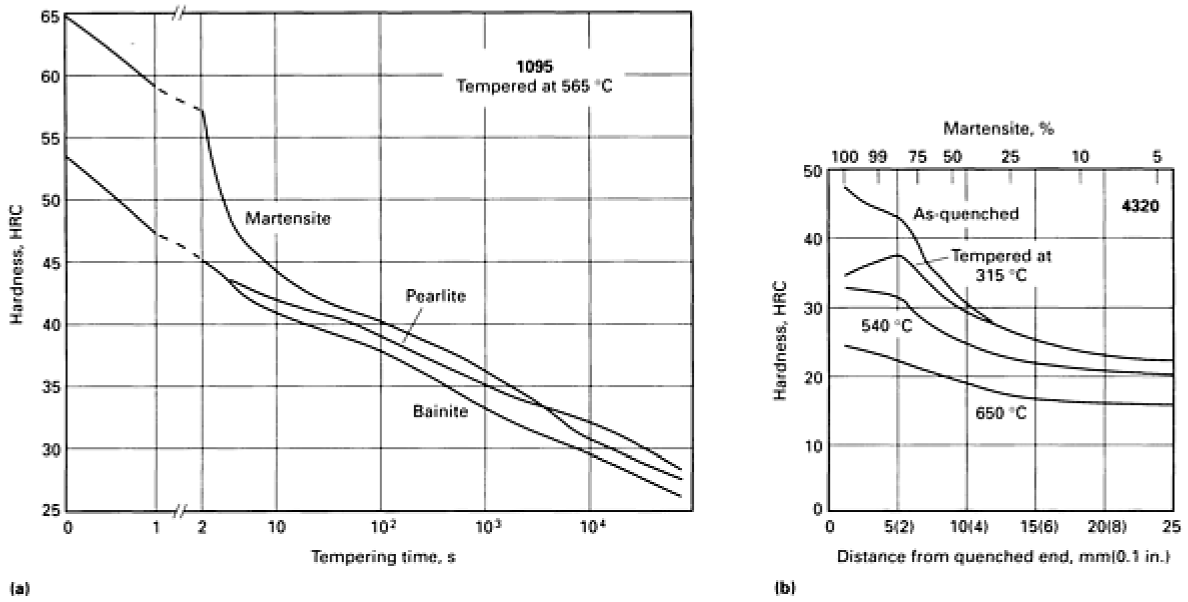

Fig. 19 Effect of prior microstructure on room-temperature hardness after tempering. (a) 1095 steel tempered at 565 °C (1050 °F) for various periods of time. (b) Room-temperature hardness before and after tempering, as well as amount of martensite present before tempering in 4320 steel end-quenched hardenability specimens tempered 2 h

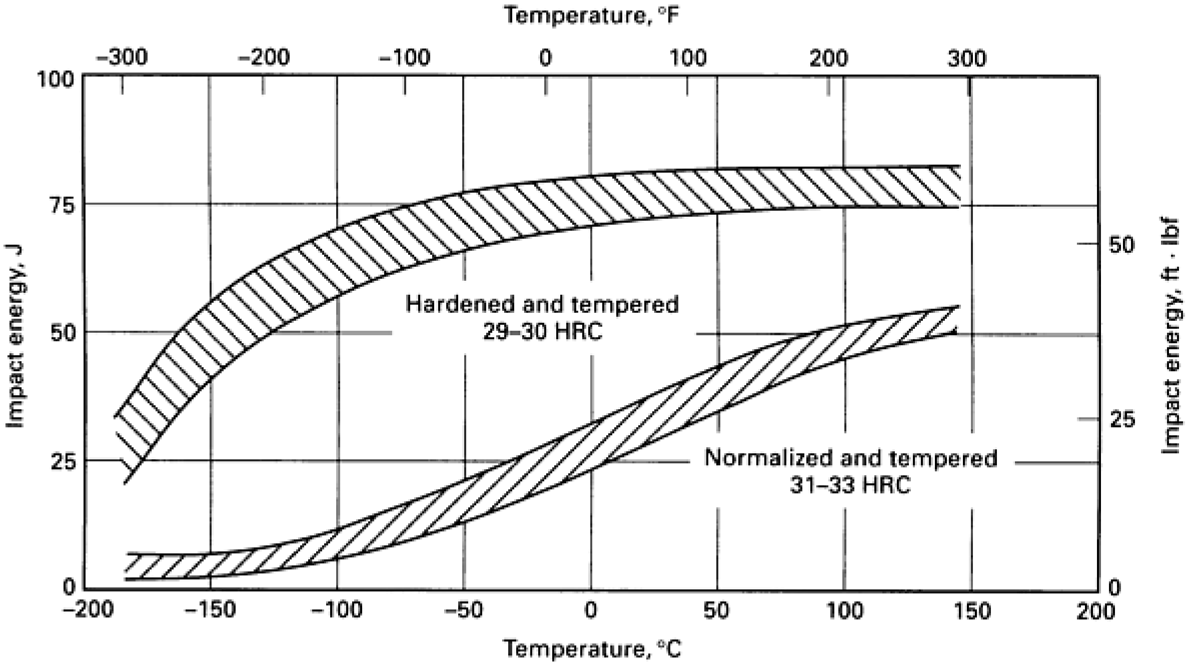

Fig. 20 Effect of microstructure on notch toughness. Variation in Charpy keyhole-notch impact energy with temperature for 4340 steel hardened and tempered to 29 to 30 HRC or normalized and tempered to 31 to 33 HRC

Induction Tempering

Extensive production experience has demonstrated the commercial success of induction tempering for many applications. Metallurgically, the success of induction tempering has been related fundamentally to the possibility of compensating for short tempering times with higher tempering temperatures. Economically, induction tempering has proved particularly adaptable to automation in production lines.

Application. At present, two principal areas of application exist for induction tempering:

- Selective tempering
- Progressive tempering of bar stock previously hardened by scanning

Many machine parts vary from one section to another with respect to load and wear requirements. Often, this variation in requirements is met by a compromise of properties obtained by uniform tempering to a single hardness level. However, it is apparent that superior performance might be expected if the mechanical properties could be adjusted to meet the particular requirements in each section by selective tempering. Within certain limitations, induction tempering is an economical means of accomplishing this. These limitations are that the parts must be of such a shape and size that they can be coupled by the inductor to heat uniformly to the desired temperature in critical sections. Although this is impossible or impracticable for some parts, many can be tempered selectively by induction to obtain different degrees of hardness in the same part, with a consequent improvement in quality.

Advantage. The principal advantage of induction tempering is the possibility of integration with machine lines to avoid excessive handling of work, thereby minimizing labor cost. This is illustrated in the preparation of bar stock of specified mechanical properties before machining into cylinder-head studs and miscellaneous machine parts. Frequently, the tempering operation is keyed to the hardening operation, or the same equipment may be used for both induction hardening and tempering either by merely changing the work coil or by reducing the power density and the heating time.

Selection of Frequency and Power Densities. Because tempering is performed below the lower transformation temperature 725 °C (1335 °F), lower-frequency induction tempering installations are generally used; such installations are necessary for tempering large sections to minimize any temperature gradient from the surface to the interior. Frequency

selection is basically related to the required depth of heating (see the article "Induction Heat Treating of Steel" in this Volume). It should be noted that line frequencies (60 Hz) may be used for tempering parts 25 to 50 mm (1 to 2 in.) in diameter or larger.

Because the usual objective of induction tempering is to produce uniform hardness throughout the cross section, rather than to heat the surface, the power density within the inductor is generally low, from 0.08 to 0.8 W/mm^2 (0.05 to 0.5 kW/in.^{2}). Power densities may be selected on the basis of experience, tests, or data such as those presented in Table 4. Furthermore, the heating time is comparatively long to help provide uniform heating throughout the part. To meet production requirements, length of the inductor can be increased, or more than one bar can be processed at a time.

Table 4 Approximate power density required for tempering

Frequency[(a)], Hz	**Input[(b)]**			
	W/mm^2		**kW/in.^{2}**	
	150-425 °C (300-800 °F)	**425-705 °C (800-1300 °F)**	**150-425 °C (300-800 °F)**	**425-705 °C (800-1300 °F)**
60	0.10	0.24	0.06	0.15
180	0.08	0.22	0.05	0.14
1,000	0.06	0.19	0.04	0.12
3,000	0.05	0.16	0.03	0.10
10,000	0.03	0.13	0.02	0.08

(a) Table is based on use of proper frequency and normal overall operating efficiency of equipment.

(b) In general, these power densities are for section sizes of 13 to 50 mm ($\frac{1}{2}$ to 2 in.). Higher inputs can be used for smaller section sizes and lower inputs may be required for larger section sizes.

In general, the control of induction tempering is achieved by selection of the power density and the rate of feed through the coil (scanning) on the basis of hardness tests of the tempered product. Automatic control may be obtained at tempering temperatures above 425 °C (800 °F) by use of a special radiation pyrometer and high-speed controller. This arrangement may be used to vary the speed of the scanning operation continuously or to control the power.

Selection of Induction Tempering Cycle. Fundamentally, the tempering cycle will be determined by the ultimate mechanical properties specified for the part. However, usual furnace tempering temperatures must be increased to compensate for the short heating times.

Figure 21 shows the increase in tempering temperature required to produce a given hardness as the tempering time is decreased from 1 h (furnace tempering) to 60 s and 5 s (induction tempering) in 1050 steel quenched in brine from 855 °C (1575 °F). Pieces with small cross section may be air cooled immediately upon reaching the tempering temperature, while slower heating rates or short periods of time at temperature (5 to 60 s) before cooling are desirable for larger sections to

allow penetration of heat. In scanning, of course, the power density, the rate of travel, and the length of the inductor will determine the time of tempering.

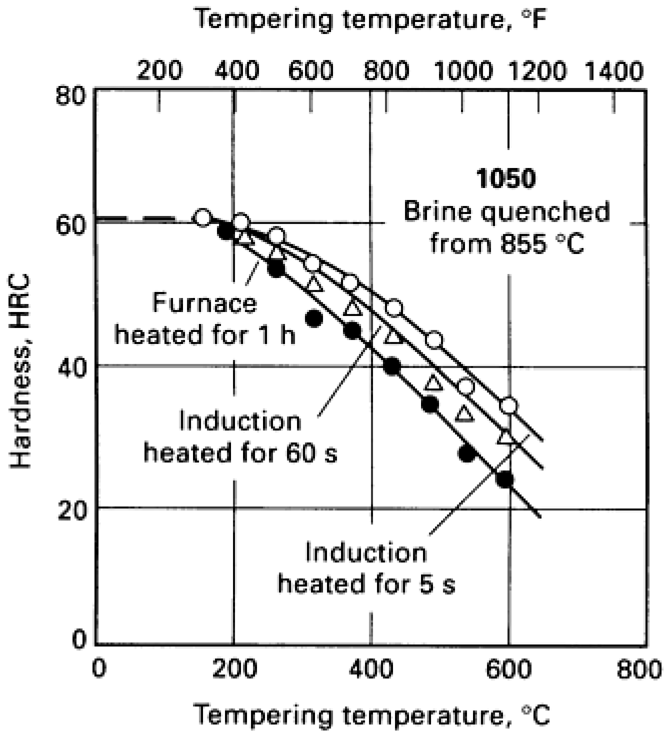

Fig. 21 Variations of room-temperature hardness with tempering temperature for furnace and induction heating

Results of Induction Tempering. Statistical studies over several years on cross-sectional hardnesses for similar bar stock that was induction hardened and tempered by scanning reveal that 67% of all average cross-sectional hardnesses resulted in a hardness spread of ±1.25 Rockwell C points and that approximately 95% were within ±2.5 points. Variations in resultant hardness occur more often from differences in hardenability between respective heats of steel than from discrepancies in the induction tempering process. If each mill beat is run separately, it is possible to compensate for differences in hardenability.

Special Tempering Procedures

Selective Tempering. Selective or localized tempering is applied to parts in which adjacent areas must have significantly different hardnesses. Chisels, punches, the upset ends of cold-formed rivets, and the threaded portions of carburized parts are typical examples. Localized tempering is also employed in preheating and postheating of weld areas when a lowering of the hardness in the beat-affected zone is desired.

Selective tempering entails heating a restricted area to the required tempering temperature without heating the remainder of the part to this temperature. Induction beating coils, special flame heads, and immersion in lead or salt baths are employed to achieve this selective heating. Selective tempering is also done by the use of defocused lasers or electron beam equipment. Induction heating and flame techniques are generally used in high-volume production applications and are easiest to control. Deeper penetration is achieved with low-frequency (3 to 10 kHz) induction heating and salt immersion than is obtained with the other techniques.

To obtain rapid heating for selective tempering by immersion in salt or lead baths, it is usually necessary that the bath temperature be considerably higher than the desired tempering temperature. Consequently, the immersion time becomes the controlling factor in obtaining the desired results. Lead, because of its higher rate of heat transfer, is more effective than salt.

Other factors, such as ease of fixturing, part configuration, heater frequency, and cost, also influence the choice of equipment for selective tempering. In induction tempering, the same heating system can be used for both hardening and tempering.

Both examples below illustrate how selective tempering can be used to produce specific hardnesses in certain areas of a workpiece.

Example 2: Use of Bulk Processing and Selective Tempering to Produce a Tack Hammer with a 50 to 55 HRC Striking Head.

An upholsterer's tack hammer, forged from 1086 steel, is hardened on all surfaces to 53 to 60 HRC and then is tempered in salt at 190 °C (375 °F). This treatment provides the desired combination of hardness, toughness, and magnetic properties for the horseshoe-magnet end of the hammer. However, the striking head must be selectively tempered in salt at 260 °C (500 °F) to produce the working hardness of 50 to 55 HRC.

Example 3: Use of Bulk Processing and Selective Tempering to Produce a Pipe Wrench with 47 to 52 HRC Chain Teeth and a 40 to 48 HRC Handle.

A chain pipe wrench handle forging, made of 4053 steel, is fully hardened and tempered for 1 h at 355 °C (675 °F) to produce an overall hardness of 47 to 52 HRC. This is an ideal hardness for the wrench teeth but does not provide sufficient toughness for the I-beam section of the handle. Thus this section is selectively tempered by induction heating for 1 min at 480 °C (900 °F) to produce a hardness of 40 to 48 HRC.

Multiple tempering is principally used to:

- Relieve the quenching and straightening stresses in irregularly shaped carbon and alloy steel parts and thereby lessen distortion
- Eliminate retained austenite and improve dimensional stability in such parts as bearing components and gear blocks
- Improve yield and impact strengths without decreasing hardness

The following examples illustrate these principal applications of the multiple-tempering process.

Example 4: Use of Multiple Tempering to Relieve Straightening-Induced Stresses in a 1046 Steel Diesel Engine Crankshaft.

A six-throw, seven-bearing, counterweighted diesel-engine crankshaft weighing 80 kg (175 lb) was distorted in rough machining to such a degree that cold straightening was required. The straightening operation induced additional stresses, which caused severe distortion in final machining. The problem was solved by first tempering the 1046 steel shaft at 455 °C (850 °F) to a hardness of about 321 HB, which allowed hot straightening. The shaft was then retempered at 480 to 540 °C (900 to 1000 °F), depending on the composition of the particular heat, to produce a hardness of 269 to 302 HB and to relieve residual stresses.

Example 5: Use of Multiple Tempering to Minimize Retained Austenite and to Improve Dimensional Stability in a W1 Tool Steel Gage Block.

In the manufacture of a gage block of W1 tool steel (final hardness, 65 to 66 HRC), the block is quench hardened after rough machining. It is then subjected to three consecutive cycles, each consisting of cold treatment at -100 °C (-145 °F) for 1 h followed by tempering at 70 °C (160 °F) for 1 h. This minimizes the retained austenite and enhances dimensional stability before the block is finish ground.

Use of Fixtures

Many high-strength steel components having a tensile strength greater than 1720 MPa (250 ksi) are finish machined before final heat treatment. To minimize distortion and satisfy stringent dimensional requirements, some of these

components, such as cylinders, pressure vessels, and thin parts, are held in fixtures during both hardening and tempering or during tempering only. Additional information is available in the article "Proper Fixturing" in Volume 16 of *ASM Handbook*, formerly 9th Edition *Metals Handbook.*

External rings, internal mandrels, jacks, screws, weights, wedges, dies, and other mechanical devices are used to aid in dimensional correction.

Example 6: Use of Tempering Fixture to Minimize Out-of-Round Condition in a 4135 Steel Welded Pressure Vessel.

A welded pressure vessel made of 4135 steel, 380 mm (15 in.) in outside diameter, 1.8 m (6 ft) long, and 3.18 mm (0.125 in.) thick, was found to be 1.3 to 3.8 mm (0.050 to 0.150 in.) out of round over its entire length when measured in the as-quenched condition. A tempering fixture consisting of a series of steel rings 125 mm (5 in.) wide reduced maximum out-of-roundness to 1.3 mm (0.050 in.) after tempering at 455 °C (850 °F) for $2\frac{1}{2}$ h.

Snap Draw. Steels that are susceptible to cracking at room temperature after hardening are given a low-temperature tempering treatment (a snap draw) immediately after hardening and prior to final tempering in fixtures

Cracking in Processing

Because of their carbon or alloy contents, some steels are likely to crack if they are permitted to cool to room temperature during or immediately following the quenching operation. This likelihood is caused by the generation of high tensile residual stresses during quenching, due to thermal gradients, abrupt changes in section thickness, decarburization, or other hardenability gradients. Another potential source is cracking due to quenchant contamination and the subsequent change in quenching severity. Accordingly, for carbon steels containing more than 0.4% C and alloy steels containing more than 0.35% C, it is recommended that the parts be transferred to tempering furnaces before they cool to below 100 to 150 °C (212 to 300 °F). Alternately, many heat-treating operations use quenching oil for the tempering operation (martempering) or to avoid cooling below 125 °C (255 °F). Steels that are known to be sensitive to this type of cracking include 1060, 1090, 1340, 4063, 4150, 4340, 52100, 6150, 8650, and 9850.

Other carbon and alloy steels are generally less sensitive to this type of delayed quench cracking but may crack as a result of part configuration or surface defects. These steels include 1040, 1050, 1141, 1144, 4047, 4132, 4140, 4640, 8632, 8740, and 9840. Some steels, such as 1020, 1038, 1132, 4130, 5130, and 8630, are not sensitive.

Before being tempered, parts should be quenched to room temperature to ensure the transformation of most of the austenite to martensite and to achieve maximum as-quenched hardness. Austenite retained in low-alloy steels will, upon heating for tempering, transform to an intermediate structure, reducing overall hardness. However, in medium- to high-alloy steels containing austenite-stabilizing elements (nickel, for example), retained austenite may transform to martensite upon cooling from tempering, and thus such steels may require additional tempering (double tempering) for the relief of transformation stresses.

Temper Embrittlement

When carbon or low-alloy steels are cooled slowly from tempering above 575 °C (1065 °F) or are tempered for extended times between 375 and 575 °C (705 and 1065 °F), a loss in toughness occurs that manifests itself in reduced notched-bar impact strength compared to that resulting from normal tempering cycles and relatively fast cooling rates (see Fig. 22). The cause of temper embrittlement is believed to be the precipitation of compounds containing trace elements such as tin, arsenic, antimony, and phosphorus, along with chromium and/or manganese. The intergranular nature of the fracture suggests that the embrittlement occurs at the prior austenite grain boundaries. Although manganese and chromium cannot be restricted, a reduction of the other elements and quenching from above 575 °C (1065 °F) are the most effective remedies for this type of embrittlement.

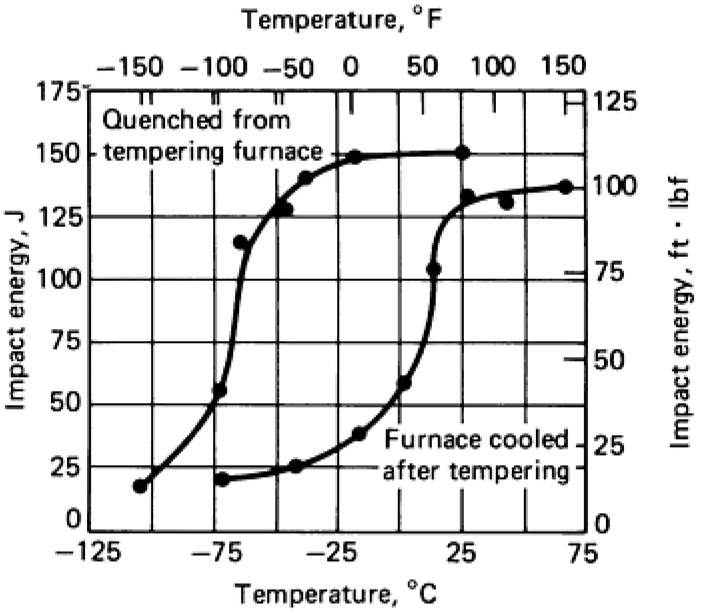

Fig. 22 Effect of temper embrittlement on notch toughness. Variation in Charpy V-notch impact energy with temperature for 5140 steel hardened and tempered at 620 °C (1150 °F); one series of specimens was quenched from the tempering temperature, and the other was furnace cooled. Slow cooling of susceptible steels causes temper embrittlement. Source: Ref 14

Steels that have been embrittled because of temper embrittlement can be de-embrittled by heating to about 575 °C (1065 °F), holding a few minutes, and subsequently, rapidly cooled or quenched. The time for de-embrittlement depends on the alloying elements present and the temperature of reheating (Ref 15). De-embrittlement is accompanied by a redistribution of impurities at the grain boundaries (Ref 16). Various surface-sensitive techniques such as x-ray photoelectron spectroscopy, Auger electron spectroscopy, and backscattering of energetic ions have been used to study the composition of grain boundaries of an embrittled steel.

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Blue Brittleness

The heating of plain carbon steels or some alloy steels to the temperature range of 230 to 370 °C (450 to 700 °F) may result in increased tensile and yield strength, as well as decreased ductility and impact strength. This embrittling phenomenon is caused by precipitation hardening and is called blue brittleness because it occurs within the blue heat range.

If susceptible steels are heated within the 230 to 370 °C (450 to 700 °F) range, they may be embrittled and thus should not be used in applications in which they are subjected to impact loads.

Tempered Martensite Embrittlement

Both intergranular (Ref 17, 18, 19) and transgranular fracture modes may be observed in tempered martensite embrittlement (Ref 17, 20). The combination of the segregation of impurities such as phosphorus to the austenitic grain boundaries during austenitizing and the formation of cementite at prior austenitic grain boundaries during tempering are

responsible for the intergranular fracture mode of tempered martensite embrittlement (Ref 17, 19). The transgranular fracture mode is caused by the formation of cementite between parallel martensitic lathes during tempering (Ref 17, 20).

Figure 23 shows the impact absorbed as a function of tempering temperature for chromium-molybdenum steels with various phosphorus and carbon contents. The figure exhibits the effect of phosphorus and carbon on the impact toughness of low-alloy steels. There is a loss in impact toughness for steels tempered in the temperature range of 250 to 300 °C (480 to 570 °F). Steels with lower phosphorus content have superior impact properties than steels with a higher phosphorus level. Also, impact toughness decreases with increasing carbon content (Ref 21). The effect of tempered martensite embrittlement on 4140 steel is shown in Fig. 4. Generally, with steels containing either potent carbide forms such as chromium or other impurities that make them susceptible to tempered martensite embrittlement, tempering between 200 to 370 °C (390 to 700 °F) should be avoided.

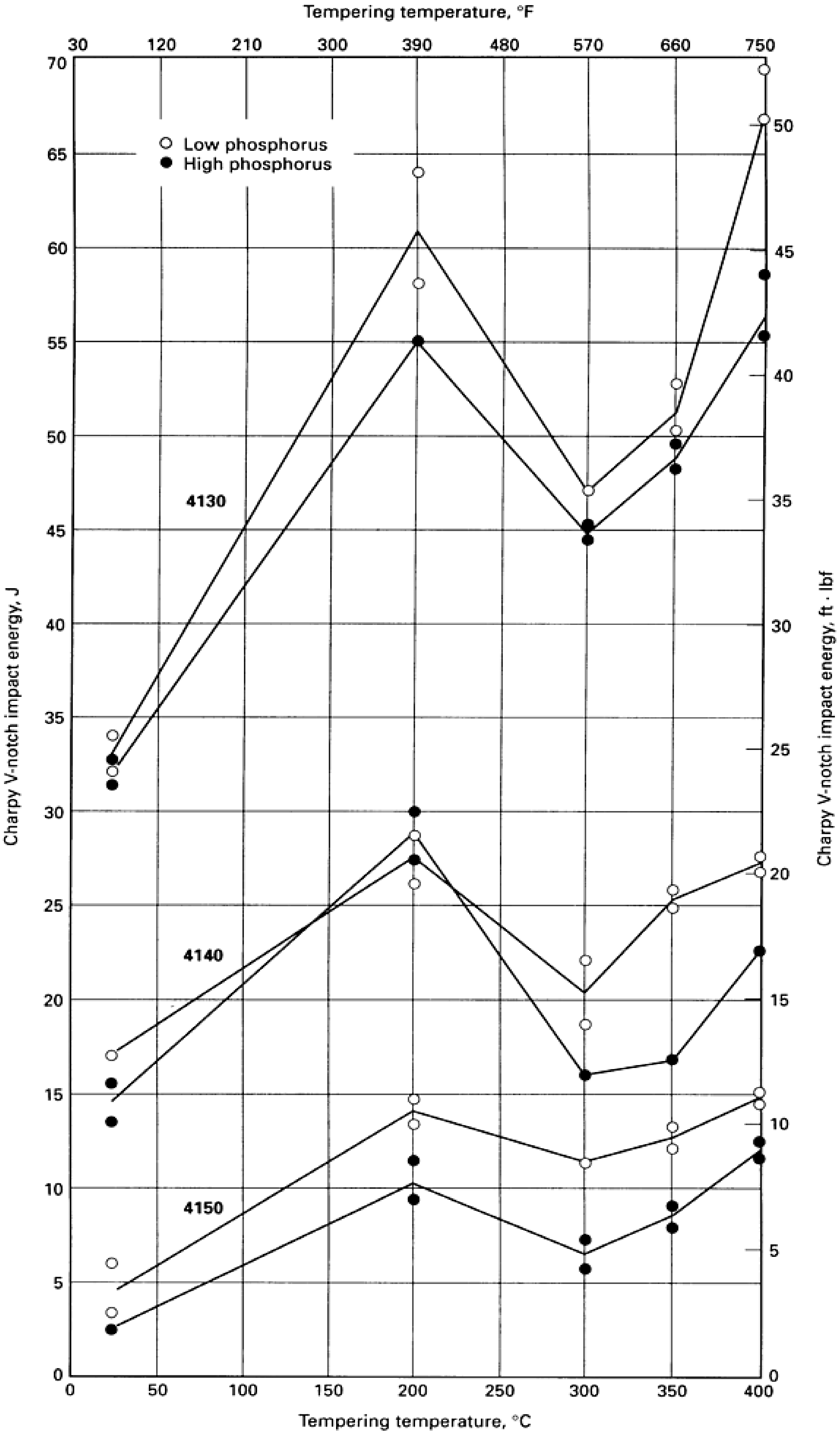
Tempering temperature, °F
30
120
210
300
390
480
570
660
750
Low phosphorus
High phosphorus
4130
4140
4150
Charpy V-notch impact energy, J
Charpy V-notch impact energy, ft · lbf
Tempering temperature, °C
0
50
100
150
200
250
300
350
400
5
10
15
20
25
30
35
40
45
50
55
60
65
70

Fig. 23 Room-temperature Charpy V-notch impact energy versus tempering temperature for 4130, 4140, and 4150 steels austenitized at 900 °C (1650 °F) and tempered 1 h at temperatures shown. Source: Ref 21

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Hydrogen Embrittlement

The selection of tempering temperature and the resultant hardness or plasticity must include the consideration of the potential problem of hydrogen embrittlement, if the part were to be exposed to hydrogen through electroplating, phosphating, or other means, or if environmental conditions cause the cathodic absorption of hydrogen during service.

Generally, the restricted notch ductility of steels with hardnesses above 40 HRC presents ideal conditions for the development of stress concentrations in parts containing notches or defects that would, in the presence of relatively low hydrogen concentrations, lead to the failure of parts at stresses far below the nominal tensile strength of the material. Thus, tempering should be carried out to achieve a hardness below 40 HRC if the part is to be subjected to relatively high stresses and probable exposure to hydrogen. Additional information is available in the articles "Elevated-Temperature Properties of Ferritic Steels" and "Embrittlement of Steels" in Volume 1 of *ASM Handbook,* formerly 10th Edition *Metals Handbook.*

Martempering of Steel

Revised by Herb Webster, Phoenix Heat Treating, Inc.; and W. James Laird, Jr., The Metal Works Industrial Furnaces, Inc.

Introduction

MARTEMPERING is a term used to describe an interrupted quench from the austenitizing temperature of certain alloy, cast, tool, and stainless steels. The purpose is to delay the cooling just above the martensitic transformation for a length of time to equalize the temperature throughout the piece. This will minimize the distortion, cracking, and residual stress. The term martempering is somewhat misleading and is better described as marquenching. The microstructure after martempering is essentially primary martensitic that is untempered and brittle.

Figure 1(a and b) shows the significant difference between conventional quenching and martempering. Martempering of steel (and of cast iron) consists of:

- Quenching from the austenitizing temperature into a hot fluid medium (hot oil, molten salt, molten metal, or a fluidized particle bed) at a temperature usually above the martensite range (M_s point)
- Holding in the quenching medium until the temperature throughout the steel is substantially uniform
- Cooling (usually in air) at a moderate rate to prevent large differences in temperature between the outside and the center of the section

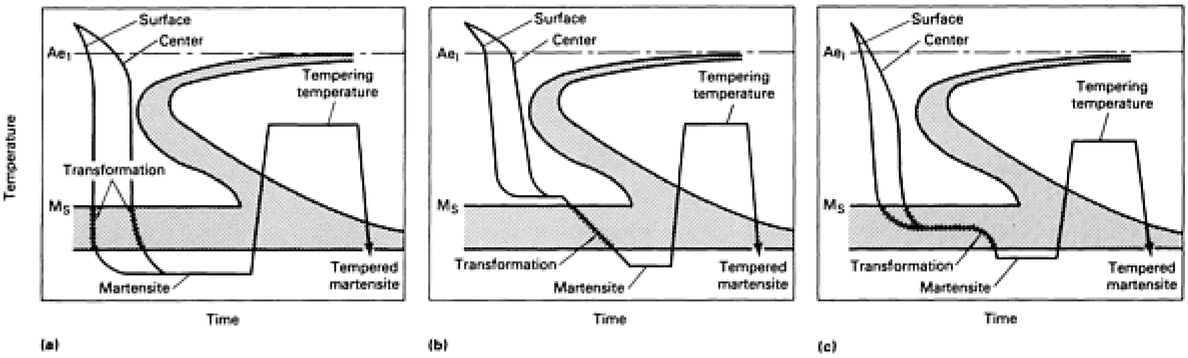


Fig. 1 Time temperature transformation diagrams with superimposed cooling curves showing quenching and tempering. (a) Conventional process. (b) Martempering. (c) Modified martempering

Formation of martensite occurs fairly uniformly throughout the workpiece during cooling to room temperature, thereby avoiding formation of excessive amounts of residual stress. Straightening or forming is also easily accomplished upon removal from the marquenching bath while the part is still hot. The piece will hold its shape upon subsequent cooling in fixturing or in air cooling after removal from the forming die. The marquenching can be accomplished in a variety of baths including hot oil, molten salt, molten metal, or a fluidized particle bed. Martempered parts are tempered in the same manner as conventional quenched parts. The time lapse before tempering is not as critical because the stress is greatly reduced.

Advantages

The advantage of martempering lies in the reduced thermal gradient between surface and center as the part is quenched to the isothermal temperature and then is air cooled to room temperature. Residual stresses developed during martempering are lower than those developed during conventional quenching because the greatest thermal variations occur while the steel is in the relatively plastic austenitic condition and because final transformation and thermal changes occur throughout the part at approximately the same time. Martempering also reduces or eliminates susceptibility to cracking.

Another advantage of martempering in molten salt is the control of surface carburizing or decarburizing. When the austenitizing bath is neutral salt and is controlled by the addition of methane gas or proprietary rectifiers to maintain its neutrality, parts are protected with a residual coating of neutral salt until immersed in the marquench bath.

Although martempering is used primarily to minimize distortion, eliminate cracking, and minimize residual stresses, it also greatly reduces the problems of pollution and fire hazard as long as nitrate-nitrite salts are used rather than martempering oils. This is especially true where nitrate-nitrite salts are recovered from wash waters with systems that provide essentially no discharge of salts into drains. Any steel part or grade of steel responding to oil quenching can be martempered to provide similar physical properties. The quenching severity of molten salt is greatly enhanced by agitation and water additions to the nitrate-salt bath. Both techniques are particularly beneficial in heat treating of carbon steels that have limited hardenability. Table 1 compares the properties obtained in 1095 steel by martempering and tempering with those obtained by conventional quenching and tempering.

Table 1 Mechanical properties of 1095 steel heat treated by two methods

Specimen number	Heat treatment	Hardness, HRC	Impact energy		Elongation[(a)], %
			J	ft · lbf	
1	Water quench and temper	53.0	16	12	0

2	Water quench and temper	52.5	19	14	0
3	Martemper and temper	53.0	38	28	0
4	Martemper and temper	52.8	33	24	0

(a) In 25 mm or 1 in.

In many instances, martempering eliminates the need for quenching fixtures that would be required for minimizing distortion during conventional quenching and thus reduces the cost of tooling and handling. However, changing from conventional quenching to martempering may require that dimensional variations in individual parts be studied before preheat-treatment dimensions are established.

Modified martempering differs from standard martempering only in that the temperature of the quenching bath is below the M_s point (Fig. 1c). The lower temperature increases the severity of quenching. This is important for steels of lower hardenability that require faster cooling in order to harden to sufficient depth, or when the M_s is high and some bainite is detrimental to the finished part. Therefore, modified martempering is applicable to a greater range of steel compositions than is the standard process.

Although hot oil is invariably the quenchant employed for modified martempering at 175 °C (350 °F) and lower, molten nitrate-nitrite salts (with water addition and agitation) are effective at temperatures as low as 175 °C (350 °F). Because of their higher heat-transfer coefficients, molten salts offer some metallurgical and operational advantages.

Martempering Media

Molten salt and hot oil are both widely used for martempering. Several factors must be considered when choosing between salt and oil. Operating temperature is the most common deciding factor. Oils are widely used for martempering at up to 205 °C (400 °F) and sometimes at temperatures as high as 230 °C (450 °F). Molten salt is used for martempering in the range of 160 to 400 °C (320 to 750 °F).

Composition and Cooling Power of Salt. A salt commonly used for martempering is composed of 50 to 60% potassium nitrate, 37 to 50% sodium nitrite, and 0 to 10% sodium nitrate. It melts at about 140 °C (280 °F) and may be used within a working range of 165 to 540 °C (325 to 1000 °F). Higher-melting-point (less costly) salts can be used for higher operating temperatures. These salts are comprised of 40 to 50% potassium nitrate, 0 to 30% sodium nitrite, and 20 to 60% sodium nitrate.

The cooling power of agitated salt at 205 °C (400 °F) is about the same as that of agitated oil in conventional oil quenching. Addition of water to salt increases its cooling power, as indicated by the cooling curves for 1045 steel in Fig. 2 and by the hardness values for 1046 steel in Fig. 3. The cooling power of salt is compared with the cooling power of water, and of three types of oil, in Fig. 3.

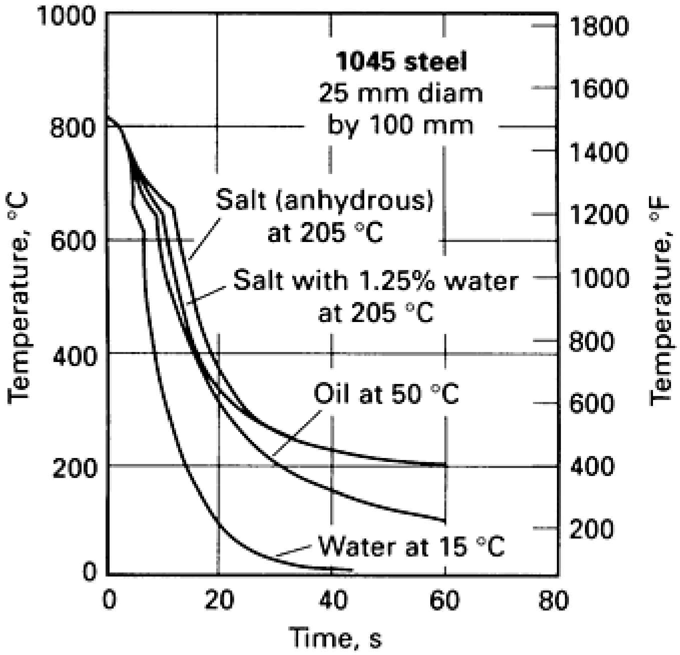


Fig. 2 Cooling curves for 1045 steel cylinders quenched in salt, water, and oil. Thermocouples were located at centers of specimens.

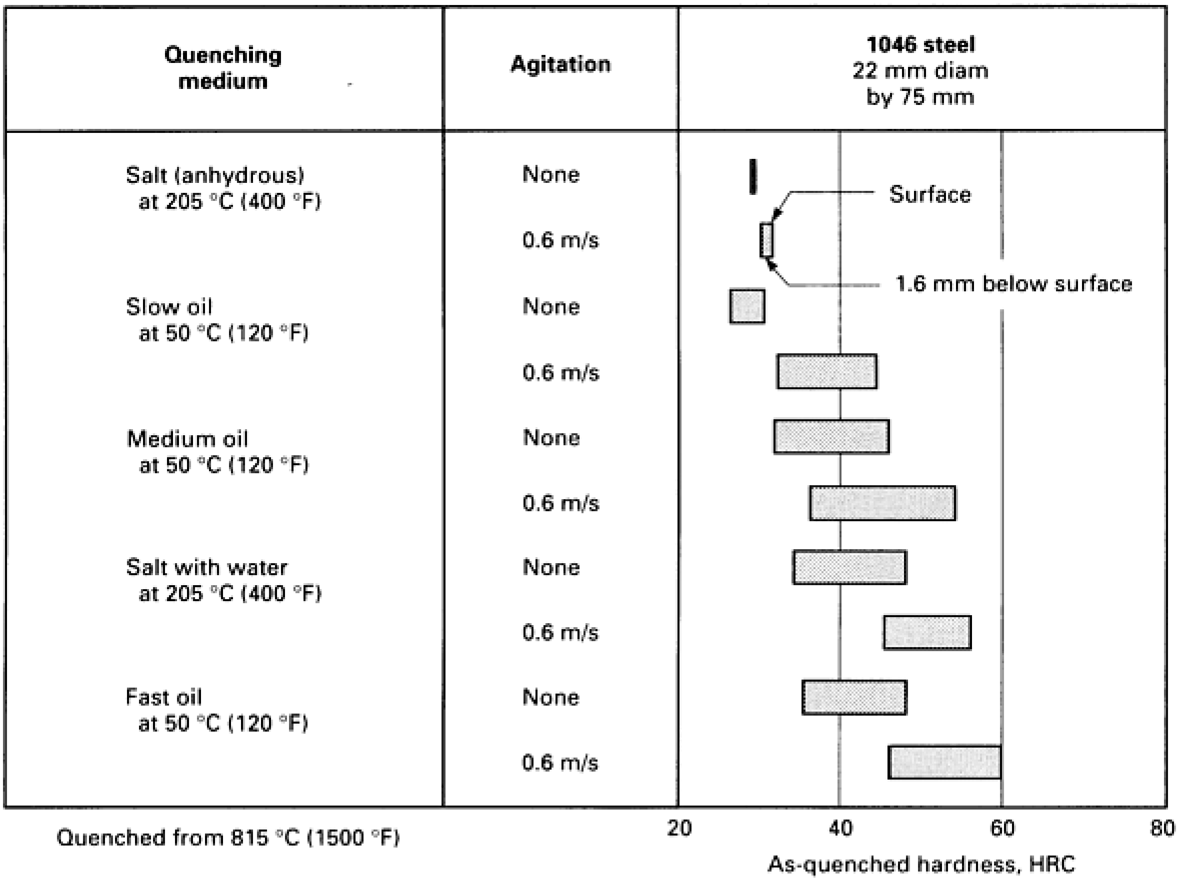


Fig. 3 Effects of quenchant and agitation on hardness of 1046 steel

Advantages of salt in comparison with oil for martempering are as follows:

- The viscosity of salt changes only slightly over a wide temperature range
- Salt retains chemical stability, so that replenishment is usually required only to replace dragout loss. This is not always the case, however. In an installation for high-volume martempering of cylinder liners, for instance, breakdown of the salt did occur, forming a carbonate. This occurred on quenching from an endothermic atmosphere into an open-top salt quench bath at 245 °C (475 °F). The same operation conducted with a nitrogen atmosphere in the heating furnace does not produce such breakdown
- Salt has a wide operating temperature range
- Salt is easily washed from the work with plain water
- Less time is required for workpieces to attain temperature equalization in salt
- No unusual disposal problems attend the rinsing operation
- Salt is relatively easy to handle in powder form and easy to clean up if spilled; however, it is necessary to keep salts separated

Disadvantages of salt in comparison with oil include the following:

- The minimum operating temperature of salt is 160 °C (320 °F)
- Quenching from cyanide-based carburizing salts is hazardous because of possible explosion
- Explosion and splatter of high-temperature salt can occur if wet or oily parts are immersed
- Potentially explosive reactions also occur with sooty atmospheres in atmosphere furnaces connected to martempering salt quenches
- Quench salt can be contaminated by high-temperature neutral salt used for heating. Sludging operations are required to maintain quenching severity

Fluidized Beds. Although fluidized beds are somewhat limited, they have the advantage of equal heat transfer throughout the entire temperature range of quenching. This leads to a quench rate that is reproducible, does not degrade with time, and can be adjusted within wide limits. In addition, fluid beds do not have the environmental drawbacks of oils or salt quenchants.

Oils for Martempering. Physical properties of two oils commonly used for martempering are listed in Table 2. Such oils are compounded especially for martempering, and in comparison with conventional quenching oils, offer higher rates of cooling during the initial stage of quenching.

Table 2 Physical properties of two oils used for martempering of steel

Property	Value, for oil with operating temperature of	
	95 to 150 °C (200 to 300 °F)[a]	150 to 230 °C (300 to 450 °F)
Flash point (min), °C (°F)	210 (410)	275 (525)
Fire point (min), °C (°F)	245 (470)	310 (595)
Viscosity, sus, at:		
38 °C (100 °F)	235-575	. . .

100 °C (210 °F)	50.5-51	118-122
150 °C (300 °F)	36.5-37.5	51-52
175 °C (350 °F)	. . .	42-43
205 °C (400 °F)	. . .	38-39
230 °C (450 °F)	. . .	35-36
Viscosity index (min)	95	95
Acid number	0.00	0.00
Fatty-oil content	None	None
Carbon residue	0.05	0.45
Color	Optional	Optional

(a) Temperature range for modified martempering

Quenching oil requires special handling when used in the temperature range from 95 to 230 °C (200 to 450 °F). To prolong its life, the oil must be maintained under a protective atmosphere (reducing or neutral). Deterioration is accelerated when oil is exposed to air at elevated temperatures. For example, for every 10 °C above 60 °C (every 18 °F above 140 °F), the rate of oxidation is approximately doubled. This causes formation of acid and sludge, which may affect both hardness and color of workpieces.

Example 1: Martempering of Carburized Transmission Components in Oil.

A manufacturer of transmission components and axles martempers carburized parts at a rate of 115 kg/h (250 lb/h) in a 7550 L (2000 gal) oil tank that is completely covered by a vestibule hood and that is located directly beneath the discharge door of the continuous carburizing furnace. The vestibule contains a protective atmosphere consisting of carburizing gases that emanate from the furnace. The vestibule is equipped with an elevator that lowers the tray of parts into the martempering oil.

The ambient temperature in the vestibule immediately above the oil is 89 to 92 °C (193 to 197 °F) when the furnace discharge door is closed. The temperature of the oil is controlled at 150 °C (300 °F). However, during high-production quenching, the temperature of the martempering oil will rise to as high as 165 °C (325 °F). The atmosphere in the vestibule protects the carburized parts and the martempering oil from oxidation. To avoid possible oil fires, the furnace discharge door is closed before the work-load is lowered into the martempering oil.

The martempering oil in this tank has not been replaced in several years of continuous operation (24 h per day, 7 days per week); makeup oil is added to the tank at a rate of about 755 L (200 gal) per month.

Bypass or continuous types of filter units with suitable filtering media (clay, cellulose cartridge, or waste cloth) or centrifugal filtering help prolong oil life and maintain clean work. Filtering units are effective and relatively inexpensive.

Oils should be circulated at a rate no lower than 0.9 m/s (180 ft/mm) to break up excessive vapor that is formed during quenching.

Continuous operation of oils above 205 °C (400 °F) can cause excessive breakdown of the oils unless the correct oil is used for each specific application. Once every one to six months, the oil should be subjected to complete physical and chemical testing to determine its condition. Such testing usually includes determinations of flash point, viscosity, degree of oxidation, quenching effect, contamination, and cooling power.

Advantages of oil in comparison with salt are as follows:

- Oil can be used at lower temperatures
- Oil is easier to handle at room temperature
- Less dragout loss occurs with oil
- Oil is compatible with all austenitizing salts

Disadvantages of oil include the following:

- Oil is limited to a maximum operating temperature of 230 °C (450 °F)
- Oil deteriorates with use, therefore requiring closer control
- When martempered in oil, workpieces require more time to attain temperature equalization
- Oil, whether hot or cold, is a fire hazard
- Soap or an emulsifier is necessary to wash off the oil. Washers must be drained and refilled periodically. Oily wastes create disposal problems

Safety Precautions

In operation of a martempering installation (salt or oil), the precautions appropriate for operating any other hot liquid bath are applicable. The following operator-safety precautions are recommended:

- Operators of equipment should be thoroughly familiar with equipment manufacturer's instructions and with company safety recommendations before attempting to operate or service the equipment
- Operators should wear gloves, face shields, and protective clothing, as required. Safety equipment contaminated with oil or nitrate-nitrite salts should be discarded
- Adequate first aid materials should be available where salts are used, and personnel should be trained and available in treating alkali burns

Nitrate-Nitrite Salts. Several precautions should be taken in operating nitrate-nitrite salt baths:

- All racks, fixtures, and cleaning tools must be thoroughly cleaned of salts (hot water preferred) and thoroughly dried before being reused; otherwise, the presence of salt could contaminate the austenitizing furnace, and residual water could cause spattering of molten salt
- All salt bath furnaces should be labeled so that the proper salt is used. Cyanide-containing salts should not be combined with nitrate-nitrite salts because such mixtures result in explosive reactions. Good house-keeping is essential to prevent accidents. Martempering salts must be stored in closed, well-marked containers. These salts are hygroscopic and will absorb water if exposed. Yellow, orange, or red coloring is commonly used for identification of nitrate-nitrite salts. Cyanide-containing materials may be identified by white, blue, or gray. Color coding is not universally practiced but is strongly recommended. Everyone handling these materials should be familiarized with the explosion hazard of intermixing. For a discussion of attendant hazards and recommended practices, see the sections of this article entitled "Salt Contamination" and "Selection of Austenitizing Equipment"
- When water is added to a nitrate-nitrite salt to increase its quenching severity, the water should be trickled or atomized onto the surface of the bath and should never be introduced below the surface or

under pressure. Otherwise, spattering or eruption can occur. Equipment manufacturers should be consulted as to recommended procedures and hardware
- The salt bath should be equipped with a high-temperature limit controller to prevent the bath from exceeding 595 °C (1100 °F). At higher temperatures, nitrate salts decompose and may cause fire or explosion. Although nitrate-nitrite salts do not burn, they are oxidizing and will support combustion. Therefore, oxidizable materials should not be stored near the bath, and combustible materials should not be introduced into the bath unless designed for the purpose. In the event of a fire, a carbon dioxide extinguisher should be used. Sand is also effective in smothering floor fires. *Caution: To avoid explosive spread of the molten medium, water should never be used to extinguish a fire in or around a molten salt (or molten metal) bath*
- Soot and carbonaceous materials should not be allowed to accumulate on the surface of the molten bath
- Signs are provided by local fire departments for placing on the outside of buildings that house salt baths. These signs tell the fire department what materials are present and what means can be used to extinguish the fire

Hot oil also requires safety precautions. Among the hazards that accompany its use are: fire; overflow caused by the increase in the volume of the oil during heating; explosion, when no atmosphere cover is used over the quench tank; and contamination by water, which can result in fire.

Equipment normally used for protection against these hazards includes:

- Alarm system on temperature-control instrument. (Recommended maximum operating temperature is 55 °C, or 100 °F, below the flash point of the quenching oil.) Often, an additional system is added for maximum temperature alarm
- An oil-level indicator
- If the oil is heated by gas-fired tubes, which are not recommended for heating martempering oils, a safety control system to prevent firing when the air cooling system is off
- Electric heating elements should have a maximum heat flux density of 0.016 $W \cdot mm^{-2}$ (10 $W \cdot in.^{-2}$)
- Expansion system to accommodate the change in volume that occurs when the oil is heated from room temperature to the operating temperature. A suitable system is a small tank equipped with an overflow return line from the main quench tank. The main tank is equipped with a small pump to return the oil from the expansion tank. The capacity of the pump is usually about 20 L/min (5 gal/min)
- A safety control to prevent oil from being heated unless it is agitated
- A carbon dioxide or foam system installed over the quench tank for fire protection
- A water-detection system, with automatic alarm, that monitors the oil for water content

Caution should be used in installing ventilating systems and any other system that could cause addition of water to the hot oil. When an atmosphere is used over the quenching medium, the general safety precautions outlined in the article "Gas Carburizing" should be followed.

Suitability of Steels for Martempering

Alloy steels generally are more adaptable than carbon steels to martempering. In general, any steel that is normally quenched in oil can be martempered. Some carbon steels that are normally water quenched can be martempered at 205 °C (400 °F) in sections thinner than 5 mm ($\frac{3}{16}$ in.), using vigorous agitation of the martempering medium. In addition, thousands of gray cast iron parts are martempered on a routine basis.

The grades of steel that are commonly martempered to full hardness include 1090, 4130, 4140, 4150, 4340, 300M (4340M), 4640, 5140, 6150, 8630, 8640, 8740, 8745, SAE 1141, and SAE 52100. Carburizing grades such as 3312, 4620, 5120, 8620, and 9310 also are commonly martempered after carburizing. Occasionally, higher-alloy steels such as type 410 stainless are martempered, but this is not a common practice.

Success in martempering is based on a knowledge of the transformation characteristics (TTT curves) of the steel being considered. The temperature range in which martensite forms is especially important. Figure 4 shows the martensite temperature ranges for 14 carbon and low-alloy steels. Two trends may be observed in these data: As carbon content increases, the martensite range widens and the martensite transformation temperature is lowered; and the martensite range of a triple-alloy (nickel-chromium-molybdenum) steel is usually lower than that of either a single-alloy or a double-alloy steel of similar carbon content.

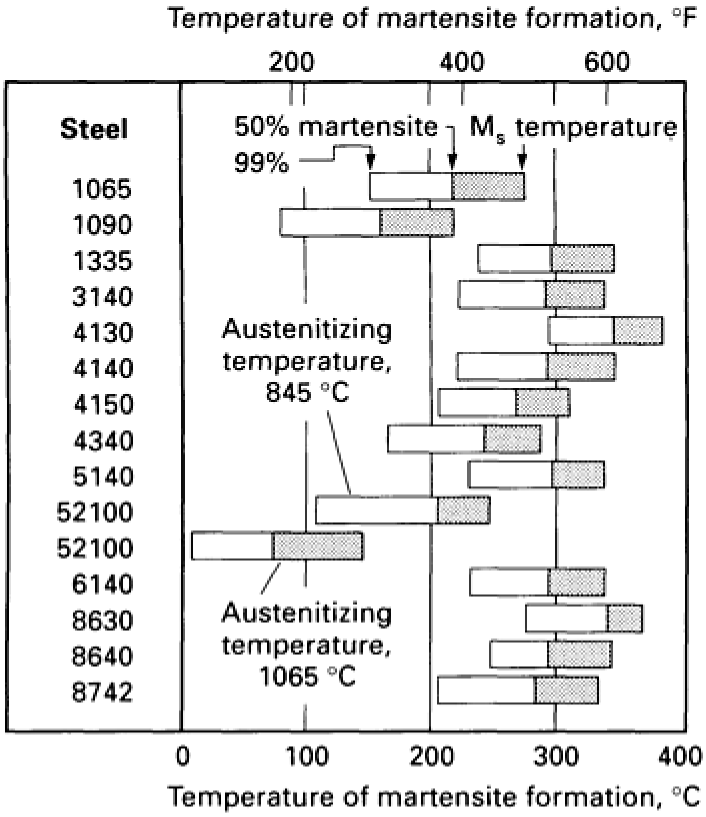


Fig. 4 Temperature ranges of martensite formation in 14 carbon and low-alloy steels

Any steel that is to be martempered successfully must contain sufficient carbon or alloying additions to move the nose of the TTT curve to the right, thus permitting sufficient time for quenching of workpieces past the nose of the TTT curve.

The TTT diagrams for a hypoeutectoid steel (1034), which is discussed later, and a hypereutectoid steel (1090) are shown in Fig. 5. The diagram for 1090 steel is the simplest form of transformation diagram because no proeutectoid constituents (free ferrite or free carbide) are involved in the transformation at temperatures above that corresponding to the nose of the curve. The speed of transformation at the nose is related to the hardenability of the steel; when the nose of the TTT curve is far to the left on the diagram, the steel has lower hardenability; when the nose is to the right, the steel has higher hardenability. To achieve full hardening during quenching, the cooling curve of the steel must pass to the left of the curve farthest to the left on the diagram. In production, some loss in as-quenched hardness is usually accepted in order to achieve minimum distortion.

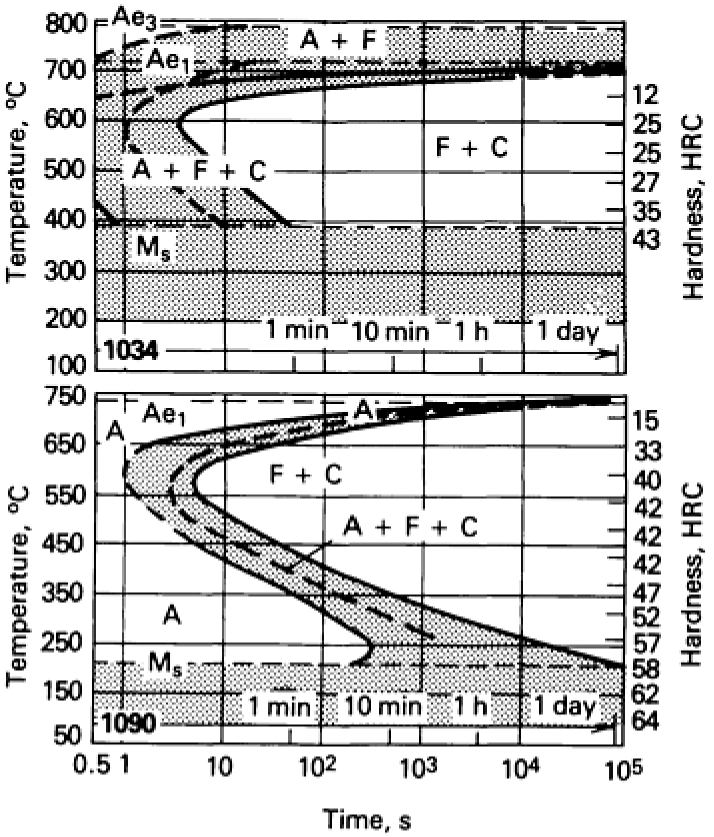


Fig. 5 Time-temperature transformation diagrams for 1034 and 1090 steels. The 1090 steel was austenitized at 885 °C (1625 °F) and had a grain size of 4 to 5.

A TTT diagram for a hypoeutectoid low-alloy steel (5140) suitable for martempering is shown in Fig. 6. The chromium in this steel causes the characteristic shape of the TTT curve near 540 °C (1000 °F).

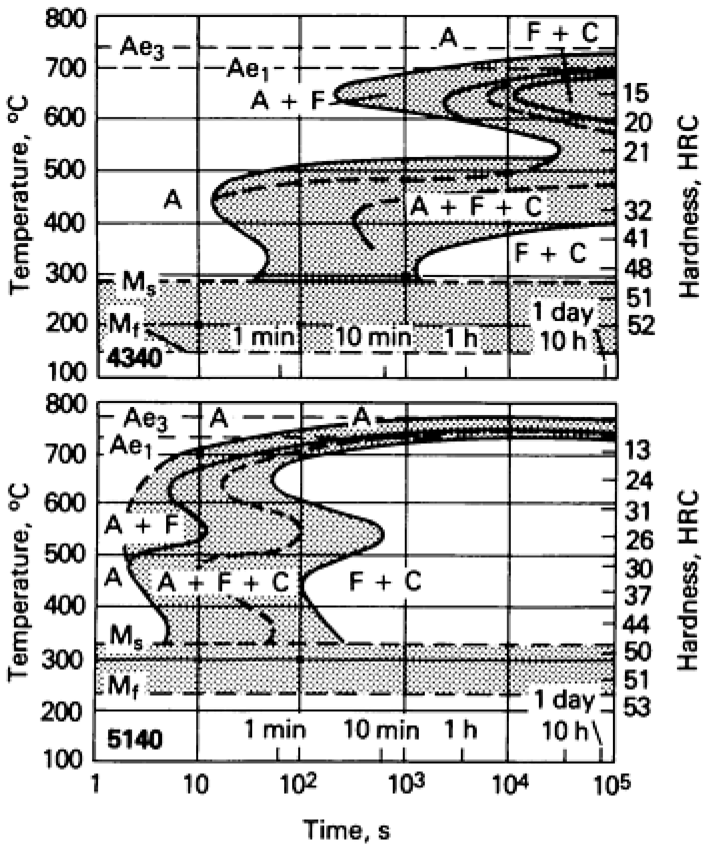


Fig. 6 Time-temperature transformation diagrams for 4340 and 5140 steels. The austenitizing temperature for both steels was 845 °C (1550 °F); grain size was 7 to 8 for 4340 and 6 to 7 for 5140.

The TTT diagram for an extremely high-hardenability steel (4340) is also shown in Fig. 6. The combined effect of nickel, chromium, and molybdenum on hardenability is illustrated in this diagram. These elements cause a double nose on the TTT curve. The nose that occurs at about 480 °C (900 °F) is more significant in martempering than the one occurring near 650 °C (1200 °F). Steels having such high hardenability are easily martempered to fully martensitic structures.

Low-carbon and medium-carbon steels 1008 through 1040 are too low in hardenability to be successfully martempered, except when carburized. The TTT curve for the 1034 steel in Fig. 5 is characteristic of a steel that is unsuitable for martempering; except in sections only a few thousandths of an inch thick, it would be impossible to quench the steel in hot salt or oil without encountering upper transformation products.

Borderline Grades. Some carbon steels higher in manganese content such as 1041 and 1141 can be successfully martempered in thin sections. Low-alloy steels that have limited applications for successful martempering are listed (the lower-carbon grades are carburized before martempering): 1330 to 1345, 4012 to 4042, 4118 to 4137, 4422 and 4427, 4520, 5015 and 5046, 6118 and 6120, 8115.

Most of these alloy steels are suitable for martempering in section thicknesses of up to 16 to 19 mm ($\frac{5}{8}$ or $\frac{3}{4}$ in.). Martempering at temperatures below 205 °C (400 °F) will improve hardening response, although greater distortion may result than in martempering at higher temperatures.

Effect of Mass. The limitation of section thickness or mass must be considered in martempering. With a given severity of quench, there is a limit to bar size beyond which the center of the bar will not cool fast enough to transform entirely to martensite. This is shown in Fig. 7, which compares the maximum diameter of bar that can be hardened by martempering, oil quenching, and water quenching for 1045 steel and five alloy steels of various hardenabilities.

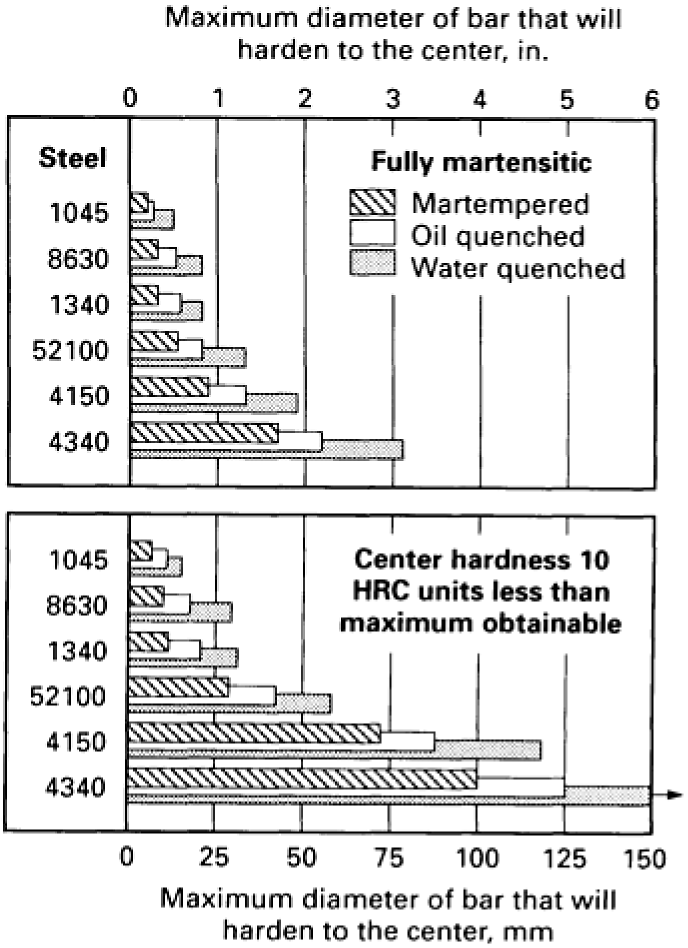


Fig. 7 Approximate maximum diameters of bars that are hardenable by martempering, oil quenching, and water quenching

For some applications, a fully martensitic structure is unnecessary and a center hardness 10 HRC units lower than the maximum obtainable value for a given carbon content may be acceptable. By this criterion, maximum bar diameter is 25 to 300% greater than the maximum diameter that can be made fully martensitic (see lower graph in Fig. 7). Non-martensitic transformation products (pearlite, ferrite, and bainite) were observed at the positions on end-quenched bars corresponding to this reduced hardness value, as follows:

Steel	Transformation
1045	15% pearlite
8630	10% ferrite and bainite
1340	20% ferrite and bainite
52100	50% pearlite and bainite

4150	20% bainite
4340	5% bainite

The influence of mixed structures such as these on the mechanical properties of the steel would have to be determined for each application.

Steels selected for martempering must be judged on hardenability and section size. To form the same amount of martensite for a given section size, the carbon content, alloy content, or both must be somewhat higher for martempering than for conventional (uninterrupted) quenching.

Control of Process Variables

The success of martempering depends on close control of variables throughout the process. It is important that the prior structure of the material being austenitized be uniform. Also, use of a protective atmosphere (or salt) in austenitizing is required because oxide or scale will act as a barrier to uniform quenching in hot oil or salt.

The process variables that must be controlled in martempering include austenitizing temperature, temperature of martempering bath, time in martempering bath, salt contamination, water additions to salt, agitation, and rate of cooling from the martempering bath.

Austenitizing temperature is important because it controls austenitic grain size, degree of homogenization, and carbide solution, and because it affects the M_s temperature, which is important in establishing martempering procedures. As indicated in Fig. 8 for 52100 steel, an increase in austenitizing temperature lowers M_s temperature and increases grain size.

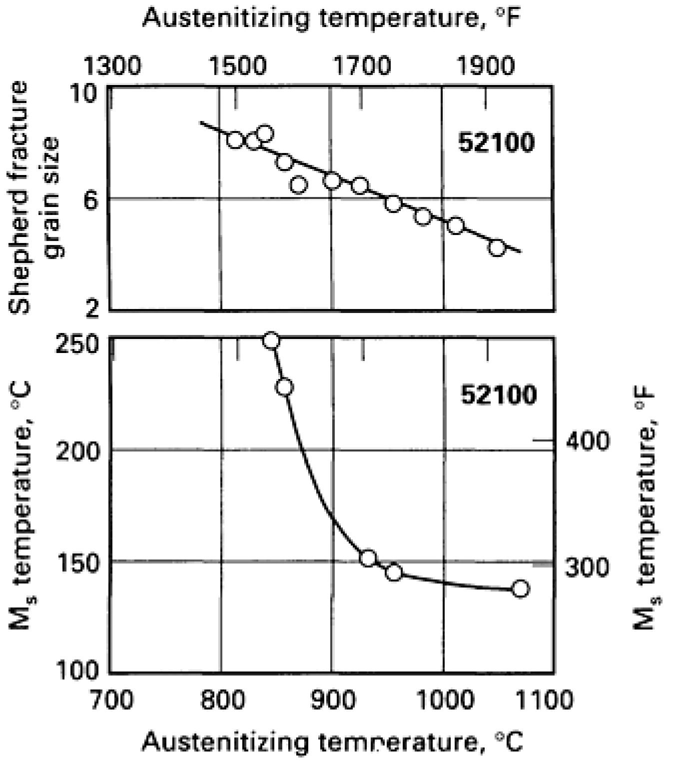


Fig. 8 Effects of austenitizing temperature on grain size and M_s temperature of 52100 steel

Temperature control during austenitizing is the same for martempering as for conventional quenching: A tolerance of 8 °C (15 °F) is common. The austenitizing temperatures most commonly used for several different steels are indicated in Table 3.

Table 3 Typical austenitizing and martempering temperatures for various steels

Grade	Austenitizing temperature		Martempering temperature			
			Oil[(a)]		Salt[(b)]	
	°C	°F	°C	°F	°C	°F
Through-hardening steels						
1024	870	1600	135	275	. . .	. . .
1070	845	1550	175	350	. . .	. . .
1146	815	1500	175	350	. . .	. . .
1330	845	1550	175	350	. . .	. . .
4063	845	1550	175	350	. . .	. . .
4130	845	1550	. . .	. . .	205-260	400-500
4140	845	1550	150	300	. . .	. . .
4140	830	1525	. . .	. . .	230-275	450-525
4340, 4350	815	1500	. . .	. . .	230-275	450-525
52100	855	1575	190	375	. . .	. . .
52100	845	1550	. . .	. . .	175-245	350-475
8740	830	1525	. . .	. . .	230-275	450-525
Carburizing steels						
3312	815	1500	. . .	. . .	175-190	350-375
4320	830	1525	. . .	. . .	175-190	350-375

4615	955	1750	190	375	. . .	. . .
4720	845	1550	. . .	. . .	175-190	350-375
8617, 8620	925	1700	150	300	. . .	
8620	855	1575	. . .	. . .	175-190	350-375
9310	815	1500	. . .	. . .	175-190	350-375

(a) Time is oil varies from 4 to 20 min, depending on section thickness.

(b) Martempering temperature depends on shape and mass of parts being quenched; higher temperatures in range (and sometimes above range) are used for thinner sections and more intricate parts.

In most instances, austenitizing temperatures for martempering are the same as those for conventional oil quenching. Occasionally, however, medium-carbon steels are austenitized at higher temperatures prior to martempering to increase as-quenched hardness.

For carburized parts, low austenitizing temperatures usually yield better size control during martempering. To obtain minimum dimensional changes, the lowest austenitizing temperature that will yield satisfactory core properties should be used. The ratio of case depth to core, as well as the prior processing history of the steel (such as forging, rolling, or drawing), can also be controlling factors, particularly for critical section shapes and sizes. Austenitizing temperatures that have been used for several carburizing steels are indicated in Table 3.

Salt Contamination. When parts are carburized or austenitized in a salt bath, they can be directly quenched in an oil bath operating at the martempering temperature. However, if the parts are carburized or austenitized in salt containing cyanide, they must *not* be directly martempered in salt because the two types of salts are not compatible and explosions can occur if they are mixed. Instead, one of two procedures should be used: Either air cool from the carburizing bath, wash, reheat to the austenitizing temperature for case and/or core in a chloride bath, and then martemper; or quench from the cyanide-containing bath into a neutral chloride rinse bath maintained at the austenitizing temperature and then martemper.

If the latter method is used, it is essential to control the amount of cyanide buildup in the neutral rinse. When tests indicate more than 5% cyanide in the chloride rinse, part of the salt should be discarded and the remainder diluted with new salt.

All fixtures must be thoroughly cleaned after martempering to prevent transfer of quenching salt to either cyanide baths or neutral chloride baths. Mixing of cyanide with nitrate-nitrite salts will cause explosion. A chloride bath that is contaminated with nitrate-nitrite salts will produce pitting and decarburization of parts immersed in it.

Temperature of the martempering bath varies considerably, depending on composition of workpieces, austenitizing temperature, and desired results. In establishing procedures for new applications, many plants begin at 95 °C (200 °F) for oil quenching, or at about 175 °C (350 °F) for salt quenching, and progressively increase the temperature until the best combination of hardness and distortion is obtained. Martempering temperatures (for oil and salt) that represent the experience of several plants are listed in Table 3.

Time in the martempering bath depends on section thickness and on the type, temperature, and degree of agitation of the quenching medium. The effects of section thickness and of temperature and agitation of the quench bath on immersion time are indicated in Fig. 9.

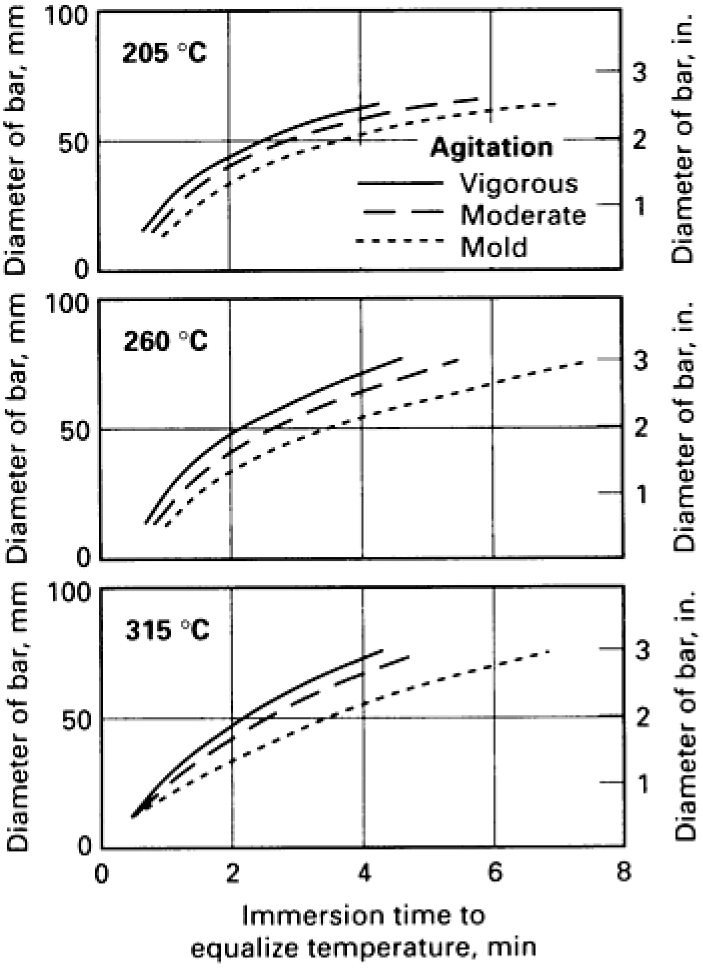


Fig. 9 Martempering time versus section size and agitation of quench bath for 1045 steel bars. Effects of bar diameter and agitation of quench bath on time required for centers of 1045 steel bars to reach martempering temperature when quenched from a neutral chloride bath at 845 °C (1550 °F) into anhydrous nitrate-nitrite martempering salt at 205, 260, and 315 °C (400, 500, and 600 °F). Length of each bar was three times the diameter.

Because the object of martempering is to develop a martensitic structure with low thermal and transformation stresses, there is no need to hold the steel in the martempering bath for extended periods. Excessive holding lowers final hardness because it permits transformation to products other than martensite. In addition, stabilization may occur in medium-alloy steels that are held for extended periods at the martempering temperature.

The martempering time for temperature equalization in oil is about four to five times that required in anhydrous salt at the same temperature. For example, for a 25 mm (1 in.) diam bar martempered in salt at 205 °C (400 °F) with moderate agitation, the customary immersion time is about $1\frac{1}{2}$ to 2 min, whereas about 8 to 10 min are required for the bath to attain temperature equalization in oil at 205 to 220 °C (400 to 425 °F). The immersion time required in salt can be reduced by as much as 50% by addition of 0.5 to 2% water.

Water Additions to Salt. The quenching severity of a nitrate-nitrite salt can be increased significantly by careful addition of water. Agitation of the salt is necessary to disperse the water uniformly, and periodic additions are needed to maintain required water content. The water can be added with complete safety as follows:

- Water can be misted at a regulated rate into a vigorously agitated area of the molten bath
- In installations where the salt is pump circulated, returning salt is cascaded into the quench zone. A controlled fine stream of water can be injected into the cascade of returning salt

- The austempering bath can be kept saturated with moisture by introducing steam directly into the bath. The steam line should be trapped and equipped with a discharge to avoid emptying condensate directly into the bath
- Steam addition of water to the bath is done on baths with operating temperatures above 260 °C (500 °F)

The addition of water to increase the severity of salt is usually made by directing a stream of water onto the molten salt at the agitator vortex. A protective shroud surrounds the water spray to prevent spattering (see the section "Safety Precautions" in this article). The turbulence of the salt carries the water into the bath without spattering or hazard to the operator. Water should never be added to a salt bath from a pail or dipper.

Water is continuously evaporating from the bath surface, and the rate of evaporation increases during quenching of hot work. Therefore, it is necessary to add water periodically to maintain the water concentration and a uniform quenching severity. The amount of water to be added varies with the operating temperature of the salt, as indicated by the following recommended concentrations:

Temperature		**Water concentration, %**
°C	**°F**	
205	400	$\frac{1}{2}$-2
260	500	$\frac{1}{2}$-1
315	600	$\frac{1}{4}$-$\frac{1}{2}$

At present, there is no known means of automatically controlling the concentration of water in molten nitrate-nitrite salt. Water is usually controlled at the discretion of the operator, who will add water as needed. On the basis of experience, however, it is possible to anticipate the need for water; here the addition of water may be simplified by use of timers that can be adjusted to time the frequency and duration of water additions.

The presence of water is visually detectable by the operator because steam is released when the hot work is immersed into the nitrate-nitrite salt. The steam causes a visible mounding of the salt above the quench area, and there is a characteristic sizzling caused by the vapor phase.

Besides visual appearance, periodic hardness checks of the work will indicate the activity of the bath. A more exact determination can be made by removing a small quantity of the salt and weighing it accurately before and after dehydrating it by heating to 370 to 425 °C (700 to 800 °F). Another method is to determine the freezing point of a small sample and to then refer to a published curve that relates freezing point to water content for that specific salt.

The use of periodic histograms is another method for determining the quenching effect of the marquench bath. Complete statistical process control is the best method to ensure consistency of the marquench process.

Agitation of the martempering salt or oil considerably increases the hardness obtainable for a given section thickness, in comparison to that possible in still quenching. This is demonstrated in Fig. 10, which presents data for 52100 steel that relate section thickness, hardness, and agitation.

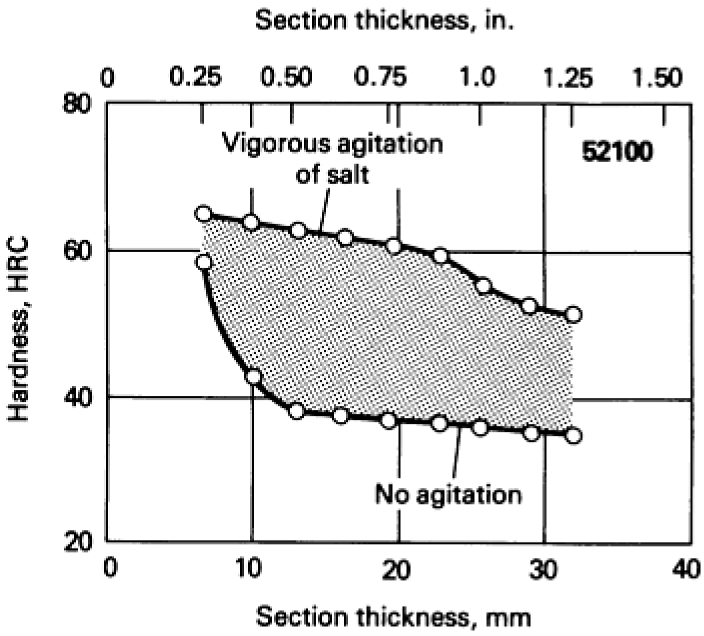


Fig. 10 Influence of agitation on surface hardness of 52100 steel in various section thicknesses martempered in hot salt

In some instances, the rapid cooling produced by the most vigorous agitation increases distortion. Thus, mild agitation is often used in combination with water addition to obtain minimum distortion without sacrificing hardness.

Cooling from the martempering bath ordinarily is done in still air to avoid large differences in temperature between the surface and the interior of the steel. Forced-air cooling by means of fans is occasionally used on sections over 19 mm ($\frac{3}{4}$ in.) thick, but caution is required if the part varies in section thickness or has more surface exposed on one section, such as on threads or serrations, because objectionable amounts of distortion can occur on rapid cooling through the martensite range. Generally, cooling of workpieces in cool oil or water after removal from the martempering bath is considered undesirable because cooling can reestablish thermal gradients and unequal stress patterns that can increase distortion.

Cooling time varies with the mass and density of the charge, the maximum section thickness of the workpiece, and the ambient air temperature. Usually, production loads of 365 to 815 kg (800 to 1800 lb) from either continuous or batch-type furnaces will require $2\frac{1}{2}$ to 5 h to reach room temperature. Figure 11 shows the effect of section thickness. As indicated, the 25 mm (1 in.) diam sections were completely cooled in about half the time required for complete cooling of the 75 mm (3 in.) diam sections.

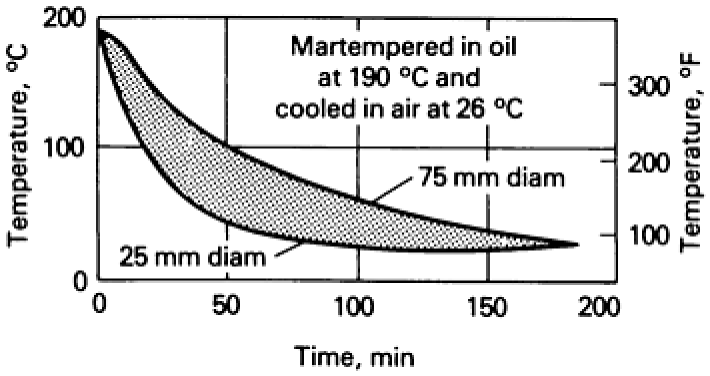


Fig. 11 Effect of section thickness on time required for air cooling of steel after martempering at 190 °C (375 °F). Temperature measurements were made at the surface. Times can be reduced by approximately 30% by forced fan cooling.

After being cooled to room temperature, martempered parts usually can be held at room temperature for several hours, and sometimes days, without risk of cracking because residual stresses are low compared to those in conventionally quenched parts. Holding of parts at room temperature also permits more nearly complete transformation of steels in which transformation is sluggish.

Dimensional Control

In many instances, distortion is significantly lower in martempered parts than in parts hardened by uninterrupted (conventional) quenching. However, prior processing often has a significant effect on distortion, regardless of the heat-treating method used. Therefore, for some applications martempering may fail to solve distortion problems because excessive dimensional changes occurred during heating prior to martempering.

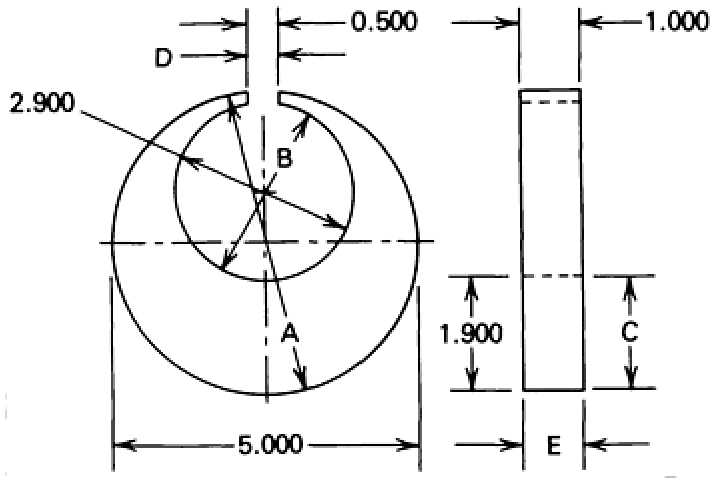
Occasionally, it is necessary to consider the effects of fabricating stresses that occur during forging, stamping, rolling, and machining. When the workpiece is heated, these stresses can cause a significant amount of distortion. A process anneal at 650 to 705 °C (1200 to 1300 °F) after rough machining or forming usually will relieve such stresses. Any resulting change in the size or shape of the part can then be corrected by finish machining prior to austenitizing and martempering. During heating, distortion also can occur as the result of temperature differences in a part having both light and heavy sections. This condition is often corrected by preheating at 650 to 705 °C (1200 to 1300 °F) prior to austenitizing.

Relatively large parts that require extreme flatness often must be press quenched. For example, a gear 178 mm (7 in.) in diameter, 13 mm ($\frac{1}{2}$ in.) thick at the rim, and with a 6.4 mm ($\frac{1}{4}$ in.) web could not be martempered with an acceptable degree of flatness. A large ring gear with internal teeth and a thin wall is another part for which martempering has been replaced by press quenching to obtain dimensions within acceptable limits.

The following examples describe specific situations in which distortion problems have been encountered. In some instances, the effects (on identical parts) of martempering and of oil quenching are presented for comparison.

Example 2: Comparison of Distortion in Navy C Specimens after Conventional Quenching and Martempering.

Figure 12 shows data for nine Navy C specimens made of a high-carbon alloy steel containing 0.95% C, 0.30% Si, 1.20% Mn, 0.50% W, 0.50% Cr, and 0.20% V were austenitized for 40 min at 845 °C (1550 °F); three of the specimens were subjected to conventional quenching in oil at 60 °C (140 °F), three were martempered for 2 min in salt at 205 °C (400 °F), and three were martempered for 2 min in salt at 245 °C (475 °F). Each quenching medium was agitated vigorously. All specimens were tempered to 63 to 64 HRC before being measured for dimensional changes.



Type of quench	Dimensional change, mm (mil)				
	A	B	C	D	E
Conventional (oil at 60 °C, or 140 °F)	0.21 (8.3)	0.24 (9.5)	0.20 (8.0)	0.61 (24)	0.075 (3)
Martempering in salt at 205 °C (400 °F)	0.137 (5.2)	0.15 (6)	0.13 (5)	0 (0)	0.025 (1)

Fig. 12 Dimensional changes in Navy C specimens austenitized at 1550 °F and quenched in three vigorously agitated mediums (Example 2). Figure dimensions given in inches

The data accompanying Fig. 12 indicate that the martempered specimens--especially those quenched in salt at 245 °C (475 °F)--exhibited less distortion in every dimension. These test results indicate that lower stresses result from martempering than from conventional oil quenching.

Example 3: Martempering of Bearing Races for Distortion Control.

Bearing races, 215 mm ($8\frac{3}{8}$ in.) in outside diameter by 190 mm ($7\frac{1}{2}$ in.) in inside diameter by 130 mm ($5\frac{1}{8}$ in.), made of 52100 steel, were austenitized in chloride salt at 850 °C (1560 °F) for 25 min, martempered in salt at 230 °C (450 °F) for $2\frac{1}{2}$ min, and air cooled to room temperature. The resulting hardness was 63 to 64 HRC. This treatment produced an average growth of 0.08 mm (0.003 in.) and an average distortion (out-of-roundness) of 0.25 mm (0.010 in.). Prior to heat treatment, the machined races had an average out-of-roundness of 0.18 mm (0.007 in.). Thus, the average increase in out-of-roundness was only 0.08 mm (0.003 in.).

In this application, martempering reduced grinding time from 50 to 7 min per race by permitting a reduction in the grinding stock required for conventionally oil-quenched parts.

Example 4: Warpage of Oil-Quenched Rods.

Rods 6.4 mm ($\frac{1}{4}$ in.) in diameter by 255 mm (10 in.) long, with a 3.2 mm ($\frac{1}{8}$ in.) hole near one end, were made from oil-hardening drill rod. The requirements were a hardness of 60 to 62 HRC and maximum warpage of 0.25 mm (0.010 in.) (indicator reading between centers).

The rods were heated by being suspended in a salt bath at 805 °C (1480 °F), and then were quenched in oil at 55 °C (135 °F). This treatment produced the required hardness, but warpage was excessive (up to 0.76 mm, or 0.030 in.). The problem was solved by replacing oil quenching with martempering in unagitated salt at 175 °C (350 °F).

Example 5: Martempering of Carburized Gears to Reduce Distortion.

Figure 13 shows a thin-wall ring gear of 8625 steel, with a flange on one end, that had to be carburized to a depth of 1.3 mm (0.050 in.) and hardened. After carburizing followed by martempering in oil at 190 °C (375 °F), out-of-roundness ranged from 0.43 to 0.66 mm (0.017 to 0.026 in.), which was not acceptable. The problem was solved by martempering and then placing the ring gears over a plug machined to the final inside diameter of the gear for cooling to room temperature. This produced acceptable parts having a maximum runout of 0.09 mm (0.0035 in.). The runout for eight gears tested before heat treating and after plug cooling is indicated in Fig. 13.

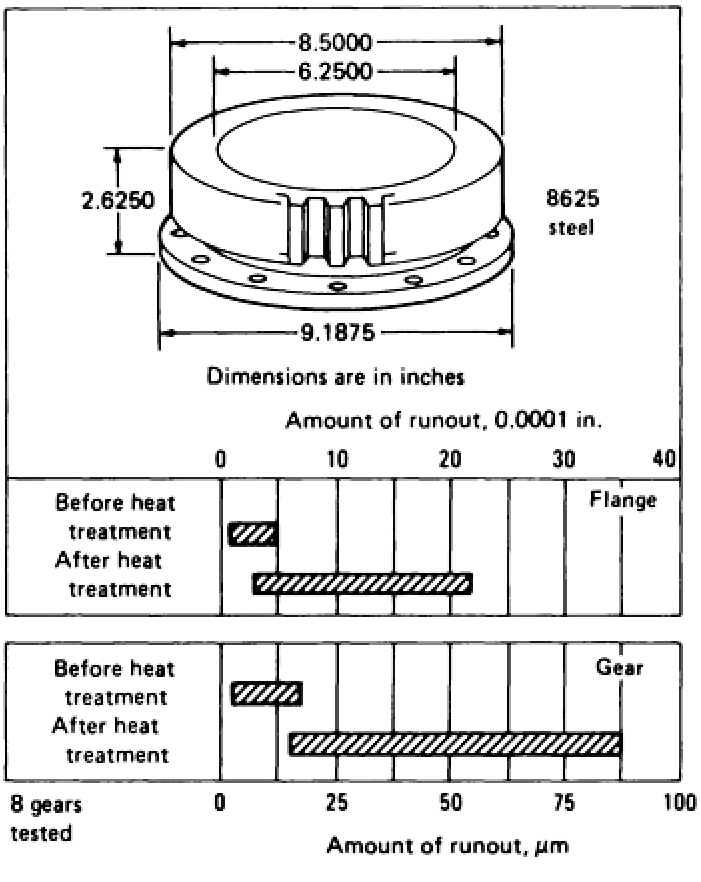


Fig. 13 Control range for 8625 steel ring gears (Example 5). Eight ring gears made of 8625 steel were carburized to a depth of 1.3 mm (0.050 in.), martempered in oil at 190 °C (375 °F), and placed on a plug for cooling to room temperature. Measurements are total indicator readings.

Figure 14 indicates the dimensional changes that occurred when different types and sizes of gears made of 8625H steel were carburized at 925 °C (1700 °F) to a depth of 1.0 to 1.5 mm (0.040 to 0.060 in.) and then martempered in oil at either 165 or 190 °C (325 or 375 °F).

Gear No.	Before treating		After treating		Weight	
	mm	in.	mm	in.	kg	lb
Size over pins						
1	99.95–100.00	3.9349–3.9370	100.02–100.06	3.9378–3.9395	2.15	4.75
2	119.85–119.91	4.7184–4.7208	119.90–119.97	4.7205–4.7234	2.38	5.25
3	163.59–163.65	6.4407–6.4429	163.69–163.76	6.4444–6.4473	2.15	4.75
4	176.53–176.63	6.9501–6.9538	176.57–176.71	6.9517–6.9569	4.31	9.50
5	234.19–234.28	9.2200–9.2235	234.17–234.30	9.2194–9.2245	4.54	10
Rolling						
1	0.008–0.023	0.0003–0.0009	0.043–0.061	0.0017–0.0024	2.15	4.75
2	0.005–0.018	0.0002–0.0007	0.018–0.084	0.0007–0.0033	2.38	5.25
3	0.020–0.041	0.0008–0.0016	0.025–0.061	0.0010–0.0024	2.15	4.75
4	0.008–0.043	0.0003–0.0017	0.010–0.046	0.0004–0.0018	4.31	9.50
5	0.013–0.038	0.0005–0.0015	0.018–0.081	0.0007–0.0032	4.54	10

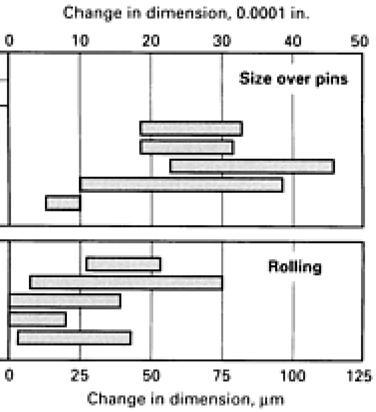


Fig. 14 Dimensional changes in carburized and martempered gears of 8625H steel (Example 5). All gears were carburized at 925 °C (1700 °F) to a depth of 1.0 to 1.5 mm (0.040 to 0.060 in.) and martempered directly from the carburizing temperature in oil at 165 °C (325 °F). Gears 1, 2, and 5 were measured over 7.32 mm (0.288 in.) diam pins; gear 3 over 3.66 mm (0.144 in.) diam pins; and gear 4 over 8.78 mm (0.3456 in.) diam pins.

Figure 15 shows the dimensional changes that were encountered in carburizing and martempering seven different sizes of automatic-transmission gears made of 8620H steel. The gears were martempered in oil at 150 °C (300 °F). Shrinkage of the largest gear is associated with lower core hardness in the considerably heavier section of the gear.

Gear No.	Before treating		After treating	
	mm	in.	mm	in.
Size over 7.32 mm diam pins				
1	153.77–153.86	6.0540–6.0575	153.86–153.95	6.0575–6.0610
2	153.70–153.77	6.0513–6.0538	153.77–153.87	6.0540–6.0580
3	166.32–166.34	6.5480–6.5490	166.40–166.43	6.5513–6.5525
4	191.75–191.81	7.5493–7.5515	191.85–191.92	7.5530–7.5560
5	200.25–200.28	7.8840–7.8850	200.34–200.38	7.8873–7.8888
6	213.10–213.13	8.3898–8.3910	213.18–213.23	8.3930–8.3950
7(a)	317.58–317.73	12.5030–12.5090	317.55–317.70	12.5020–12.5080
Out-of-roundness				
1	0.000–0.000	0.0000–0.0000	0.000–0.033	0.0000–0.0013
2	0.000–0.005	0.0000–0.0002	0.025–0.051	0.0010–0.0020
3	0.000–0.008	0.0000–0.0003	0.000–0.030	0.0000–0.0012
4	0.000–0.000	0.0000–0.0000	0.005–0.025	0.0002–0.0010
5	0.000–0.008	0.0000–0.0003	0.005–0.020	0.0002–0.0008
6	0.000–0.005	0.0000–0.0002	0.013–0.038	0.0005–0.0015
7	0.000–0.013	0.0000–0.0005	0.000–0.018	0.0000–0.0007

(a) Size over 12.2 mm (0.480 in.) diam pins

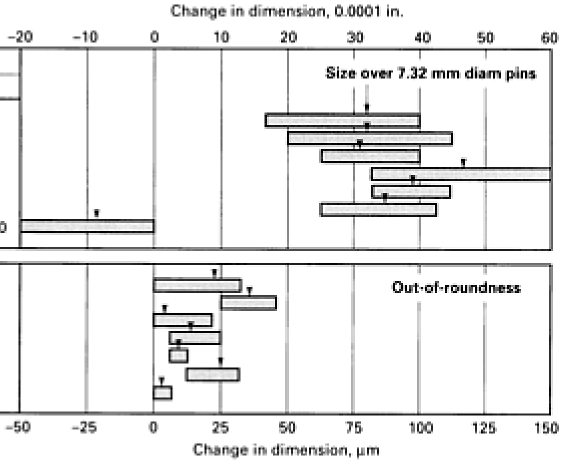


Fig. 15 Dimensional changes in carburized and martempered automatic-transmission gears made of 8620H steel. All gears were carburized at 925 °C (1700 °F) and then martempered directly from the carburizing temperature in oil at 150 °C (300 °F).

Figure 16 indicates the effects of various combinations of carburizing and quenching methods on the dimensions of 25-tooth reverse-idler gears for power-grader transmissions. All gears were carburized to a depth of 0.76 to 1.0 mm (0.030 to 0.040 in.). The smallest dimensional changes occurred in gears that were liquid carburized and then martempered in salt at 205 °C (400 °F); the greatest changes occurred in those that were gas carburized and quenched in agitated oil at 45 °C (110 °F).

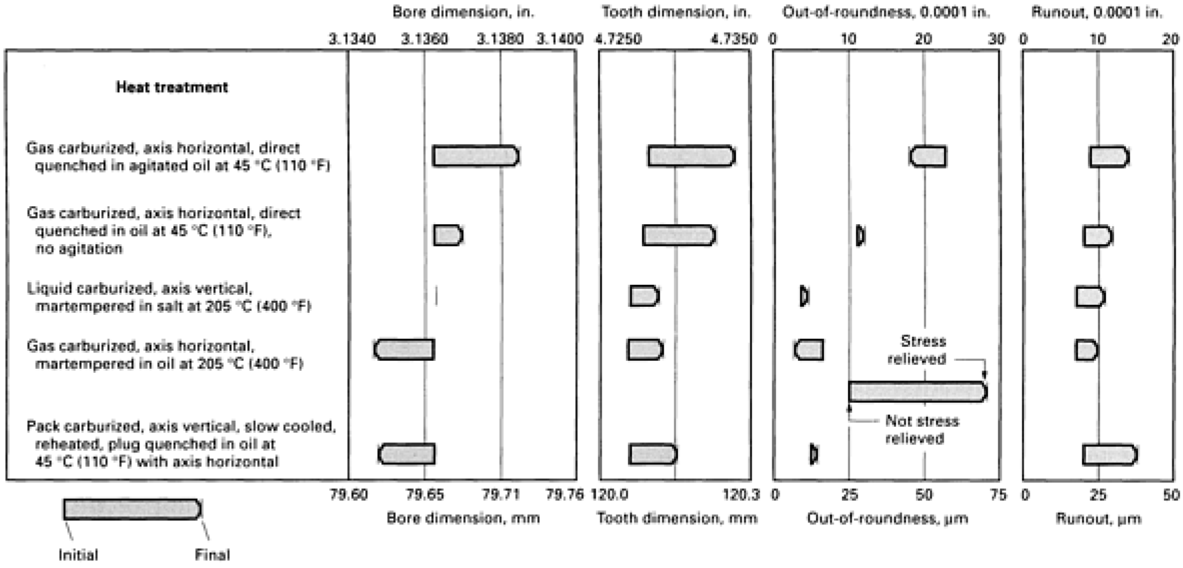


Fig. 16 Effects of various carburizing and quenching methods on dimensions of 4620H steel reverse-idler gears for power-grader transmissions. Gears were carburized to a depth of 0.8 to 1.0 mm (0.030 to 0.040 in.) and quenched to a hardness of 58 to 63 HRC.

The effect of stress relieving on out-of-roundness is also indicated in Fig. 16. The data for bore, teeth, and runout are for gears that were stress relieved before heat treating.

Example 6: Distortion in Martempering of 8625 Steel Shafts.

Figures 17 and 18 are histograms of distortion data, in terms of total indicator readings, for various shafts made of 8625 steel. The shafts depicted in Fig. 17 were machined from bar stock, whereas those in Fig. 18 were forged. All shafts were carburized at 925 °C (1700 °F) and martempered in oil at 165 °C (325 °F). Also, all shafts were in the vertical position during heat treating--some suspended, and some supported on one end--as indicated in Fig. 17 and 18.

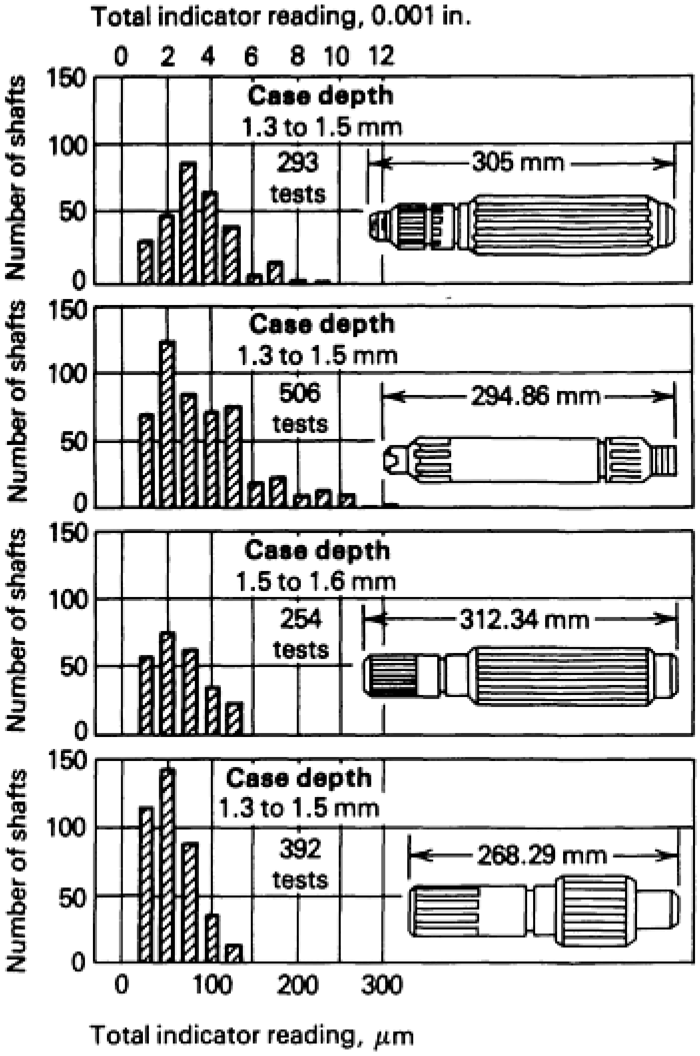
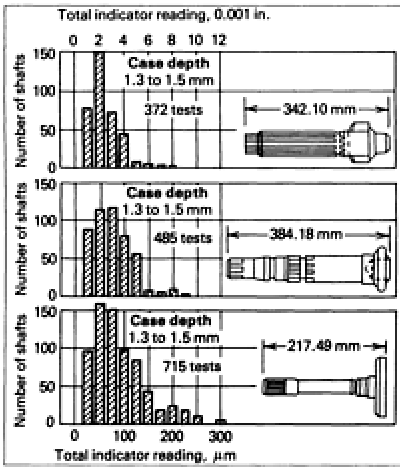


Fig. 17 Distortion in martempering (Example 6). Histograms of distortion data on shafts of 8625 steel (machined from bar stock) after carburizing at 925 °C (1700 °F) and martempering in oil at 165 °C (325 °F). Shafts were heat treated in the vertical position: the top two shafts were suspended vertically from the threaded end; the lower two shafts were supported on one end.



Type of quench	Dimensional change									
	A		B		C		D		E	
	μm	0.0001 in.	μm	0.0001 in.	μm	0.0001 in.	μm	0.0001 in.	μm	0.0001 in.
Conventional, oil at 60 °C (140 °F)	210	83	240	95	205	80	610	240	75	30
Martempering in salt at										
205 °C (400 °F)	130	52	150	60	125	50	0	0	25	10
245 °C (475 °F)	115	45	75	30	2.5	1	−50	−20	25	10

Type of quench	Dimensional change									
	A		B		C		D		E	
	µm	0.0001 in.	µm	0.0001 in.	µm	0.0001 in.	µm	0.0001 in.	µm	0.0001 in.
Conventional, oil at 60 °C (140 °F)	210	83	240	95	205	80	610	240	75	30
Martempering in salt at										
205 °C (400 °F)	130	52	150	60	125	50	0	0	25	10
245 °C (475 °F)	115	45	75	30	2.5	1	-50	-20	25	10

Fig. 18 Distortion in martempering (Example 6). Histograms of distortion data on forged shafts of 8625 steel after carburizing at 925 °C (1700 °F) and martempering in oil at 165 °C (325 °F). Shafts were supported vertically on one end during heat treatment.

Stabilizing after Martempering. Parts such as shafts, chain-saw guides, washers, and springs require straightening or re-forming after heat treatment. This is sometimes not feasible after normal quenching and tempering. However, after such parts are removed from a martempering bath, straightening is readily accomplished, either by hand pressure or in a die press, while the parts are still essentially austenitic.

When parts are clamped between plates held at approximately 150 °C (300 °F), the parts cool to the temperature of the plate. At this temperature, depending on the M_f temperature of the steel, the transformation to martensite may be only partial, but it is usually near enough to completion for the part to set permanently before it is removed from the clamped position. At this temperature, the film of salt (melting point, about 145 °C, or 290 °F) adhering to the part will not freeze, and therefore removal of the part from the clamps or die can be accomplished without difficulty. The transformation of martensite is completed during subsequent air cooling to room temperature, and the part is within dimensional tolerance.

Forming after Martempering. Difficult-to-form materials, such as hot-work die steels (H11) and some martensitic stainless steels used for missiles, rockets, and high-speed aircraft, can be accurately formed and hardened by austenitizing, martempering, and hot forming to shape immediately after they are extracted from the quench bath, if the martempering temperature is above the martensite transformation temperature for the specific alloy being treated. During hot forming by rolling, forging, drawing, or extruding, the metal consists of metastable austenite, which transforms to martensite on subsequent cooling to room temperature.

Parts of both simple and complex shape have been formed in this manner; after being air cooled to room temperature in or out of the forming die, the parts will accurately maintain their as-formed dimensions and yet be in the fully heat-treated condition, requiring only a subsequent tempering operation.

This method of heat treating and forming has been successfully applied to sheet and plate that require nearly perfect flatness. It also has been used for forming type 420 stainless steel sheet into cups that require close dimensional tolerances and hardness values of 55 to 58 HRC. Working of metastable H11 that results in deformation of 58 to 94% at 480 °C (900 °F) produces a 19 to 32% increase in tensile strength.

Applications

Typical applications of martempering in salt and oil are indicated in Tables 4 and 5, which list and describe steel parts commonly treated and give details of martempering procedures and hardness requirements. From these tables, it is evident that martempering is used for parts of diverse shapes, weights, section sizes, and steel compositions.

Table 4 Typical applications of martempering steel parts in salt

Part	Grade	Maximum section thickness		Weight		Martempering conditions			Required hardness, HRC
						Temperature of salt		Minimum time in salt, min	
		mm	in.	kg	lb	°C	°F		
Compliant tube	4130	0.8	0.03	0.11	0.25	160[a]	320[a]	5	50[b]
Thrust washer	8740	5.1	0.20	0.05	0.1	230	450	1	52 min[b]
Chain link	1045	5.6	0.22	0.11	0.25	205[c]	400[c]	1	45-50[b]
Cotton-picker spindle[d]	Type 410	6.4	0.25	0.05	0.12	315	600[c]	$1\frac{1}{2}$	44-48[b]
Accessory drive shaft	9310[e]	6.4	0.25	0.45	1.0	190	375	$2\frac{1}{2}$	90 (15N scale)
Clutch-adjustment nut	8740	7.6	0.30	0.14	0.3	230	450	2	52 min[b]
Seal ring	52100	7.6	0.30	0.18	0.4	190	375	10	65[b]
Spur pinion	3312[e]	7.6	0.30	0.23	0.5	175	350	$1\frac{1}{2}$	90 (15N scale)
Internal gear	4350	8.9	0.35	0.36	0.8	245	475	2	54 min[b]
Dual gear[f]	4815[e]	9.4	0.37	2.13	4.7	260	500	2	62-63[b]
Drive coupling	4340	10.2	0.40	0.27	0.6	230	450	$2\frac{1}{2}$	52 min[b]
Spline shaft	8720[e]	10.2	0.40	0.50	1.1	190	375	$2\frac{1}{2}$	90 (15N scale)
Arbor sleeve	1117L[e]	10.2	0.40	0.59	1.3	205	400	3	. . .

Screw-machine spindle	8620[e]	10.2	0.40	6.35	14.0	205	400	3	. . .
Driving barrel	4350	12.7	0.50	0.45	1.0	245	475	3	48-52[g]
Bearing race[h]	52100	12.7	0.50	13.2	29.2	220	425	$2\frac{1}{2}$	63-64[b]
Hog knife	9260	15.2	0.60	8.16	18.0	175[i]	350[i]	15	62[b]
Landing-gear spring	6150	19.1	0.75	14.7	32.5	260	500	$2\frac{3}{4}$	56-57[b]
Internal gear	1117L[e]	25.4	1.00	1.36	3.0	205	400	3	. . .
Spur pinion gear[j]	4047	25.4	1.00	16.4	36.2	230[c]	450[c]	3	50-52[k]
Screw-machine sprocket	8620[e]	38.1	1.50	9.07	20.0	205	400	3	. . .

Note: OD, outside diameter: ID, inside diameter.

(a) Salt contained $1\frac{1}{2}$% water.

(b) As-quenched.

(c) Salt contained water.

(d) 6.4 mm ($\frac{1}{4}$ in.) diam by 203 mm (8 in.) long.

(e) Carburized.

(f) 124 mm ($4\frac{7}{8}$ in.) OD by 32 mm ($1\frac{1}{4}$ in.) ID by 102 mm (4 in.).

(g) Final.

(h) 224 mm ($8\frac{13}{16}$ in.) ID by 251 mm ($9\frac{7}{8}$ in.) OD.

(i) Salt contained 1% water.

(j) 19 mm ($\frac{3}{4}$ in.) OD by 92 mm (5 $\frac{5}{8}$ in.) ID by 140 mm (5 $\frac{1}{2}$ in.).

(k) As-quenched hardness of teeth

Table 5 Typical applications of martempering steel parts in oil

Part	Grade	Maximum section thickness		Outside diameter		Weight		Carburizing temperature, °C	Depth of case		Quenching, temperature, °C	Temperature of martempering oil[(a)], °C	Surface hardness, HRC
		mm	in.	mm	in.	kg	lb		μm	0.001 in.			
Sleeve	52100	3.2	0.125	. . .	. . .	0.1	$\frac{1}{4}$	. . .	. . .	. . .	790	165	58-59
Spacer plate	1065	3.2	0.125	. . .	. . .	0.1	$\frac{1}{4}$	. . .	. . .	. . .	790	165	56-57
Bushing	1117	4.8	0.1875	51.0	2.009	0.2	$\frac{1}{2}$	910	1015-1220	40-48	910	190	58-62
	1117	6.4	0.25	76.3	3.0034	0.6	$1\frac{1}{4}$	910	1015-1220	40-48	910	190	55-60
Shifter rail	1018	9.5	0.375	. . .	. . .	1.0	$2\frac{1}{8}$	845[(b)]	255-455	10-18	845	165	55-60
	1018	9.5	0.375	. . .	. . .	1.4	$3\frac{1}{8}$	845[(b)]	355-610	14-24	845	165	55-60
Spur gear	8620	12.7	0.5	320.6	12.620	12.7	28	925	1145-1525	45-60	845	150	55-60
Helical gear	4620H	19.1	0.75	331.5	13.050	16.9	37.2	925	760-1015	30-40	845	150	58-63

Part	**Grade**	**Maximum section thickness**		**Outside diameter**		**Weight**		**Carburizing temperature, °C**	**Depth of case**		**Quenching, temperature, °C**	**Temperature of martempering oil[(a)], °C**	**Surface hardness, HRC**
		mm	**in.**	**mm**	**in.**	**kg**	**lb**		**μm**	**0.001 in.**			
Herringbone gear	4820	19.1	0.75	283.2	11.150	16.3	36	925	1145-1525	45-60	845	150	55-61
Shifter rail	1141	25.4	1.0	25.4	1.0	0.9	$1\frac{7}{8}$	885[(b)]	455-660	18-26	885	165	45-50
Spiral bevel gear	4620	25.4	1.0	210.6	8.29	5.1	11.25	925	1015-1270	40-50	845	150	55 min
Helical pinion	8617H	25.4	1.0	35.8	1.409	0.4	0.9	925	510-710	20-28	845	150	58-63
Spur gear	8625	31.8	1.250	83.8	3.300	4.3	$9\frac{3}{8}$	925	1525-1725	60-68	925	190	58-62
	4817H	34.0	1.340	186.7	7.350	8.6	19	925	1400-1780	55-70	845	150	58-63
	8625	38.1	1.500	165.1	6.500	2.5	$5\frac{1}{2}$	925	1525-1725	60-68	925	190	58-62
Splined shaft	8625	39.7	1.564	39.7	1.564	2.7	$5\frac{7}{8}$	925	1400-1980	70-78	925	190	58-62

Part	Grade	Maximum section thickness		Outside diameter		Weight		Carburizing temperature, °C	Depth of case		Quenching, temperature, °C	Temperature of martempering oil[(a)], °C	Surface hardness, HRC
		mm	in.	mm	in.	kg	lb		µm	0.001 in.			
Spur gear	8625	44.4	1.750	108.0	4.250	3.5	$7\frac{3}{4}$	925	1525-1725	60-68	925	165	58-62
Splined shaft	8625	44.4	1.750	44.4	1.750	2.0	$4\frac{1}{2}$	925	1525-1725	60-68	925	190	58-62
	8620	50.8	2.000	50.8	2.000	5.1	$11\frac{1}{4}$	925	1525-1725	60-68	925	165	58-62
	8625	65.0	2.559	65.0	2.559	6.8	15	925	1525-1725	60-68	925	165	58-62
Spur gear	8625	84.7	3.3343	245.5	9.667	11.9	$26\frac{1}{4}$	925	1525-1725	60-68	925	190	58-62

(a) Minimum time in oil, 5 min.

(b) Carbonitriding temperature

Although about a third of the applications in Table 4 and most of the applications in Table 5 are carburized parts, it is believed that in current industrial practice the tonnage of martempered through-hardening steels markedly exceeds that of martempered carburized steels. However, martempering is especially appropriate for carburized parts (particularly for splined shafts, cams, and gears) because these parts generally are more difficult to grind and more costly to fabricate, and are made to closer dimensions, than are parts made of through-hardening steels.

Special adaptations of martempering are sometimes employed to achieve desired characteristics and to solve specific problems. Such modified techniques, however, usually require that all conditions be closely controlled, lest still greater problems result. One special technique that has been employed is described in the following example.

Example 7: Adaptation of Martempering Involving a Brief Quench in Brine.

A problem was encountered in obtaining a sufficient depth of hardness in forged balls made of 52100 steel, which ranged in diameter from 25 to 64 mm (1 to $2\frac{1}{2}$ in.). Investigation ruled out both conventional oil quenching and martempering because of low hardness penetration and the existence of quenching pearlite (an intermediate transformation product) in the microstructure.

This problem was solved by preceding martempering with a brief, timed quench in agitated brine at 23 °C (74 °F). Heat treatment of the balls then consisted of:

- Austenitizing in salt at 855 °C (1575 °F) for times ranging from 15 min for 25 mm (1 in.) diam balls to 50 min for 64 mm ($2\frac{1}{2}$ in.) diam balls
- Quenching in agitated brine at 23 °C (74 °F) for times ranging from 15 s for 25 mm diam balls to 40 s for 64 mm diam balls and removing parts while hot (above 100 °C, or 212 °F) to accelerate evaporation of moisture
- Martempering in salt at 165 °C (325 °F) for 8 min (all diameters)
- Air cooling
- Tempering at 140 °C (285 °F) for 3 h (all diameters). By use of this treatment, the parts were successfully hardened to the desired depth. Surface hardness values were as follows:

Diameter of ball		Surface hardness, HRC
mm	in.	
27	$1\frac{1}{16}$	64.0-64.5
29	$1\frac{1}{8}$	64.5-65.5
32	$1\frac{1}{4}$	63.5-64.5

33	$1\frac{5}{16}$	64.0-64.5
35	$1\frac{3}{8}$	63.0-64.0
38	$1\frac{1}{2}$	63.0-63.5
41	$1\frac{5}{8}$	63.5-64.5
43	$1\frac{11}{16}$	63.0-64.0
44	$1\frac{3}{4}$	63.5-64.5
48	$1\frac{7}{8}$	63.5-64.0
49	$1\frac{15}{16}$	63.5-64.0
54	$2\frac{1}{8}$	61.5-63.5

-

Selection of Austenitizing Equipment

Austenitizing of steel prior to martempering may be done in virtually any furnace. This phase of the operation has been successfully accomplished in furnaces ranging from small, simple box furnaces to large, fully automated, high-production installations. Both atmosphere-controlled furnaces and molten salt baths are widely used. Fluid beds are also being used to austenitize loads prior to martempering.

The choice of austenitizing equipment depends mainly on availability, shape and size of workpieces, production requirements, and permissible distortion.

Work that is austenitized in a gaseous atmosphere can be oxidized while being transferred to an oil or salt martempering furnace. However, no special considerations are necessary when salt media are used for austenitizing before martempering in salt because chloride salts are compatible with, and are easily separated from, the martempering bath. The composition and characteristics of a typical chloride salt medium are as follows. composition, 45 to 55% NaCl and 45 to 55% KCl; melting range, 650 to 675 °C (1200 to 1250 °F); working range, 705 to 900 °C (1300 to 1650 °F).

If it is necessary to austenitize in a bath that contains cyanide, such as a liquid carburizing bath, the work should be transferred to a neutral salt (chloride-type) rinse at the austenitizing temperature prior to martempering in salt. Direct quenching from a noncyanide-type liquid carburizing bath is permissible (see the article "Liquid Carburizing and Cyaniding" in this Volume).

Salt bath furnaces for austenitizing (and neutral rinsing, if used) are most commonly of the submerged- or immersed-electrode type, although externally heated pots are also satisfactory.

Selection of Martempering Equipment

The furnace used for martempering is essentially a heat exchanger. Its basic functions are to absorb heat from the work being quenched, and then to dissipate this heat to the surroundings to maintain a constant temperature.

In its simplest form, the martempering furnace consists of a steel pot that contains the oil or nitrate-nitrite salt and that is heated internally or externally. Such a simple furnace can be successfully used for martempering in limited production quantities.

For continuous production, more complex equipment is needed to maintain optimum quenching conditions.

Fuel-fired (usually gas-fired) immersion tubes, electrodes, or immersion heaters, located across the back wall and sides of the furnace, are also used for internal heating. Occasionally, furnaces are externally heated by fuel or electricity, but such furnaces are limited to relatively small installations because they are difficult to control.

With internal heating, furnace size is unlimited and is based on production requirements. Sizes may range from 0.06 m^3 (2 ft^3) to lengths of more than 18 m (60 ft) and depths of more than 14 m (45 ft).

The operating temperature range for martempering usually is 165 to 595 °C (325 to 1100 °F). Temperature is measured by one or more thermocouples (depending on the size of the furnace), which are connected to controlling pyrometers that automatically control temperature within by actuating the heating or cooling systems as required.

In continuous production, heat input from the work usually exceeds heat losses by radiation. Therefore, arrangements for cooling as well as for heating the martempering medium are required. To supplement heat losses by radiation from the surface of the bath, the exterior surface of the pot may be designed with cooling fins so that additional heat can be removed by forcing air through the cooling chamber between the pot and the casing walls. To increase heat dissipation, atomized water may be added to the stream of air. The mixture is then passed through a heat exchanger placed in the bath.

Agitation of the molten salt greatly improves the rate at which heat is extracted from the work. The furnace can be provided with a propeller-type pump that delivers the molten salt to the quench header into which the hot work is placed for quenching. By directing the flow of salt upward or downward through this quench header, effective control of the quenching severity of the salt is maintained, particularly if the speed of the pump can be varied. The salt also may be agitated by propeller mixers, centrifugal pumps, or air bubblers located to produce effective agitation in the quench area. The use of air bubblers is not recommended because they are not efficient and may cause carbonate buildup in the bath.

The furnace may have a second chamber in which the contaminating chlorides of barium, sodium, and potassium that may be carried over from the austenitizing salt bath are separated by gravity from the nitrate-nitrite martempering salt. Contaminated salt is continuously circulated through the separating chamber, and with a drop in salt temperature, more chlorides are precipitated from solution and settle to the bottom of the separating chamber. Because clarification is continuous, a uniform quenching condition is provided at all times. When work is austenitized in an atmosphere-controlled furnace, this chamber is not required.

The equipment required for martempering in hot oil is essentially the same as that for martempering in salt. Although the operating temperature range of oil baths is lower (95 to 230 °C, or 200 to 450 °F), the problem of maintaining a constant bath temperature is the same for salt.

Examples of equipment requirements for several specific operations are given in Tables 6, 7, 8, 9, 10, 11, and 12. Each example is described further below.

Table 6 Equipment requirements for oil martempering carburized parts made of 4024 and 4028 steels

Production requirements	
Production rate, kg/h (lb/h)	455 (1000)
Weight of each piece, kg (lb)	70 g-1.0 (0.15-2.2)
Number of pieces per hour	Variable
Equipment requirements	
Capacity of quench tank, 1 (gal)	18,925 (5000)
Type of oil	Mineral oil (viscosity at 99 °C, or 210 °F; 110 sus)
Temperature of oil, °C (°F)	190 (375)
Agitation	High and low, as required

Table 7 Equipment requirements for oil martempering carburized parts made of 8617 steel

Production requirements	
Weight of load, kg (lb)	455 (1000) net
Weight of each piece, kg (lb)	1.5 (3.3)
Number of pieces treated per hour	75
Equipment requirements	
Capacity of quench tank, 1 (gal)	7570 (2000)
Type of oil	Mineral oil with additives (viscosity at 38 °C, or 100 °F, 250 sus)
Temperature of oil, °C (°F)	150 (300)
Agitation	Direct flow[(a)]

(a) Agitation provided by two 3.7 kw (5 hp) motors driving 455 mm (18 in.) propellers at 370 rpm, causing the oil to flow at a rate of 915 mm/s (36 in./s)

Table 8 Equipment requirements for salt martempering automotive transmission shafts of 5040 steel

Production requirements	
Weight of each piece, kg (lb)	1.1 (2.5)
Pieces per fixture	14
Production per hour	
Number of loaded fixtures	10.7
Number of pieces	150
Weight of pieces, kg (lb)	170 (375)
Equipment requirements	
Martempering furnace	Steel salt pot with resistance immersion heaters (70 kW)
Size of chamber[(a)]	1.22 m by 510 mm by 560 mm (48 by 20 by 22 in.)
Size of chloride-separating chamber, mm (in.)	380 by 815 by 940(15 by 32 by 37)
Capacity of salt pot, kg (lb)	3630 (8000)
Type of salt	Nitrate-nitrite
Operating temperature. °C (°F)	260 ± 3 (500 ± 5)
Agitation, kW (hp); mm (in.)	One 2.2 (3) 150 (6) propeller pump
Cooling system[(b)], kW (hp); m^3/min (ft^3/min)	One 0.25 ($\frac{1}{3}$) blower (25.5, or 900)

(a) Total depth of salt was 940 mm (37 in.)

(b) Cooling capacity of system was 215 kg/h (475 lb/h) (gross) from 845 to 230 °C (1550 to 450 °F) without exceeding 230 °C.

Table 9 Equipment requirements for salt martempering gears made of 6150 steel

Production requirements

Weight of each piece, kg (lb)	0.9 (2)
Pieces per furnace load	32
Production per hour[a]	
Number of pieces	128
Net work load, kg (lb)	116 (256)
Gross furnace load[b], kg (lb)	152 (336)
Equipment requirements	
Martempering furnace	Immersion-heated salt pot[c]
Size of salt pot, mm (in.)	610 by 380 by 840 (24 by 15 by 33)
Capacity of salt pot, kg (lb)	270 (600)
Type of salt	Nitrate-nitrite (2% water added)
Quenching capacity of salt pot, kg/h (lb/h)	180 (400)
Operating temperature, °C (°F)	205 (400)
Agitation	Air-operated stirrer

(a) Cycle time, 15 min.

(b) Work plus fixtures: each fixture had an empty weight of 9.1 kg (20 lb) and contained eight gears.

(c) Salt pot rated at 21 kV · A (3 phase, 60 cycle, 220 to 440 V) for heating to temperature range of 175 to 400 °C (350 to 750 °F); 0.37 kW ($\frac{1}{2}$ hp) blower (3 phase, 60 cycle, 220 V) used for cooling by driving room-temperature air between wall of pot and exterior shell of furnace

Table 10 Equipment requirements for salt martempering a variety of steel parts

Martempering furnace	Steel salt pot
Method of heating, mm (in.)	100 (4) immersion tube fired by natural gas[a]

Rated heat input, kW (Btu/h)	38.4 (131 000)
Operating temperature range[(b)], °C (°F)	205-400 (400-750)
Capacity of salt pot, kg (lb)	1725 (3800)
Type of salt	Nitrate-nitrite
Size of chloride-separating chamber[(c)]	205 mm by 1.07 m (8 by 42 in.)
Agitation method, kW (hp)	0.19 ($\frac{1}{4}$) propeller mixer
Cooling method[(d)]	Air through immersion tube

(a) Gas rated at 39.12 MJ/m^3 (1050 Btu/ft^3).

(b) Temperature automatically controlled to ±3 °C (±5 °F).

(c) Depth of salt, 760 mm (30 in.).

(d) Cooling capacity, 180 kg/h (400 lb/h) (gross) from 845 to 260 °C (1550 to 500 °F) without exceeding 260 °C

Table 11 Equipment requirements for salt martempering piston rings made of 52100 steel

Production requirements	
Production rate[(a)]	
Gross, kg/h (lb/h)	210 (465)
Net, kg/h (lb/h)	68 (150)
Equipment requirements	
Martempering furnace	Immersion-heated steel salt pot[(b)]
Size of work chamber[(c)], mm (in.)	915 by 455 (36 by 18)
Size of chloride-separating chamber[(d)], mm (in.)	380 by 785 (15 by 31)

Capacity of salt pot, kg (lb)	1950 (4300)
Type of salt	Nitrate-nitrite
Operating temperature of salt pot[e], °C, (°F)	260 (500)
Agitation, kW (hp); mm (in.)	One 2.2 (3), 150 (6) propeller pump
Cooling system, kW (hp); m^3/min (ft^3/min)	One 0.25 ($\frac{1}{3}$) blower (25.5, or 900)
Cooling capacity, kg/h (lb/h); °C (°F)	210 (465) (gross) from 845 to 260 (1550 to 500)

(a) Heavy mandrels were used as fixtures to retain shape of piston rings, which accounts for wide difference between gross and net weights.

(b) Resistance immersion heaters (60 kW).

(c) Depth of salt, 760 mm (30 in.).

(d) Depth of salt, 1.04 m (41 in.).

(e) Automatically controlled to ±3 °C (±5 °F)

Table 12 Equipment requirements for salt martempering aircraft landing-gear parts of 4330 steel

Production requirements	
Production per hour, kg (lb)	One load of 270 (600)
Equipment requirements	
Martempering furnace	Immersion-heated steel salt pot[a]
Size of work chamber[b], m (in.)	1.5 by 1.9 (60 by 75)
Capacity of salt pot, kg (lb)	21,850 (48,200)
Type of salt	Nitrate-nitrite
Operating temperature of salt pot[c], °C (°F)	205 (400)

Agitation, kW (hp); mm (in.)	Two 2.2 (3), 180 (7) propeller agitators
Cooling system	Natural draft
Cooling capacity, kg/h (lb/h); °C (°F)	455 (1000) (gross) from 845-205 (1550-400)[d]

Note: Parts were treated as follows: austenitize for 45 to 60 min at 845 °C (1550 °F), martemper for 5 to 7 min at 205 °C (400 °F), air cool to room temperature, and then temper at 425 °C (800 °F) to produce a hardness of 37 to 42 HRC.

(a) Resistance immersion heaters (120 kW).

(b) Depth of salt, 4.72 m (186 in.).

(c) Temperature automatically controlled to ±3 °C (±5 °F).

(d) Maximum temperature rise to 215 °C (415 °F)

Examples in Table 6. The equipment required for martempering miscellaneous carburized parts (70 g to 1.0 kg, or 0.15 to 2.2 lb, per piece) made from 4024 and 4028 steels, at a rate of 455 kg/h (1000 lb/h), is listed in Table 6. Oil at 190 °C (375 °F) was the martempering medium used in this installation.

The parts were carburized at 915 to 925 °C (1680 to 1700 °F) to a depth of 0.5 to 0.75 mm (0.020 to 0.030 in.) in a radiant-tube, gas-fired, three-row continuous pusher furnace with automatic quenching facilities. Parts were quenched from the final zone at 895 to 905 °C (1640 to 1660 °F). The carburizing atmosphere consisted of endothermic gas provided by a gas generator and 4.8 m^3/h (170 ft^3/h) of natural gas.

Example in Table 7. In the operation for which equipment requirements are detailed in Table 7, oil at 150 °C (300 °F) was used as the martempering medium. In this operation, a 455 kg (1000 lb) load of 1.5 kg (3.3 lb) parts made of 8617 steel was quenched from an automatic batch-type furnace.

These parts were carburized to a depth of 1.0 mm (0.040 in.) in a radiant-tube, gas-fired batch furnace with automatic quenching facilities. The parts were carburized at 925 °C (1700 °F) and cooled in the furnace to a quenching temperature of 845 °C (1550 °F). The carburizing atmosphere consisted of endothermic gas and natural gas.

Example in Table 8. Table 8 lists details of equipment required for salt martempering 1.1 kg (2.5 lb) transmission shafts made of 5040 steel at a rate of 170 kg/h (375 lb/h). The complete treatment was as follows:

- Austenitize for 35 min in neutral chloride salt at 845 °C (1550 °F)
- Martemper for 5 min at 260 °C (500 °F)
- Air cool (30 min) to 65 to 95 °C (150 to 200 °F)
- Temper for 45 min at 425 °C (800 °F)
- Air cool (5 min) to 95 to 120 °C (200 to 250 °F)
- Wash, rinse, and dry

Hardness after tempering and cooling to room temperature was 40 to 42 HRC (required hardness was 38 to 42 HRC).

Example in Table 9. Table 9 lists equipment requirements for salt martempering 0.9 kg (2 lb) gears made of 6150 steel at a rate of 128 pieces per hour. The gears were austenitized in a 60 kV · A submerged-electrode salt pot capable of

heating 180 kg/h (400 lb/h) to 870 °C (1600 °F). The austenitizing pot measured 455 by 380 by 760 mm (18 by 15 by 30 in.) and contained 180 kg (400 lb) of alkali-chloride salt at an operating temperature of 845 °C (1550 °F). Table 9 gives martempering requirements.

Example in Table 10. Details of a salt martempering furnace used in a commercial heat-treating plant for quenching up to 180 kg/h (400 lb/h) are given in Table 10. This salt bath is capable of being operated at up to 400 °C (750 °F) and therefore can also be used for austempering.

Example in Table 11. Table 11 shows details of a salt martempering bath capable of cooling 210 kg/h (465 lb/h) from 845 to 260 °C (1550 to 500 °F). This specific installation is used exclusively for heat treating piston rings made of 52100 steel.

Example in Table 12. The equipment used in one installation for martempering aircraft landing-gear parts made of 4330 steel is detailed in Table 12. Following martempering, these parts are tempered at 425 °C (800 °F), which results in a hardness of 37 to 42 HRC.

Maintenance of Equipment

Lack of an established maintenance schedule may result in loss of process control, damage to the equipment, or both.

Salt System. Because martempering baths vary widely in design, shape, size, and method of operation, it is not feasible to set forth a standard maintenance schedule. Manufacturers' recommendations for specific equipment should be followed; however, typical schedules for maintaining a salt bath are as follows:

Each 8-h shift

- Check instruments and thermocouples against a standard
- Check neutrality of austenitizing bath (if salt containing cyanide is used for austenitizing, the cyanide content should be less than 2%)
- Remove sludge from martempering bath; mechanical separators (filter baskets or pans) eliminate the need for this operation
- Check salt level
- Check agitation of bath and adjust as needed

Weekly

- Lubricate all moving parts
- Remove sludge or contamination from the surface of the immersion heaters (radiant tubes or electrodes), and from the walls, bottom, and top of the furnace

Monthly

- Check operation of all moving parts, such as blowers and pumps; adjust belt tension and alignment of shafts
- Check electrical contacts of all contactors and relays, and repair as required; examine all electrical devices for proper operation
- Remove fallen parts or debris from the quench header or quench area to avoid fouling
- Check heating and cooling facilities

Semiannually or annually

- Remove the salt from the furnace and check the condition of the pot, pumps, and heating system

- Clean and repair all electrical parts, such as contactors, relays, motors, and motor starters (it is especially important to remove condensed salt from all terminals and transformers)
- Clean and repair all moving parts and lubricate as required

Oil System. Following is a typical procedure for maintaining a high-temperature (175 to 205 °C, or 350 to 400 °F) oil-quench system:

Daily

- Observe oil-temperature indicators every hour; verify the indicated temperature with a potentiometer each day
- Check oil level in sight gage to ensure proper level and function of the automatic makeup unit
- Check closed system frequently for proper pressure of the atmosphere blanket over the quenching oil; pressure of this blanket should be equal to furnace-atmosphere pressure
- Check oil agitation by either observing through sight doors and noting if the pump shaft is operating at the proper speed, or, preferably, by monitoring the load on the pump motor
- Check condition of oil on parts emerging from quench. Undue discoloration or varnishing may indicate deterioration of oil
- Visually check the performance of gas-fired immersion-heating tubes

Weekly

- Check condition of oil visually and by viscosity testing; record findings on graph to note trends
- Check speed of pump shaft with tachometer to ensure consistent oil flow
- Check performance of temperature-control devices through on-off range to ensure positive control
- Check thermocouple
- Check for proper operation and elevations of quenching mechanism or elevator
- Check and clean pilot lights
- Check and clean electrodes in ignition system of gas burners
- Check safety control on gas lines for heating tubes
- Check makeup oil supply
- Check motor-operated venting systems for proper operation and remove carbon buildup to prevent jamming

Semiannually

- Drain oil from, and clean, quench tank
- Operate, and inspect functioning of mechanical elements such as elevator, oil pumps, and adjustable oil deflectors
- Check gas-fired heating tubes
- Inspect V-belts for pump drive and agitators; replace if necessary
- Check condition of temperature-measuring system
- Determine condition of oil by physical and chemical testing of various properties

Racking and Handling

The techniques for handling parts to be martempered may be similar to those for conventional oil quenching. However, racking and fixturing can be simplified for some martempering applications because distortion is less.

Example 8: Elimination of Heavy Fixturing with Martempering.

Extensive fixturing was required during conventional oil quenching of shaftlike parts made of 52100 steel. These parts were about 180 mm (7 in.) long and had a major diameter of 25 mm (1 in.). The fixtures weighed about the same as the work load.

A change from conventional quenching to martempering for 5 min in salt at 245 °C (475 °F) eliminated the need for the heavy, expensive fixtures and made it possible to hold distortion within the required limits. For martempering, the parts were placed vertically in simple fabricated baskets. This practice also resulted in a greater "payload."

The manner in which workpieces enter the bath generally is less critical in martempering than in conventional oil quenching. For example, large flat parts do not dish as much when martempered. However, the shape of each part must be considered individually, and some trial and error often is necessary before an optimum handling technique can be developed.

Nesting of small parts can be a problem, and development of a handling method that will result in uniform quenching often requires experimentation. A technique that proved successful for one application is described below.

Example 9: Techniques to Improve Uniform Quenching during Martempering.

Flat blades that were not well suited to fixturing or wiring had a tendency to nest, which caused nonuniform quenching during martempering. This problem was overcome by use of a pump that directed a heavy flow of molten salt upward through a perforated metal basket, which kept the parts separated. This technique requires that the flow of salt be regulated to the floating characteristics of the workpieces.

For fixturing of parts, one of the following considerations may apply:

- Long, slender parts should be suspended
- Symmetrical parts, such as bearing races and cylinders, can be stacked and supported on a rack or grid
- Flat parts, such as circular saw blades, mower blades, and clutch plates, are best supported on horizontal slotted rods that provide the necessary separation
- Coils of wire are supported either vertically on a spider-type grid or horizontally on support rods
- Small parts can be loaded into a perforated ladle or basket and then dumped into the quench to obtain intimate quenching of all parts
- Fixture design should be simple, free of welds (if possible), and easy to maintain. For example, fixtures supporting vertical stacks of bearing races should be removable for periodic grinding to maintain flatness

Proper spacing of workpieces to permit good flow of the quenchant around each part is an important consideration in martempering. Also, the combined weight of workpieces and fixtures must be limited to the extent that the heat they contain is insufficient to cause a sharp increase in the temperature of the quenchant. In this regard, the size of a salt bath furnace is determined not only by the physical size of the work, but also by design requirements such as salt-separating systems, a means for agitation of the salt, and sufficient area for dissipation of heat through sidewalls.

Washing the Work

Regardless of the martempering medium used, the work load should not be washed until transformation is complete (all portions of workpieces should be near room temperature).

Martempering salts are completely water soluble, and any hot-water soaking tank or spray washer will remove all salt from accessible areas. Cold water can be used, but its washing action is much slower.

The speed of washing will depend on how much hot water unsaturated with salt flows over the salt-coated surface. Therefore, agitation will increase the washing action, and a device such as an open-impeller sump pump can be used in a soaking tank to direct a stream of hot water into recessed areas. Steam jets may be used as supplementary equipment to remove salt from sections of intricately shaped parts with difficult-to-reach recesses for which conventional washing equipment is inadequate.

Quenching oils often present washing problems. Martempering oil adheres more tenaciously to workpieces than does conventional quenching oil because of its higher viscosity, as high as 1200 Saybolt Universal Seconds (SUS) at 38 °C (100 °F), compared with 100 SUS at 38 °C for conventional oil.

Basically, the washing equipment is the same for both types of quenching oils, but a heavy-duty cleaner must be used to remove martempering oil. Several proprietary heavy-duty silicate-alkaline cleaners are available for cleaning parts martempered in hot oil. Vapor degreasing and steam cleaning without detergent may be used in special applications.

Austempering of Steel

Revised by John R. Keough, Atmosphere Group, Inc.; W. James Laird, Jr., The Metal Works Industrial Furnaces,Inc.; and A.D. Godding, Heatbath Corporation

Introduction

AUSTEMPERING is the isothermal transformation of a ferrous alloy at a temperature below that of pearlite formation and above that of martensite formation. Austempering of steel offers several potential advantages:

- Increased ductility, toughness, and strength at a given hardness (Table 1)
- Reduced distortion, which lessens subsequent machining time, stock removal, sorting, inspection, and scrap
- The shortest overall time cycle to through-harden within the hardness range of 35 to 55 HRC, with resulting savings in energy and capital investment

Table 1 Mechanical properties of 1095 steel heat treated by three methods

Specimen No.	Heat treatment	Hardness, HRC	Impact strength		Elongation in in 25 mm, or 1 in., %
			J	ft · lbf	
1	Water quenched and tempered	53.0	16	12	. . .
2	Water quenched and tempered	52.5	19	14	. . .
3	Martempered and tempered	53.0	38	28	. . .
4	Martempered and tempered	52.8	33	24	. . .
5	Austempered	52.0	61	45	11

Steel is austempered by being:

- Heated to a temperature within the austenitizing range, usually 790 to 915 °C (1450 to 1675 °F)
- Quenched in a bath maintained at a constant temperature, usually in the range of 260 to 400 °C (500 to 750 °F)
- Allowed to transform isothermally to bainite in this bath
- Cooled to room temperature

The process is described in detail by the inventors E.S. Davenport and E.C. Bain in U.S. Patent 1,924,099. The fundamental difference between austempering and conventional quenching and tempering is shown schematically in Fig. 1. For true austempering, the metal must be cooled from the austenitizing temperature to the temperature of the austempering bath fast enough so that no transformation of austenite occurs during cooling, and then held at bath temperature long enough to ensure complete transformation of austenite to bainite. Modifications of these procedures, constituting departures from true austempering, are discussed in the section "Modified Austempering" in this article.

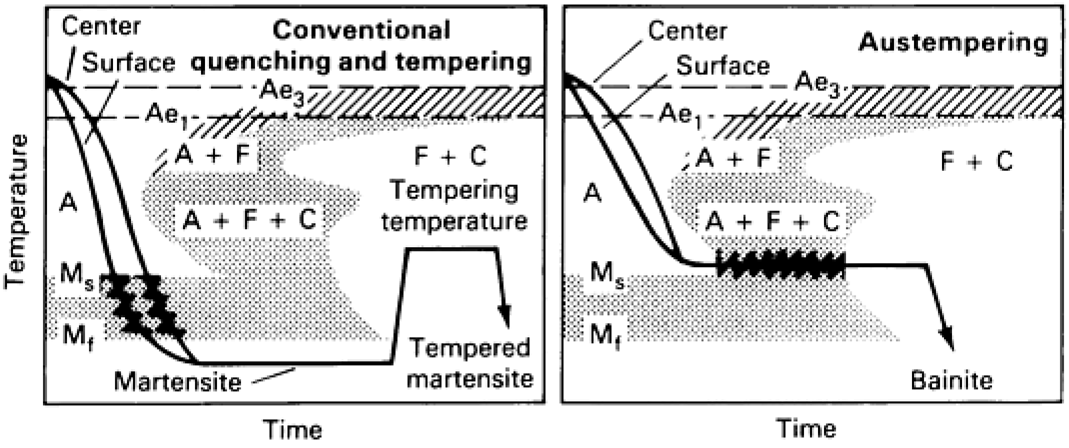


Fig. 1 Comparison of time-temperature transformation cycles for conventional quenching and tempering and for austempering

Austempering is also the isothermal transformation used to form a unique acicular matrix of bainitic ferrite and stable high-carbon austenite in hardenable cast irons. The process of austempering ductile iron (ADI) is described in detail in the article "Heat Treating of Ductile Iron" in this Volume.

Quenching Media for Austempering

Molten salt is the quenching medium most commonly used in austempering because:

- It transfers heat rapidly
- It virtually eliminates the problem of a vapor phase barrier during the initial stage of quenching
- Its viscosity is uniform over a wide range of temperature
- Its viscosity is low at austempering temperatures (near that of water at room temperature), thus minimizing dragout losses
- It remains stable at operating temperatures and is completely soluble in water, thus facilitating subsequent cleaning operations
- The salt can be easily recovered from wash waters by evaporative methods

Formulations and characteristics of two typical salt quenching baths are given in Table 2(a). The high-range salt is suitable for austempering only, whereas the wide-range salt may be used for austempering, martempering, and modifications thereof. Table 2(b) compares quench severity for salt quenches.

Table 2(a) Compositions and characteristics of salts used for austempering

	High range	Wide range
Sodium nitrate, %	45-55	0-25

Potassium nitrate, %	45-55	45-55
Sodium nitrite, %	. . .	25-55
Melting point (approx), °C (°F)	220 (430)	150-165 (300-330)
Working temperature range, °C (°F)	260-595 (500-1100)	175-540 (345-1000)

Table 2(b) Quench severity comparison for salt quenches

Numbers given are estimated Grossmann H-values as described in the article "Quenching of Steel" in this Volume.

Agitation	At temperature	
	180 °C (360 °F)	370 °C (700 °F)
Still and dry	0.15-0.20	0.15
Agitated and dry	0.25-0.35	0.20-0.25
Agitated with 0.5% water	0.40-0.50	0.30-0.40
Agitated with 2% water	0.50-0.60	0.50-0.60[a]

(a) Requires special enclosed quenching apparatus

Water Additions to Nitrate-Nitrite Salt. The quenching severity of a nitrate-nitrite salt can be increased significantly by careful addition of water. Agitation of the salt is necessary to disperse the water uniformly. Periodic water additions are needed to maintain required water content (see the article "Martempering of Steel" in this Volume). Water can be added with complete safety as follows:

- Water may be misted at a regulated rate into a vigorously agitated area of the molten bath
- In installations where the salt is pump circulated, returning salt is cascaded into the quench zone. A controlled fine stream of water may be injected into the cascade of returning salt
- The austempering bath may be kept saturated with moisture by introducing steam directly into a bath. The steam line should be trapped and equipped with a discharge to avoid emptying condensate directly into the bath
- Steam additions of water to ADI baths is done with operating temperatures above 260 °C (500 °F)

Addition of water to increase the quenching severity of salt usually is made by directing a stream of water onto the molten salt at the agitator vortex. A protective shroud surrounds the water spray to prevent spattering. The turbulence of the salt

carries the water into the bath without spattering or hazard to the operator. Water should never be added to a salt bath from a pail or dipper.

Water is continuously evaporating from the bath surface, and the rate of evaporation increases during quenching of hot work. Thus, it is necessary to add water periodically to maintain the water concentration and a uniform quenching severity. The amount of water to be added to an open salt bath varies with the operating temperature of the salt, as indicated by the following recommended concentrations:

Temperature		**Water concentration, %**
°C	**°F**	
205	400	$\frac{1}{2}$ to 2
260	500	$\frac{1}{2}$ to 1
315	600	$\frac{1}{4}$ to $\frac{1}{2}$

The numbers shown in this table represent the amounts of water soluble in salt baths maintained at atmosphere pressure. Some newer types of equipment with enclosed quenches have been reported to allow in excess of 10% water at 200 °C (400 °F) with a resultant increase in quench severity (see Table 2(b)).

Water additions are usually controlled at the discretion of the operator, who will add water as needed. On the basis of experience, however, it is possible to determine the need for water by freezing-point depression (Fig. 2); here, the addition of water may be simplified by use of timers that can be adjusted to time the frequency and duration of water additions.

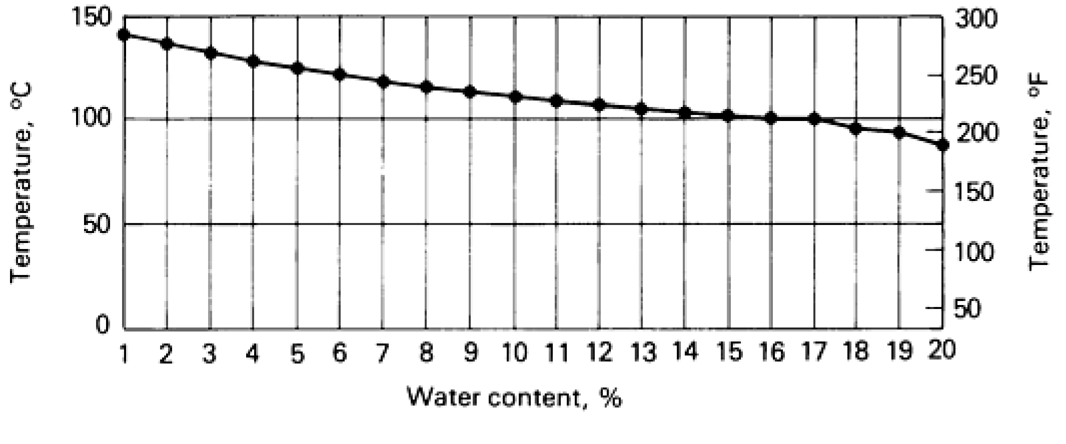


Fig. 2 Effect of water content on the freezing point of nitrate-nitrite salt bath

The presence of water is visually detectable by the operator because steam is released when the hot work is immersed in the nitrate-nitrite salt. The steam causes a visible mounding of the salt above the quench area, and there is a characteristic sizzling caused by the vapor phase.

Besides visual appearance, periodic hardness checks of the work will indicate the activity of the bath. Another determination can be made by removing a small quantity of the salt and weighing it accurately before and after dehydrating it by heating to 370 to 425 °C (700 to 800 °F).

Several other devices now exist for measuring quench severity and controlling water additions automatically. These devices are based on the slope of the cooling curve. In general, a heating element is placed in the bath and the time to cool between the initial temperature and a preset lower temperature is measured. If the cooling time is greater than the set point, water is automatically added. These devices aid the operator in maintaining a uniform quench severity and improve process capability.

Oil is sometimes used for austempering, but because of its chemical instability and resulting change in viscosity at austempering temperatures, its use is restricted to applications below 245 °C (470 °F). Because of its persistent vapor phase, oil is a slower quenchant than salt at elevated temperatures and presents a fire hazard.

Steels for Austempering

The selection of steel for austempering must be based on transformation characteristics as indicated in time-temperature transformation (TTT) diagrams. Three important considerations are:

- The location of the nose of the TTT curve and the speed of the quench being utilized
- The time required for complete transformation of austenite to bainite at the austempering temperature
- The location of the M_s point

As indicated in Fig. 3, 1080 carbon steel possesses transformation characteristics that provide it with limited suitability for austempering Cooling from the austenitizing temperature to the austempering bath must be accomplished in about 1 s to avoid the nose of the TTT curve, and thus prevent transformation to pearlite during cooling. Depending on the temperature, isothermal transformation in the bath is completed within a period ranging from a few minutes to about 1 h. Because of the rapid cooling rate required, austempering of 1080 can be successfully applied only to thin sections of about 5 mm (0.2 in.) maximum.

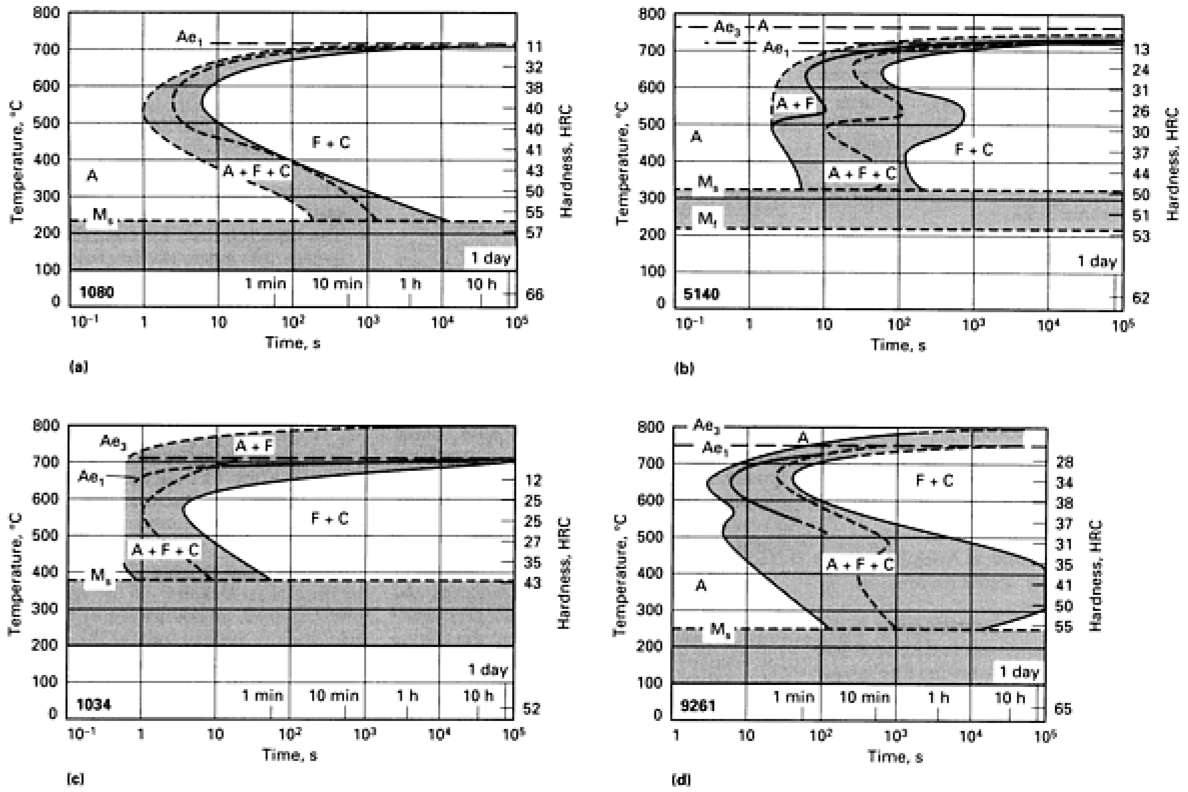


Fig. 3 Transformation characteristics of 1080, 5140, 1034, and 9261 steels, in relation to their suitability for austempering. 1080, limited suitability for austempering because pearlite reaction starts too soon near 540 °C (1000 °F); 5140, well suited to austempering; 1034, impossible to austemper because of extremely fast pearlite reaction time at 540 to 595 °C (1000 to 1100 °F); 9261, not suited to austempering because of slow reaction to bainite at 260 to 400 °C (500 to 750 °F). See text for discussion of steel selection.

5140 low-alloy steel is well suited to austempering, as indicated by the TTT curve for this steel shown in Fig. 3. Approximately 2 s are allowed in which to bypass the nose of the curve, and transformation to bainite is completed within 1 to 10 min at 315 to 400 °C (600 to 750 °F). Parts made of 5140 steel or of other steels with similar transformation characteristics are adaptable to austempering in larger section sizes than are feasible for 1080 steel because of the greater time allowed for bypassing the nose of the curve.

In addition to the steels previously indicated (1080 and 5140), steels adaptable to austempering include:

- Plain carbon steels containing 0.50 to 1.00% C and a minimum of 0.60% Mn
- High-carbon steels containing more than 0.90% C and, possibly, a little less than 0.60% Mn
- Certain carbon steels (such as 1041) with a carbon content of less than 0.50% but with manganese content in the range from 1.00 to 1.65%
- Certain low-alloy steels (such as the series 5100 steels) containing more than 0.30% C; the series 1300 to 4000 steels with carbon contents in excess of 0.40%; and other steels, such as 4140, 6145, and 9440

Some steels, although they have sufficient carbon or alloy content to be hardenable, are borderline or impractical for austempering because transformation at the nose of the TTT curve starts in less than 1 s, thus making it virtually impossible to quench other than thin sections in molten salt without forming some pearlite, or they require excessively long periods of time for transformation. A typical example of a steel belonging to the first category is 1034, whose transformation characteristics are shown in Fig. 3. Transformation characteristics for 9261 (also shown in Fig. 3) indicate no difficulty in quenching past the nose of the curve, but the time required for isothermal transformation to bainite (about 24 h) is excessive. Other alloy steels with excellent hardenability that require long transformation times include those in series 4300, 4600, and 4800.

The chemical composition of the steel is the major determinant of the martensite-start (M_s) temperature. Carbon is the most significant variable affecting the M_s. The direct effects of other alloying elements on the M_s point are much less pronounced than the effect of carbon. However, carbide-forming elements (such as molybdenum and vanadium) can tie up the carbon as alloy carbides and prevent complete solution of carbon. The approximate M_s temperature, in degrees Centigrade, of a completely austenitized steel can be calculated by means of the following formula:

$$
\begin{aligned}
M_s = 538 &- (361 \times \%C) \\
&-(39 \times \% Mn) \\
&-(19 \times \% Ni) \\
&-(39 \times \% Cr)
\end{aligned}
$$

Expressed in degrees Fahrenheit, the formula is:

$$
\begin{aligned}
M_s = 1000 &- (650 \times \% C) \\
&-(70 \times \% Mn) \\
&-(35 \times \% Ni) \\
&-(70 \times \% Cr)
\end{aligned}
$$

Austenitizing temperature has a significant effect on the time at which transformation begins. As the austenitizing temperature is increased above normal (for a specific steel), the nose of the TTT curve shifts to the right because of grain coarsening. In Fig. 3, for example, approximately $\frac{3}{4}$ s is allowed for quenching 1080 steel in order to avoid the nose of the curve. However, this is based on an austenitizing temperature of 790 °C (1450 °F); higher austenitizing temperatures move the TTT curve to the right, allowing more time before transformation begins.

Practical use is sometimes made of this phenomenon in order to process compositions or section sizes that would otherwise be borderline for austempering. However, the coarser grain sizes resulting from higher austenitizing temperatures may be detrimental to some desired properties. Therefore, it is recommended that standard austenitizing temperatures be given preference for austempering. If experience with specific compositions and parts proves that advantages can be gained from the use of a higher temperature and that no harm will be incurred from grain coarsening, higher austenitizing temperatures may be employed.

As the austenitizing temperature of a high-carbon steel increases, the M_s temperature decreases marginally because of more complete solution of carbon. This effect on the M_s temperature, however, is small compared to the effects of the chemical composition.

Section Thickness Limitations

Maximum thickness of section is important in determining whether or not a part can be successfully austempered. For 1080 steel, a section thickness of about 5 mm (0.2 in.) is the maximum that can be austempered to a fully bainitic structure. Carbon steels of lower carbon content will be restricted to a proportionately lesser thickness. Lower-carbon steels containing boron, however, can be successfully austempered in heavier sections. In some alloy steels, section thicknesses up to about 25 mm (1 in.) can be austempered to fully bainitic structures.

Nevertheless, sections of carbon steel significantly thicker than 5 mm (0.2 in.) are regularly austempered in production when some pearlite is permissible in the microstructure. This is demonstrated in Table 3, which lists section sizes of austempered parts made of various steels.

Table 3 Hardness of various steels and section sizes of austempered parts

Steel	Section size		Salt temperature		M_s temperature[(a)]		Hardness, HRC
	mm	in.	°C	°F	°C	°F	

1050	3[b]	0.125[b]	345	655	320	610	41-47
1065	5[c]	0.187[c]	[d]	[d]	275	525	53-56
1066	7[c]	0.281[c]	[d]	[d]	260	500	53-56
1084	6[c]	0.218[c]	[d]	[d]	200	395	55-58
1086	13[c]	0.516[c]	[d]	[d]	215	420	55-58
1090	5[c]	0.187[c]	[d]	[d]	. . .	. . .	57-60
1090[e]	20[c]	0.820[c]	315[f]	600[f]	. . .	. . .	44.5 (avg)
1095	4[c]	0.148[c]	[d]	[d]	210[g]	410[g]	57-60
1350	16[c]	0.625[c]	[d]	[d]	235	450	53-56
4063	16[c]	0.625[c]	[d]	[d]	245	475	53-56
4150	13[c]	0.500[c]	[d]	[d]	285	545	52 max
4365	25[c]	1.000[c]	[d]	[d]	210	410	54 max
5140	3[b]	0.125[b]	345	655	330	630	43-48
5160[e]	26[c]	1.035[c]	315[f]	600[f]	255	490	46.7 (avg)
8750	3[b]	0.125[b]	315	600	285	545	47-48
50100	8[c]	0.312[c]	[d]	[d]	. . .	. . .	57-60

(a) Calculated.

(b) Sheet thickness.

(c) Diameter of section.

(d) Salt temperature adjusted to give maximum hardness and 100% bainite.

(e) Modified austempering: microstructure contained pearlite as well as bainite.

(f) Salt with water additions.

(g) Experimental value

The effects of section thickness on the hardness of austempered 1090 and 5160 steels are shown in Fig. 4. Hardness remains reasonably consistent to the center of a 17 mm (0.680 in.) diameter of 1090, but it becomes erratic when the diameter is increased to 21 mm (0.820 in.). A similar difference is evident for 5160 steel when the diameter is increased from 24.6 to 26 mm (0.967 to 1.035 in.).

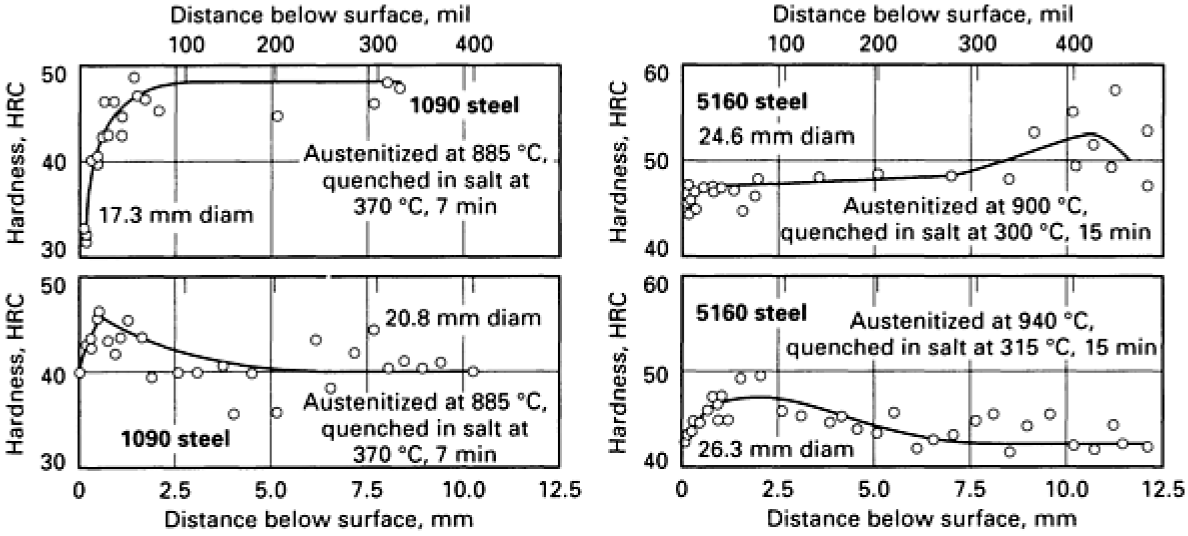


Fig. 4 Effect of section thickness on the hardness of austempered carbon and alloy steels. The 5160 steel was quenched in agitated salt containing some water. HRC values were converted from microhardness readings taken with a 100 g load. Low values of surface hardness result from decarburization. High hardness at center of 24.6 mm (0.967 in.) 5160 is due to segregation.

The lower surface hardnesses indicated for 1090 and 5160 were the result of surface decarburization and/or grain refinement. The high core hardness of the 24.6 mm (0.967 in.) diameter of 5160 is attributed to chemical segregation in the center portion of the bar and the absence of appreciable grain refinement.

Applications

Austempering usually is substituted for conventional quenching and tempering for the following reasons:

- To obtain improved mechanical properties (particularly higher ductility or notch toughness at a given high hardness). Figure 5 compares the fracture morphologies of austempered versus quenched and tempered 10B53 steel
- To decrease the likelihood of cracking and distortion
- To improve wear resistance for a given hardness
- To improve resistance to subsequent embrittlement

In some applications, austempering is less expensive than conventional quenching and tempering. This is most likely when small parts are treated in an automated setup wherein conventional quenching and tempering comprise a three-step operation--that is, austenitizing, quenching, and tempering. Austempering requires only two processing steps: austenitizing and isothermal transformation in an austempering bath.

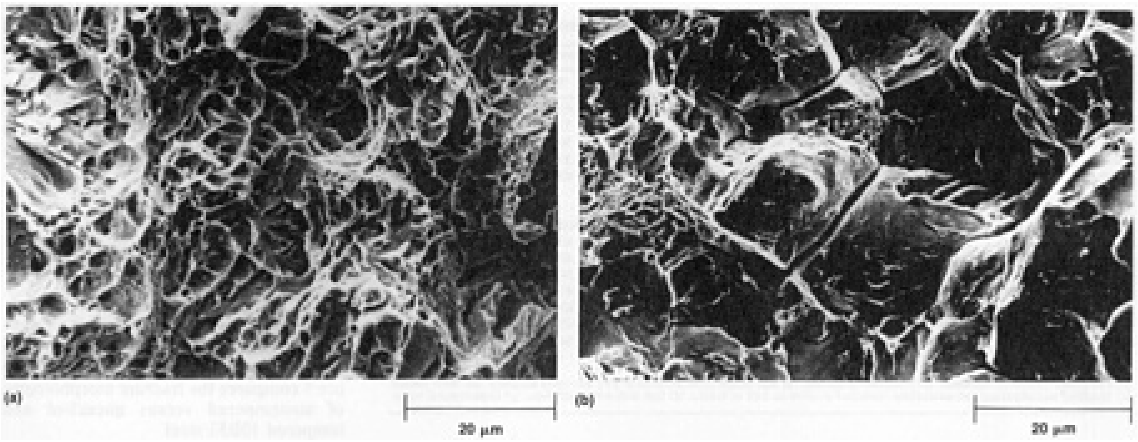


Fig. 5 Effect of heat treatment on the fracture appearance of 10B53 steel. (a) Ductile fracture surface of specimen austempered to 53 HRC. (b) Brittle fracture of specimen quenched and tempered to 53 HRC. Courtesy of Vermont America Corporation

The range of austempering applications generally encompasses parts fabricated from bars of small diameter or from sheet or strip of small cross section. Austempering is particularly applicable to thin-section carbon steel parts requiring exceptional toughness at a hardness between 40 and 50 HRC.

In austempered carbon steel parts, reduction in area is usually much higher than in conventionally quenched and tempered parts, as indicated in the following tabulation for 5 mm (0.180 in.) diam bars of 0.85% C plain carbon steel:

Austempered mechanical properties	
Tensile strength, MPa (ksi)	1780 (258)
Yield strength, MPa (ksi)	1450 (210)
Reduction in area, %	45
Hardness, HRC	50
Quenched and tempered mechanical properties	
Tensile strength, MPa (ksi)	1795 (260)
Yield strength, MPa (ksi)	1550 (225)

Reduction in area, %	28
Hardness, HRC	50

The mechanical properties of sway bars made of 1090 steel and hardened by these two processes are listed in Table 4 (see also Table 1).

Table 4 Comparison of typical mechanical properties of austempered and of oil-quenched and tempered sway bars of 1090 steel

Property[(a)]	**Austempered at 400 °C (750 °F)**[(b)]	**Quenched and tempered**[(c)]
Tensile strength, MPa (ksi)	1415 (205)	1380 (200)
Yield strength, MPa (ksi)	1020 (148)	895 (130)
Elongation, %	11.5	6.0
Reduction of area, %	30	10.2
Hardness, HB	415	388
Fatigue cycles[(d)]	105,000[(e)]	58,600[(f)]

(a) Average values.

(b) Six tests.

(c) Two tests.

(d) Fatigue specimens 21 mm (0.812 in.) in diameter.

(e) Seven tests; range, 69 050 to 137 000.

(f) Eight tests; range, 43 120 to 95 220

It is more important that austempered parts possess desired mechanical properties than that they have a 100% bainitic structure. In Table 3, it is evident from the hardness values indicated that several of the austempered steels have mixed structures. Higher-than-normal hardness indicates that some martensite has formed, and below-normal hardness indicates the presence of some pearlite. The formation of pearlite is more common and results from a quenching speed too slow for complete avoidance of the nose of the TTT curve.

In industrial austempering practice, a sizable percentage of applications are successful with less than 100% bainite. In fact, 85% bainite has been found to be satisfactory for some applications. Obviously, austempering is often "modified" to some degree in commercial application, and whether or not the metallurgical properties obtained conform to those obtained in true austempering is at least partially ignored if the treated parts meet service requirements. However, variations in hardenability from heat to heat may give rise to erratic results from variations in the amount of pearlite when borderline conditions are involved in modified austempering.

Table 5 presents processing data for a number of specific parts made of various plain carbon, alloy, and carburizing steels; these data are representative of austempering practice in at least a dozen different manufacturing plants.

Table 5 Typical production applications of austempering

Parts listed in order of increasing section thickness

Part	Steel	Maximum section thickness		Parts per unit weight		Salt temperature		Immersion time, min	Hardness, HRC
		mm	in.	kg^{-1}	lb^{-1}	°C	°F		
Plain carbon steel parts									
Clevis	1050	0.75	0.030	770/kg	350/lb	360	680	15	42
Follower arm	1050	0.75	0.030	412/kg	187/lb	355	675	15	42
Spring	1080	0.79	0.031	220/kg	100/lb	330	625	15	48
Plate	1060	0.81	0.032	88/kg	40/lb	330	630	6	45-50
Cam lever	1065	1.0	0.040	62/kg	28/lb	370	700	15	42
Plate	1050	1.0	0.040	0.5 kg	$\frac{1}{4}$ lb	360	675	15	42
Type bar	1065	1.0	0.040	141/kg	64/lb	370	700	15	42
Tabulator stop	1065	1.22	0.048	440/kg	200/lb	360	680	15	45
Lever	1050	1.25	0.050	. . .	. . .	345	650	15	45-50
Chain link	1050	1.5	0.060	573/kg	260/lb	345	650	15	45
Shoe-last link	1065	1.5	0.060	86/kg	39/lb	290	550	30	52
Shoe-toe cap	1070	1.5	0.060	18/kg	8/lb	315	600	60	50

Lawn mower blade	1065	3.18	0.125	1.5 kg	$\frac{2}{3}$ lb	315	600	15	50
Lever	1075	3.18	0.125	24/kg	11/lb	385	725	5	30-35
Fastener	1060	6.35	0.250	110/kg	50/lb	310	590	25	50
Stabilizer bar	1090	19	0.750	22 kg	10 lb	370	700	6-9	40-45
Boron steel bolt	10B20	6.35	0.250	100/kg	45/lb	420	790	5	38-43
Alloy steel parts									
Socket wrench	6150	. . .	. . .	0.3 kg	$\frac{1}{8}$ lb	365	690	15	45
Chain link	Cr-Ni-V[a]	1.60	0.063	110/kg	50/lb	290	550	25	53
Pin	3140	1.60	0.063	5500/kg	2500/lb	325	620	45	48
Cylinder liner	4140	2.54	0.100	15 kg	7 lb	260	500	14	40
Anvil	8640	3.18	0.125	1.65 kg	$\frac{3}{4}$ lb	370	700	30	37
Shovel blade	4068	3.18	0.125	. . .	. . .	370	700	15	45
Pin	3140	6.35	0.250	100/kg	45/lb	370	700	45	40
Shaft	4140[b]	9.53	0.375	0.5 kg	$\frac{1}{4}$ lb	385	725	15	35-40
Gear	6150	12.7	0.500	4.4 kg	2 lb	305	580	30	45
Carburized steel parts									
Lever	1010	3.96	0.156	33 kg	15 lb	385	725	5	30-35[c]
Shaft	1117	6.35	0.250	66/kg	30/lb	385	725	5	30-35[c]
Block	8620	11.13	0.438	132/kg	60/lb	290-315	550-600	30	50[c]

(a) Contains 0.65 to 0.75% C.

(b) Leaded grade.

(c) Case hardness

Equipment and Processing Procedures

Austenitizing prior to austempering can be performed in molten salt baths, in one of several types of standard heat-treating furnaces (including belt, batch, pusher, rotary retort, and shaker-hearth furnaces), or in other special types of furnaces that employ a protective gas atmosphere. In the types of austenitizing furnaces that employ a gaseous atmosphere, atmosphere control is extremely important because the formation of scale on parts will inhibit the rapid heat exchange that is essential in a successful austempering operation. Protective atmospheres do not contaminate the quench and are routinely controlled using oxygen probes, CO_2 analyzers, and continuous-reading dew-point devices in conjunction with a process controller.

Molten salt baths for austenitizing are widely used for batch-type operation; they can also be mechanized for continuous operation. Heating in salt for batch-type operation is advantageous because the film of adhering salt prevents scaling during transfer from the austenitizing operation to the austempering bath. Salt bath furnaces heated by either immersed or submerged electrodes are most common, although externally heated pots are also used.

Because most austempering is performed in molten salt, the salt bath used for austenitizing must be compatible with the austempering salt. Chloride salts are recommended for austenitizing; the composition and characteristics of a typical chloride salt bath for austenitizing are as follows:

Sodium chloride, %	45-55
Potassium chloride, %	45-55
Melting temperature. °C (°F)	650-675 (1200-1250)
Working temperature range, °C (°F)	705-900 (1300-1650)

Caution: Austenitizing salt baths should not contain cyanide because it reacts violently with quenching salts. Carbonate compositions and mixtures containing barium salts are not recommended because they are difficult to separate from quenching salts.

Shaker-hearth furnaces with atmosphere control are widely used for austenitizing, especially where large quantities of small parts are being processed. In a typical automated installation, the workpieces enter the shaker from a feeder, and after being heated to the austenitizing temperature, are dropped through a chute into the austempering bath, thus avoiding exposure in air and the possibility of scaling. The parts are transported through the austempering bath on variable-speed mesh or plate belt-type conveyors at a speed that allows complete transformation before they are automatically transferred to a constant-speed conveyorized washing and drying setup. These systems are relatively inexpensive to install and operate, but are restricted to a few hundred pounds per hour capacity.

Feeders for shaker-hearth furnaces vary widely in design, depending on the size, shape, and fragility of workpieces. In one type of equipment, parts are fed by gravity from the hopper onto a reciprocating hearth, on which they are transported through the shaker-hearth furnace and then into the austempering furnace. This mechanism is used for small round or flat parts that will not be distorted by the vibrating action. Other methods of feeding to the moving hearth include "Walmil"-style ram volumetric feeders, weigh loaders, and special magnetic conveyor-and-bin combinations that disentangle parts that bundle.

Rotary retort furnaces are widely used for products in the saw-chain, concrete, explosive drive, and air-driven nail industries and in similar applications where both hardness and ductility are prime factors in the end product, and reasonably large quantities of similar small parts are being processed without the threat of damage by the tumbling action of the retort. One of the advantages of the rotary retort, which advances the work by means of the internal spiral, is the absolute control of the retention time within the heated chamber. This control ensures uniformity of metallurgical properties of the product. Excellent atmosphere control is also attained because the work progresses through a sealed retort, is sealed at the quench chute by the quench media, and the process has a restricted part entry area. Consistent production rates and uniformity of results are obtained by controlling the loading rate with a weigh loader that is fed from a storage hopper by discharging the workpieces to a loading elevator that in turn transports the load through a chute into the partially sealed entry of the retort. These Systems are moderately expensive to install but inexpensive to operate and are capable of up to 200 to 500 kg (500 to 1000 lb) per hour of production.

Belt-type furnaces ensure controlled retention time for repeatability of metallurgical properties of the product. The integrity of the atmosphere is controlled by sealing the charge end of the furnace either mechanically or with a positive-atmosphere seal. The discharge chute into the molten salt also is sealed. Conveyorized transport through the austempering salt bath and wash tanks as described for shaker-hearth furnaces is also employed with both the rotary retort and belt furnace systems.

Belt furnaces may use either a cast-link or mesh-type part-carrier belt. In some belt furnace designs, the belt is totally enclosed in the austenitizing furnace. These units are loaded utilizing a charge conveyor or a shaker feeder. Belt units that use a positive-atmosphere seal allow the belt to return outside of the furnace, thus allowing either mechanical or hand loading outside of the furnace. The mesh-belt type of furnace is primarily used to process relatively thin sheet metal stampings that would become distorted if loaded directly onto a heavy cast-link belt or would become tangled or distorted if processed through a rotary retort.

Continuous automated parts feeding may be accomplished by use of specialized magnetic conveyor feeders. These feeders strip the parts that tend to tangle from one edge of the pile in the feeding bin and carry them up to a vibratory trough. The trough in turn feeds the workpieces to the hearth that enters the furnace.

The cast-link belt types are used to handle heavier parts that would not be subject to distortion upon loading onto the hot cast-link belt. Continuous feeding is accomplished with Walmil volumetric feeders, charge conveyors, automated orienters, or simple bin and vibratory trough types, depending upon part configuration. Each feeding system delivers parts to the hearth, which enters the furnace.

Direct-fired tunnel-type furnaces are employed for heat treating large quantities of similar parts that must be hung from hooks or fixtures to minimize distortion. In a typical installation, the hooks or fixtures carrying the work travel in front of the operators and can be easily loaded. The work is conveyed through the tunnel-type heating zone, automatically removed after heating and dropped into the austempering bath, and then conveyed to washing and drying. During austenitizing, parts are in a protective atmosphere provided by the controlled gas-to-air ratio of the burners. The entire operation is automatic except for the hand loading of parts onto hooks.

Austempering Lines. Simple salt baths, either fuel-fired or electrically heated, are suitable for low-production austempering Circulation can be provided by a propeller-type mixer. Most of these furnaces have no provision for cooling and depend on heat losses to equal the heat input acquired from workpieces.

Sufficient production quantities warrant the use of salt lines specifically designed for austempering. These furnaces usually provide for automatic handling. The salt bath units are heated with immersion heaters, immersed electrodes, or gas-fired immersion tubes. To maintain a constant temperature, heat is dissipated by forced air that cools the pot sidewall or by immersed plate coils. Both heating and cooling are automatically controlled. A salt-separating system is required to separate chloride salts dragged over from the austenitizing furnace. Chlorides, scale, and other contaminants are removed by:

- *Gravity separation:* Providing a separate chamber for the suspensions to settle; settled solids are then removed by manual desludging or sludge pans
- *Continuous filtration:* Suspended contaminants are continuously passed through filter baskets; the baskets are periodically removed and dumped
- *Solubility separation:* The temperature of the entire quench bath is periodically dropped, or the separating chamber is held at a lower temperature by insulating or cooling to drop chlorides (hardening salt) out of solution (Fig. 6) where they can be removed by manual desludging or through the use of sludge pans

An analysis for the amount of chloride in quench baths can also be made (Table 6). To provide uniform quenching, one or more propeller agitators are used to agitate the salt.

Table 6 Titration procedure for determination of chloride in quench baths

Reagents
1. 0*N* NaOH, 5% acetic acid, 0.1*N* $AgNO_3$, saturated potassium chromate, and phenolphthalein indicator
Procedure
1. Weigh out about 0.1-0.2 g sample and transfer into a 600 ml beaker
2. Add about 250 ml of distilled H_2O. Dissolve
3. Add 2 drops phenolphthalein (if pink, go to Step 5)
4. Add 1.0*N* NaOH dropwise until pink
5. Add 5% acetic acid until clear
6. Add 7-10 drops potassium chromate
7. Titrate with 0.1*N* $AgNO_3$ until orange color persists

Calculations

$$Chloride = \frac{Milliliters\ \text{of 0.1N AgNO}_3\ \text{x 0.3546}}{\text{Sample weight in grams}} = \%Cl$$

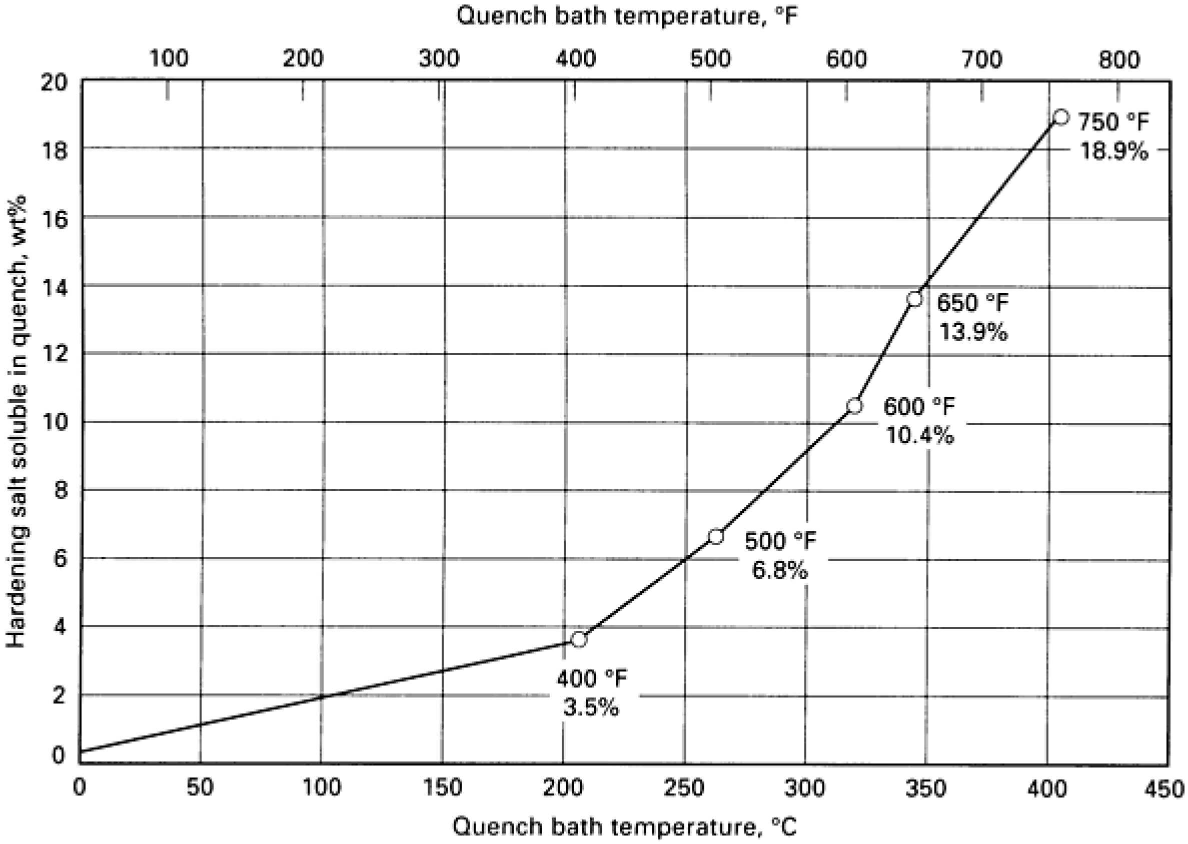


Fig. 6 Solubility of hardening salt in quench salt

Pusher-type furnaces utilize special alloy baskets or trays for holding the workpieces. The time at temperature and in the quench is controlled by the indexing time. Each time a basket exits the line, a basket of green parts is charged. These types of units are used extensively to austemper gears, shafts, heavier stampings, and forgings that are hand racked.

Pusher furnaces are relatively expensive to install and are suited best to processing large volumes (up to 900 kg, or 2000 lb, per hour) of parts that have the same austempering cycle. For high volumes, they are relatively inexpensive to operate, but as volumes drop and cycles are varied (that is, differing austenitizing and austempering temperatures and times), the effectiveness of the pusher furnace is reduced.

A pusher furnace can be fitted with a special, enclosed salt quench for adding larger amounts of water, thus realizing quench severities as fast as those for oil at room temperature.

Batch furnaces with either integral hot oil or salt quenches are used to process parts similar to those run in pusher furnaces. As with pusher furnaces, parts are racked in trays or baskets prior to being charged in the furnace. In the case of salt quenches, either open or enclosed quenches may be utilized. With hot oil quenches, an enclosed quench is utilized.

Batch furnaces are moderately expensive to install, but have the flexibility to change cycles, a feature that is lacking in pusher furnaces. For austempering high volumes of heavier stampings, forgings, and machined parts with a variety of cycles, the batch furnace is a cost-effective option. In addition, an enclosed batch salt-quench can be fitted with an enhanced water-addition system to through harden parts that could not be run in continuous or salt-to-salt systems.

Specialty Equipment Applications. Many specially designed types of austempering equipment have, and are utilized for, specific applications. Some examples include:

- *Gantry furnaces* are used to austemper long parts such as rollers, shafts, and tubes
- *Fluidized bed furnaces* are used to austemper small lots of highly alloyed parts such as tool bits, gun

components, and small, complex castings

- *Induction heating systems* are used in conjunction with hot oil or salt quenches to austemper parts in localized areas. These systems are used to locally harden parts requiring improved fatigue strength and/or wear resistance with minimum distortion
- *Multiple-quench batch-type systems* utilize one furnace servicing several quenches which may include salt, water-based, oil, or gas quenches
- *Carboaustempering systems* provide a carburizing atmosphere in conjunction with an austempering quench. Parts processed in systems with this capability have a high-carbon bainitic core and exhibit excellent fatigue and wear resistance with minimum distortion. These systems are used to process gears, rollers, and other wear parts

Racking and handling procedures for austempering are not necessarily different from those used for other heat-treating operations. Racking or other means of keeping parts separated are often essential to the process. To minimize distortion, delicate parts must be handled with particular care.

For heating in tunnel-type or other special furnaces, a standard form of racking (Fig. 7) is usually employed. (Provision must also be made for lowering of parts into the austempering bath.) Parts similar to those illustrated in Fig. 7 may be batch treated by using fixtures such as those shown in Fig. 8(a). Another common type of rack, useful for handling disks or rings, is shown in Fig 8(b). The well-known Christmas tree type of rack is used for parts that can be hung. Some parts are strung on wires that can be suspended into the austenitizing and quenching media. Heavier parts, or parts that cannot be hung, may be placed in baskets, provided that rapid and uniform quenching can be obtained. Parts must not be stacked together because this will result in nonuniform quenching.

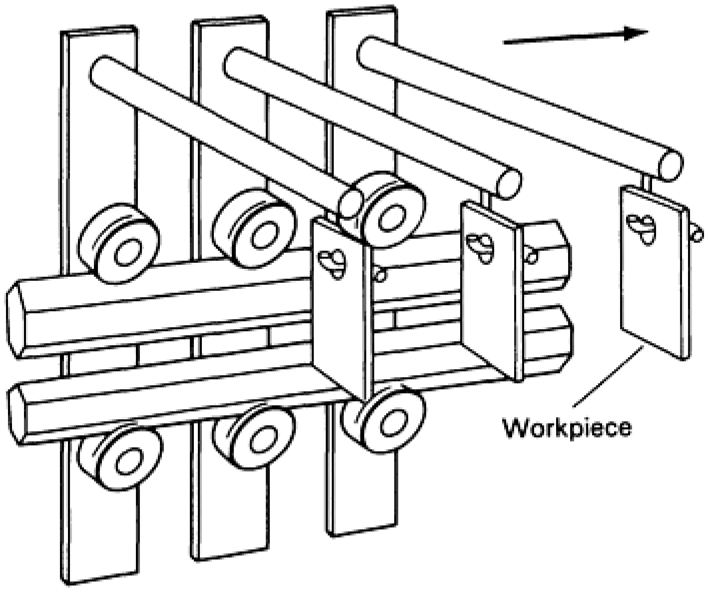


Fig. 7 Method of continuously transporting parts on fixtures through an austenitizing furnace and into an austempering bath

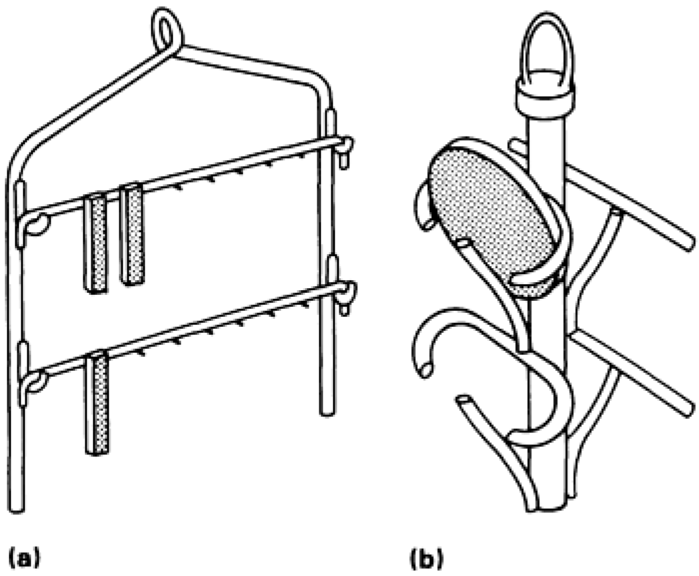


Fig. 8 Racking for batch-type austempering. See text for discussion of these two types of racks.

Racks, baskets, and other fixtures may be made of carbon steel, but if they are expected to last for many cycles it is usually more economical to make them of a heat-resisting alloy such as 35Ni-18Cr or another nickel-base alloy (see the article "Heat-Resistant Materials for Furnace Parts, Trays, and Fixtures" in this Volume).

Washing and Drying. Salts used in the austempering bath are water soluble, and no special equipment is needed for their removal. Normal practice is to use clean, hot water, with agitation, for dissolving and removing salt from austempered parts. Cold water may be used, but its dissolving action is much slower. Hot water may not suffice to dissolve all salt from parts with deep blind holes, small crevices, laps, hidden corners, or ledges. If it is not completely removed, salt may bleed from such crevices or joints long after heat treating. Quenching into hot water directly from the austempering salt bath is often used to blow out trapped salt. Large parts may be cleaned with high-pressure steam. However, rapid cooling may cause distortion.

Equipment requirements for specific austempering operations are detailed in the three production-base examples that follow.

Example 1: Two Methods of Austenitizing and Austempering Small Steel Parts.

Table 7 compares equipment required for two different methods of austenitizing and austempering small mechanical stops and levers. Parts of this type weighing 0.007 kg (0.015 lb) were processed at the rate of 4000/h by being austenitized at 845 °C (1550 °F) in an electrically heated salt-pot furnace and austempered in salt at 370 °C (700 °F). Parts weighing 0.002 kg (0.005 lb) were processed at the rate of 3700/h by being austenitized at 870 °C (1600 °F) in a controlled-atmosphere shaker-hearth furnace and austempered in salt at 360 °C (680 °F).

Table 7 Equipment requirements for two methods of austenitizing and austempering mechanical stops and levers

Requirements	Method 1	Method 2
Production requirements		
Weight of each piece, kg (lb)	0.007 (0.015)	0.002 (0.005)

Weight of each load, kg (lb)	12 (27)	[(a)]
Number of pieces per hour	4000	3700
Equipment requirements		
Type of austenitizing furnace	Salt pot[(b)]	Shaker hearth[(c)]
Size of furnace, mm (in.)	380 by 760 by 560	305 by 2900
	(15 by 30 by 22)	(12 by 114)[(d)]
Heat input, kJ (Btu) per hour	290,000 (275,000)[(e)]	90,000 (85,500)[(e)]
Amount of chloride salt, kg (lb)	770 (1700)	. . .
Operating temperature, °C (°F)	845 (1550)	870 (1600)
Type of austempering furnace	Salt bath[(f)]	Salt bath[(g)]
Size of furnace, mm (in.)	380 by 915 by 760 (15 by 36 by 30)[(h)]	610 by 1830 by 1220 (24 by 72 by 48)
Amount of nitrate-nitrite salt, kg (lb)	1770 (3900)	2720 (6000)
Heat input, kJ (Btu) per hour	215,000 (204,000)	70,800 (67,200)
Operating temperature, °C (°F)	370 (700)[(i)]	360 (680)
Agitation	Propeller-type pump	. . .
Cooling system	Blower[(j)]	. . .

(a) Shaker hearth.

(b) Electric furnace with internally heated ceramic pot.

(c) Electrically heated furnace with endothermic atmosphere (dew point, -1 °C, or 30 °F) generator.

(d) Size of hearth.

(e) At 845 °C (1550 °F).

(f) Salt heated with electric resistance elements.

(g) Electrically heated radiant tubes.

(h) Quench area: salt-separating chamber, 305 by 710 by 1040 mm (12 by 28 by 41 in.).

(i) Temperature of salt-separating chamber, 315 °C (600 °F).

(j) Blower between pot and furnace wall, pyrometer controlled

Example 2: Austempering 1.8 kg (3.9 lb) Parts at 1500 Pieces per Hour.

Table 8 gives details of equipment required for austempering parts made of 1080 steel at the rate of 1500/h. These parts, which varied in weight from 1.1 to 1.8 kg (2.4 to 3.9 lb), were austenitized at 925 °C (1700 °F) before being austempered.

Table 8 Equipment for austempering parts made of 1080 steel

Parts austenitized at 925 °C (1700 °F)

Production requirements	
Weight of each piece, kg (lb)	1.1 to 1.8 (2.4 to 3.9)
Production per hour	1500 pieces
Equipment requirements	
Austempering furnace	Submerged fuel-fired salt pot
Size of furnace, m^3 (ft^3)	6.6 (233)
Nitrate-nitrite salt, kg (lb)	11,340 (25,000)
Temperature, °C (°F)	345-360 (650-675)
Agitation	Pump, directed at delivery chute
Cooling	Forced air through burner tube

Example 3: Equipment for Austempering with Manually Operated Monorail Line.

Table 9 lists details of the equipment comprising a manually operated monorail line for preheating, austenitizing, austempering, washing and rinsing, and corrosion protection, and indicates production capacities for processing tubes, plates, and disks made of 1035 and 1060 steels.

Table 9 Equipment requirements for austenitizing, austempering, and corrosion protection of parts made of 1035 and 1060 steels

Equipment comprises a manually operated monorail heat-treating line.

Production requirements			
Part	Fabricated disk	Rectangular tube	Rectangular plate
Steel	1035	1060	1060
Section thickness, mm (in.)	12.5 (0.492)	1.4 (0.055)	0.8 (0.032)
Weight of part, kg (lb)	1.1 (2.5)	0.2 (0.425)	0.01 (0.024)
Load weight (gross), kg (lb)	163 (360)	35.7 (78.75)	7.3 (16)
Number of pieces per h	432	720	3900
Preheating, °C (°F); min	705 (1300); 10	705 (1300); 5	705 (1300); 5
Austenitizing, °C (°F); min	845-870 (1550-1600); 10	830 (1525); 10	830 (1525); 10
Austempering, °C (°F); min	425 (800); 10	345 (650); 6	330 (630); 6
Equipment requirements			
Preheating furnace	Immersed-electrode salt bath, 0.45 by 0.6 by 1.6 m (18 by 24 by 62 in.)		
Amount of chloride salt, kg (lb)	590(1300)		
Austenitizing furnace	Immersed-electrode salt bath, 0.45 by 0.6 by 1.6 m (18 by 24 by 62 in.)		
Amount of chloride salt, kg (lb)	590 (1300)		
Austempering furnace	Gas-fired salt bath, 0.6 by 1.2 by 1.8 m (24 by 48 by 72 in.)		
Amount of nitrate-nitrite salt, kg (lb)	2270 (5000)		
Heat input, kJ (Btu) per h	740,000 (700,000)		

Agitation	Two 150 mm (6 in.) impellers
Two washing and rinsing tanks	Gas-fired, hot water; each 0.5 by 0.9 by 1.2 m (20 by 36 by 48 in.)
Capacity, each tank	570 L (150 gal)
Heat input, each tank, kJ (Btu) per h	316,000 (300,000)
Tank for corrosion protection, m (in.)	0.5 by 0.9 by 1.2 (20 by 36 by 48)

Control of Process Variables

The achievement of desired results from austempering processes depends on control of the bath temperature and the immersion time of the work being processed, and on agitation of the bath.

Temperature control of austempering baths is important because:

- Bath temperature determines the hardness and other properties obtained in the part being heat treated
- Unintended freezing of a salt bath can result in unwarranted expense
- At temperatures exceeding 455 °C (850 °F), nitrate-nitrite salt mixtures will cause pitting attack of steel pots, and more importantly, steel workpieces
- *Caution: Local temperatures above 595 °C (1100 °F) anywhere in a nitrate-nitrite salt bath can cause violent exothermic reactions inthe salt that may result in fire or explosion even after the source of furnace heat has been shut off.* Equipment manufacturers should be consulted as to their recommendations regarding safe *average* bath temperatures

The potential hazard of nitrate-nitrite salt mixtures overheating as the result of failure of a thermocouple or control instrument must be recognized, and appropriate safeguards must be provided. A second instrument and thermocouple are recommended. These may be set 28 °C (50 °F) higher than the desired operating temperature and arranged to take over in the event of malfunction.

Usually, a variation in bath temperature of ±6 °C (±10 °F) is permissible. However, variations greater than ±6 °C have been known to cause unacceptable variations in the hardness of austempered parts.

Time in the bath should be sufficient to allow complete transformation. Allowing parts to remain in the bath for longer than the required time will increase the cost of the operation, but it is not harmful to mechanical properties (Table 10). In one instance, parts that had fallen from racks were unintentionally held at 265 °C (510 °F) for several months. Subsequent tests revealed that their properties were not harmed by the prolonged immersion.

Table 10 Effect of austempering time on hardness of three steels

Steel	Austempering temperature		Rockwell hardness[a] after austempering times of						
	°C	°F							
			30 min	60 min	90 min	120 min	240 min	300 min	360 min

1095[(b)]	230[(c)]	450[(c)]	91	90	90	90	90	90	90
	265[(d)]	510[(d)]	90	89	89	89	89	89	89
			1 min	2 min	5 min	10 min	20 min	40 min	80 min
8735[(e)]	260[(f)]	500[(f)]	51	51	49	49	48	48	47
	315[(f)]	600[(f)]	49	45	46	46	46	46	46
	370[(f)]	700[(f)]	40	39	38	38	38	38	37
8750[(g)]	260[(f)]	500[(f)]	58	56	53	51	52	52	51
	315[(f)]	600[(f)]	58	52	48	47	47	47	47
	370[(f)]	700[(f)]	54	42	39	39	39	38	39

(a) Rockwell 15-N hardness values for the 1095 steel; Rockwell C hardness values for the 8735 and 8750 steels.

(b) Steel contained 0.90% C; specimen thickness, 0.25 mm (0.010 in.). Each hardness value is an average of 12 specimens; range of test values did not exceed one point on Rockwell 15-N scale.

(c) Time for 100% transformation was 170 min.

(d) Time for 100% transformation was 85 min.

(e) Steel contained 0.37% C; specimen size, 16 by 32 by 2 mm (0.622 by 1.250 by 0.087 in.).

(f) Time for complete transformation was 5 to 10 min.

(g) Steel contained 0.49% C; specimen size, 25 by 25 by 3 mm (1 by 1 by $\frac{1}{8}$ in.)

Bath agitation can be a significant variable in austempering because it affects quenching speed. Quench rates can be two to three times greater for thinner parts as linear flow rates are increased from 0 m/min (0 ft/min) to 15 m/min (50 ft/min). Mechanical stirring, pumping, and air agitation have all proved successful for specific operations. Pumping provides the greatest amount of salt movement, although it requires a more expensive installation. In many applications, the other methods have provided a sufficiently rapid quench. The suitability of stirring as compared to pumping is indicated in the following example.

Example 4: Redesign of Salt-Bath Quenching System from Mechanical Stirrers to Pump Flow Agitation.

Mechanical stirring devices were originally used in the quenching system of a rotary retort furnace used for austempering (Fig. 9a). Although the pattern of agitation could be varied by changing the location and altitude of the impellers, this did not provide for displacement of the static salt within the chute; consequently, parts failed to quench adequately because the static salt allowed parts to remain in clusters. Changing the angles of the mechanical stirrers failed to eliminate inadequate quenching.

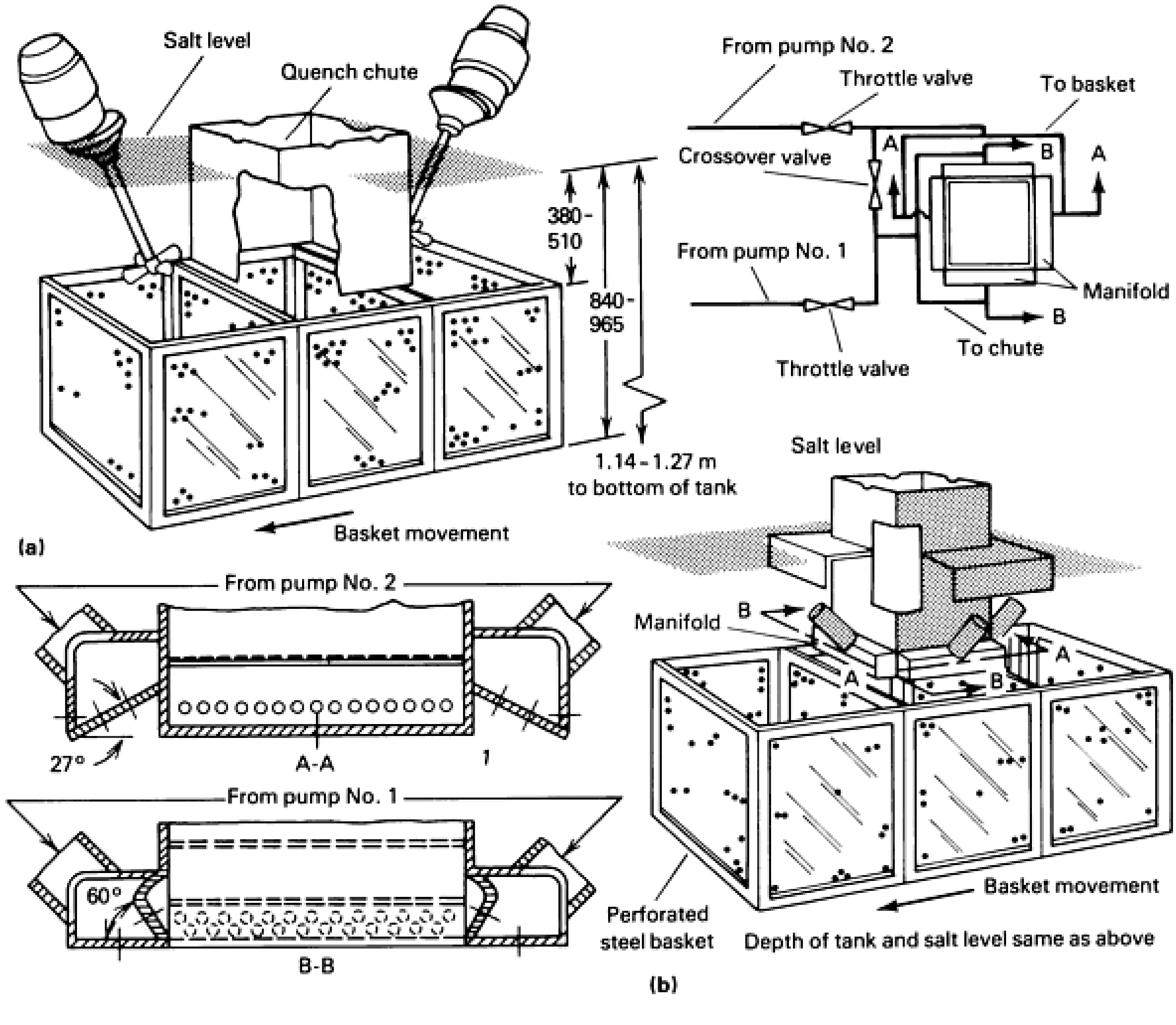


Fig. 9 Mechanical and pump methods of agitation discussed in Example 4. (a) Mechanical stirring. (b) Pump agitation. This example illustrates a problem of salt bath quenching efficiency in which extensive redesign of the quenching system proved to be necessary. After redesign, the system could be used at full flow for heavier parts 3 mm (0.125 in.) thick and at about half flow for parts about half this thickness. Accompanying text indicates methods of adjusting the pump throttle valve for control.

The lower section of the quench chute was redesigned for pump agitation (Fig. 9b). The output of a 950 L/min (250 gal/min) pump was directed upward into the chute at an angle of 60° above the horizontal from two oppositely inclined multiple orifice plates located at the bottom of the chute. Salt entering the chute was returned to the bath through a perforated section of the chute located just below the normal salt level. A skirt, extending outward from the chute above the perforated section and draped on all sides to a level below the salt level, maintained the atmosphere seal.

The output of a second 950 L/min (250 gal/min) pump was directed downward into the receiving basket at an angle of 27° below the horizontal. The salt entering the basket was returned to the bath through the perforated bottom and walls of the basket and over the top rim of the basket. A throttle valve was installed in the discharge line of each pump to control

the discharge velocity at the orifice plates. A crossover line with shutoff valve made it possible to supply salt to the two pairs of orifice plates, independently, from either or both pumps. The degree of agitation could then be adjusted for maximum quenching to match the mass of the parts being processed.

Experience has proved that the output from one pump to all four orifice plates provides adequate agitation for all parts being treated. Full flow is used for heavier parts 3 mm (0.125 in.) thick, and an estimated half flow is used for lighter parts 1.5 mm (0.060 in.) thick. Rough adjustment of the pump throttle valve is made by observing the stream of salt discharged from a hole drilled in the manifold piping (this hole serves primarily to drain these lines when the pumps are shut off). Final adjustment is based on the contour of the surface of the bath as formed by the parts in the baskets. A markedly dished (concave) contour, with the parts sloped upward against all sides and corners of the basket, indicates that agitation is sufficient to avoid clustering of parts. A feathering of the parts to an acute angle against the sides of the basket indicates excessive agitation that could result in loss of parts over the basket rim.

Dimensional Control

Parts can usually be produced with less dimensional change by austempering than by conventional quenching and tempering. Austempering may be the best way to hold close tolerances without extensive straightening or machining after heat treatment. The data in Fig. 10 and 11 indicate the degree of improvement in dimensional stability attainable by austempering as compared to water or oil quenching and tempering.

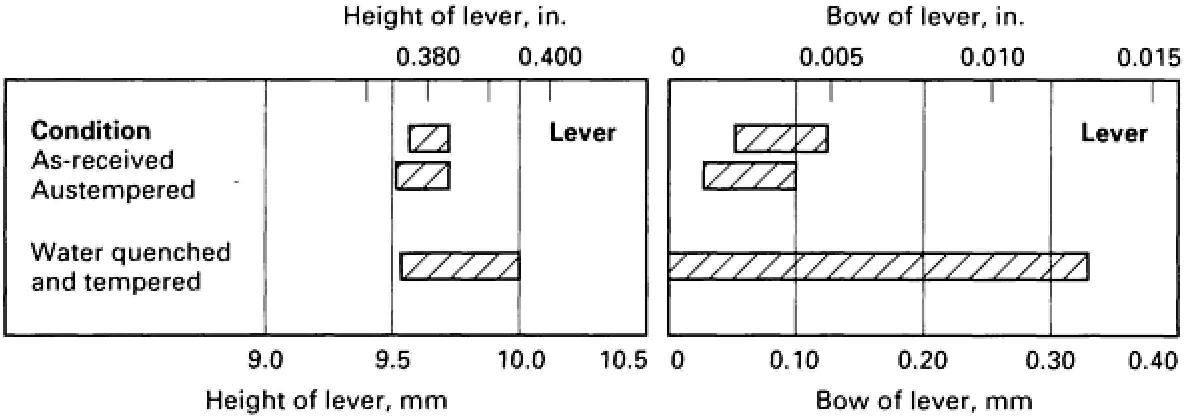


Fig. 10 Variation in dimensions of 3 mm (0.125 in.) thick levers after austempering and after water quenching and tempering. Horizontal bars represent groups of ten samples.

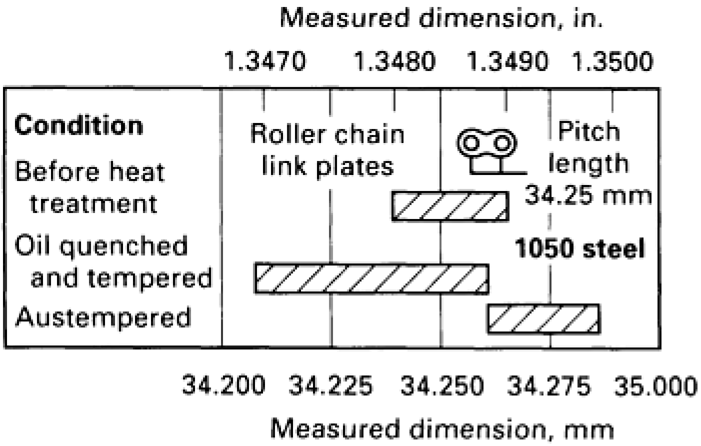


Fig. 11 Variation in pitch length of 2 mm (0.080 in.) thick link plates after austempering and after oil quenching and tempering. All link plates were austenitized at 855 °C (1575 °F) for 11 min; austempered link plates were held in salt at 340 °C (640 °F) for approximately 1 h, a time dictated by convenience in processing

but not required to attain complete transformation.

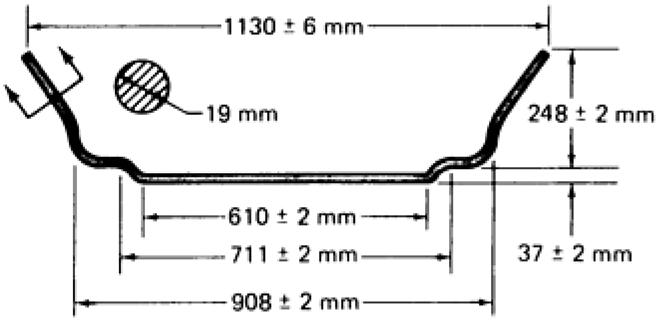
Example 5: Reduced Distortion in U-Bolts by Austempering.

In one application, a U-shape part was formed from 1095 steel strip, 0.25 mm (0.010 in.) thick. The open end of the U varied within 0.25 mm (0.010 in.) after forming. When these parts were oil quenched from 800 °C (1475 °F) and tempered at 260 °C (500 °F), the open end of the U varied over a range of 1.3 mm (0.050 in.). However, when the parts were austempered for 90 min at 265 °C (510 °F), the dimensional spread was decreased to about 0.8 mm (0.030 in.).

Example 6: Reduction in Straightening Operations with Austempering.

Table 11 compares the dimensional changes that occurred in stabilizer bars as a result of oil quenching and tempering with those that resulted from austempering. About 20% of these bars require straightening when oil quenched. This percentage is sharply reduced when austempering is used. With a new die setup, about 1 to 5% will require straightening for the first 3000 pieces while the dies are being trimmed for precise fit. Once the correct fit and setup are established, straightening will drop to less than $\frac{1}{2}$%. This will carry through until the die wear becomes appreciable (approximately 40,000 pieces), at which point the amount of straightening required begins to increase.

Table 11 Effects of oil quenching and tempering and of austempering on dimensions of stabilizer bars



Specified dimensions		Process	Measured dimension[(a)]					
			High		Low		Average	
mm	in.		mm	in.	mm	in.	mm	in.
1130 ± 6	$44\frac{1}{2} \pm \frac{1}{4}$	OQ & T	1133	$44\frac{5}{8}$	1127	$44\frac{3}{8}$	1130	$44\frac{1}{2}$
		Austemper	1130	$44\frac{1}{2}$	1126	$44\frac{5}{16}$	1127	$44\frac{3}{8}$
908 ± 2	$35\frac{3}{4} \pm \frac{1}{16}$	OQ & T	911[(b)]	$35\frac{7}{8}$ [(b)]	905[(b)]	$35\frac{5}{8}$ [(b)]	910	$35\frac{13}{16}$
		Austemper	910	$35\frac{13}{16}$	910	$35\frac{13}{16}$	910	$35\frac{13}{16}$

711 ± 2	$28 \pm \frac{1}{16}$	OQ & T	714[b]	$28\frac{1}{8}$ [b]	711	28	713	$28\frac{1}{16}$
		Austemper	713	$28\frac{1}{16}$	711	28	711	28
610 ± 2	$24 \pm \frac{1}{16}$	OQ & T	614[b]	$24\frac{3}{16}$ [b]	611	$24\frac{1}{16}$	613[b]	$24\frac{1}{8}$ [b]
		Austemper	611	$24\frac{1}{16}$	610	24	611	$24\frac{1}{16}$
248 ± 2	$9\frac{3}{4} \pm \frac{1}{16}$	OQ & T	249	$9\frac{13}{16}$	246	$9\frac{11}{16}$	248	$9\frac{3}{4}$
		Austemper	248	$9\frac{3}{4}$	246	$9\frac{11}{16}$	246	$9\frac{11}{16}$
37 ± 2	$1\frac{15}{32} \pm \frac{1}{16}$	OQ &T	38	$1\frac{1}{2}$	36.5	$1\frac{7}{16}$	38	$1\frac{1}{2}$
		Austemper	38	$1\frac{1}{2}$	38	$1\frac{1}{2}$	38	$1\frac{1}{2}$
2[c]	$\frac{1}{16}$ (0.0625)[c]	OQ & T	1.3	0.050	0.13	0.005	0.8	0.032
		Austemper	1.5	0.060	0.25	0.010	0.9	0.036

OQ & T, oil quenching and tempering.

(a) Data represent measurements made on 12 samples of bars processed by each method.

(b) Out or specification.

(c) Arm-to-arm parallel

Austempering Problems and Solutions

Problems encountered in austempering, together with their solutions, are discussed in the following examples.

Example 7: Normalizing before Austenitizing and Austempering to Achieve Carbide Solution and Adequate Ductility.

Threaded fasteners made of 1060 steel, designed to be embedded in concrete by explosive discharge, exhibited insufficient ductility after austempering. These parts were hardened by being heated to 845 °C (1550 °F) and quenched in a salt bath at 290 °C (550 °F) for 30 min. The lack of ductility was attributed to insufficient carbide solution. Parts with acceptable ductility after austempering were obtained by normalizing before final austenitizing and austempering.

Example 8: Austempering Procedure for a Steel with Borderline Hardenability.

Lawn mower blades, approximately 3 mm ($\frac{1}{8}$ in.) thick and made of 0.50 to 0.60% C steel, exhibited low hardness after austempering. Low hardenability due to lower-than-normal manganese content proved to be the cause. The manganese content desired for this application should be near the high side of the allowable range (0.60 to 0.90%), but the steel for these blades contained less than 0.50% Mn.

The problem was solved by first quenching the blades in a lower-temperature bath (just above M_s) for $\frac{1}{2}$ min and then transferring them to the normal austempering bath at 315 °C (600 °F) and holding for $\frac{1}{2}$ h. This technique has been successfully applied to many carbon steels that were borderline for austempering because of low hardenability in relation to the section being quenched.

Example 9: Use of Pump Agitation in Quenching Part Clusters.

A small percentage of parts made of medium-carbon and low-alloy steels had low hardness after austempering. The parts had been heated in a rotary retort furnace. Microscopic examination disclosed high-temperature transformation products caused by underquenching.

Investigation disclosed that this condition resulted when the parts were quenched in clusters rather than in a continuous sequence. Clustering resulted in a slow cooling rate at the center of the clusters. The problem was solved by redesigning the submerged portion of the quench chute to allow for high-velocity multiple jets of molten salt that could be directed upward into the chute and downward into the receiving basket (see Example 4 and Fig. 9).

Example 10: Reduced Salt Bath Temperature to Eliminate Nonuniform Quenching from Chloride Contamination.

Nonuniform hardness was found in some parts hardened in an automated austempering cycle. The parts, made of 1050 steel, were 13 mm ($\frac{1}{2}$ in.) wide, 125 mm (5 in.) long, and 1 mm (0.040 in.) thick. Heat treatment consisted of austenitizing at 845 °C (1550 °F) in a neutral salt, followed by quenching at 345 °C (650 °F) and holding for 15 min. The problem was traced to chloride contamination of the nitrate-nitrite quenching bath, a condition that caused the quenching bath to be sluggish. Inspection of the filtering screens indicated that they were not functioning adequately.

The problem was solved by establishing a procedure for reducing the bath temperature to 290 °C (550 °F) twice a week and thus precipitating the chlorides to a screen at the bottom of the bath for removal. This procedure eliminated the need for filtering screens and provided uniform quenching.

Example 11: Prehardening Treatment to Dissolve the Abnormally Large Carbides Produced during Spheroidization.

Chain saw components made of low-alloy Cr-Ni-V steel containing 0.65 to 0.75% C exhibited excessive brittleness in a torque test. The parts had been austenitized in a shakerhearth furnace at 830 °C (1525 °F) and quenched in an agitated salt bath at 290 °C (550 °F). Examination disclosed excessive martensite and undissolved carbides in the microstructure. Overspheroidization prior to hardening was determined to be the cause of brittleness. This resulted in the formation of abnormally large carbides that were not dissolved during the 11-min furnace cycle, thus lowering the carbon content of the matrix and raising the M_s temperature. This caused partial transformation to martensite instead of 100% lower bainite. The problem was solved by prehardening and tempering prior to the regular heat-treating cycle.

Modified Austempering

As mentioned previously, modifications of austempering practice that give rise to mixed structures of pearlite and bainite are quite common in industrial practice. The amounts of pearlite and bainite may vary widely in different modifications of processing.

Patenting, a treatment used in the wire industry, is a significant and useful form of modified austempering, in which austenitized wire or rod is continuously quenched into a bath maintained at 510 to 540 °C (950 to 1000 °F) and held in the bath for periods ranging from 10 s (for small wire) to 90 s (for rod). Patenting provides a combination of moderately high strength and high ductility. As indicated in Fig. 12 by the line designated Modified practice, the process varies from true austempering in that the quenching rate, instead of being rapid enough to avoid the nose of the TTT curve, is sufficiently slow to intersect the nose, which results in the formation of fine pearlite.

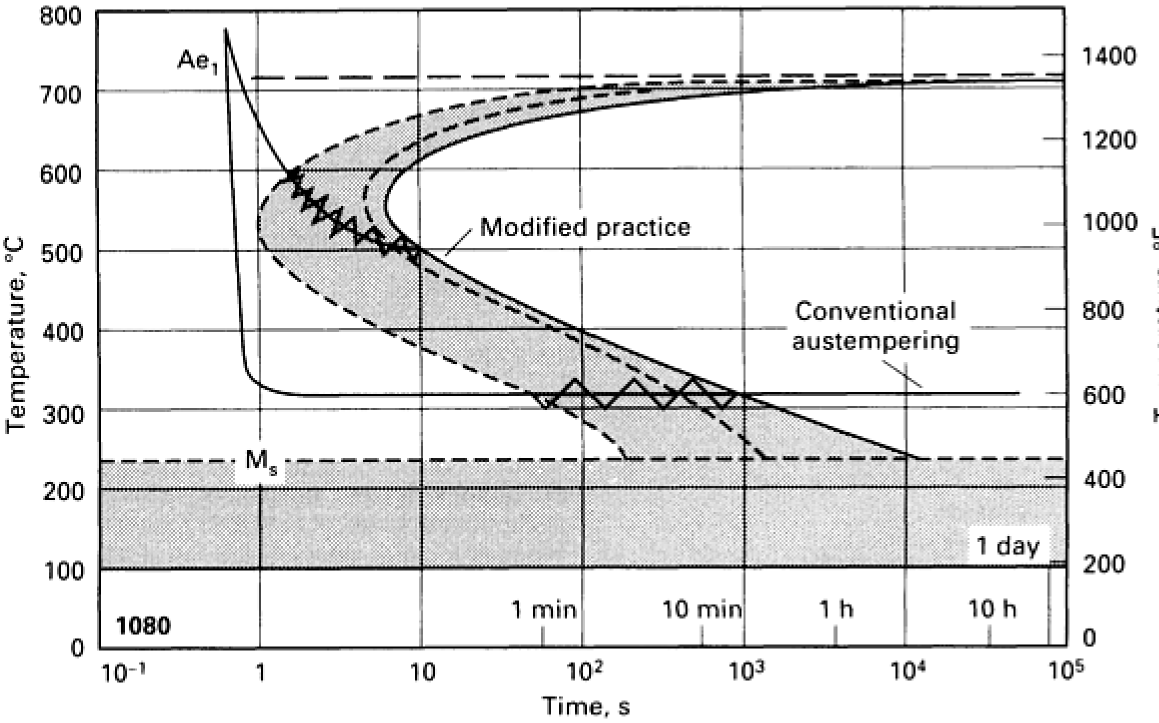


Fig. 12 Time-temperature transformation diagram for 1080 steel, showing difference between conventional and modified austempering. When applied to wire, the modification shown is known as patenting.

Similar practice is usefully employed in applications involving plain carbon steels when a hardness between about 30 to 42 HRC is desirable or acceptable. The hardness of plain carbon steel quenched at a rate that intersects the nose of the TTT curve will vary with carbon content (Fig. 13).

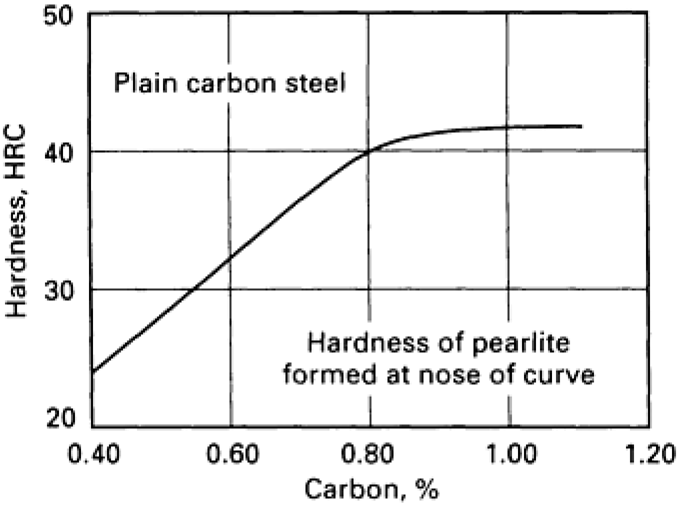


Fig. 13 Effect of carbon content in plain carbon steel on the hardness of fine pearlite formed when the quenching curve intersects the nose of the time-temperature diagram for isothermal transformation

Modified practices can be applied to parts having sections thicker than are normally considered practicable for austempering. These practices, however, also are subject to certain metallurgical limitations, such as the following that apply to the modified austempering of 1080 steel:

- The part to be quenched must be of sufficient mass or weight that cooling to the quench bath temperature cannot be accomplished in the time (about $\frac{3}{4}$ s) allowed for avoiding the nose of the TTT curve; otherwise, the part will undergo true austempering and may be harder than desired. The temperature of the quenching medium should not be raised above 370 °C (700 °F) in an effort to retard the cooling rate, or temper brittleness may result. For small parts, isothermal annealing at 565 °C (1050 °F) is preferred to austempering for obtaining hardness in the range of 30 to 42 HRC
- The part to be quenched is subject to a maximum, as well as a minimum, weight limit. If more than about 20 s is required for the center of the part to transform, or if there is a rise in bath temperature, some upper bainite may form, resulting in a variable hardness and mixed structure
- The lower temperature limit of the quench bath depends on the weight of the part. For pieces weighing 1 to 2 kg (2 to 4 lb), the lower limit of bath temperature is about 330 °C (625 °F)

From the above it is evident that modified practices are limited by several critical factors and that some trial and error is necessary in developing an optimum cycle for parts of specific composition and section thickness.

Another form of modified austempering also entails the use of a special technique but produces results that are similar to those obtained in true austempering. This modification is employed for parts that, because of their size and the type of steel from which they are made, are difficult to quench rapidly enough to avoid the nose of the TTT curve before transformation begins. In such applications, the cooling rate can be increased by first quenching the part into a bath that is slightly above the M_s temperature. For 1080 steel, this is about 260 °C (500 °F), as shown in Fig. 12. The part is held at this temperature for only the brief time necessary to obtain temperature equalization throughout the section, and is then transferred to the austempering bath at a higher temperature and allowed to transform isothermally in the normal manner (see Example 8).

Washing and Drying

Plain water, preferably warm or hot, is most suitable for cleaning austempering salts from parts. A single overflowing tank can be used. In automated systems, it is common practice to use two conveyorized tanks, the first heated by incoming parts and the second separately heated. Fresh water is added to the second tank, with the overflow going to the

first tank. In some cases, the concentrated salt solution is pumped back to the salt tank with available salt-recovery systems to recover both the salt and the water. This recovery reduces salt and water consumption and alleviates the disposal problem. The parts should be dried by warm forced air or treated with a rust preventative immediately after washing.

Safety Precautions

In operating an austempering installation, the same precautions should be taken that are appropriate for operation of any other hot liquid bath. These include the wearing of gloves and face masks. Several other special precautions are unique to operation of nitrate-nitrite baths:

- *Caution: Local temperatures above 595 °C (1100 °F) anywhere in a nitrate-nitrite salt bath can cause violent exothermic reactions in the salt that may result in fire or explosion even after the source of furnace heat has been shut off.* (Overheating might be caused by instrument failure or by overloading of the bath with hot workpieces.) Equipment manufacturers should be consulted for their recommendations regarding safe *average* bath temperatures
- *Caution: Nitrate-nitrite mixtures are oxidizing and should not be intermixed with materials that are readily oxidized. Cyanide and cyanide-bearing salts are especially incompatible with nitrate-nitrite salt mixtures.* Austempering should never be done directly from an austenitizing bath containing cyanide. When it is desirable to austemper cyanided or liquid carburized parts, they should first be immersed in a bath of neutral salt. This bath should be operated at the desired austenitizing temperature and controlled to prevent the accumulation of more than 2% sodium cyanide or potassium cyanide
- When austempering is carried out in the same area where cyanide-containing salts also are used, the salt pots and salt containers should be color coded. Yellow, orange, or red are commonly used for identification of nitrite and nitrite-containing salts. Cyanide-containing materials may be identified by white, blue, or gray. *Caution: Anyone handling these materials should be made aware that explosions can occur if they are intermixed*
- Finely divided carbonaceous materials should not be used. For example, it is common practice to use graphite, coal, or powdered coke as an insulating cover on lead baths. *Caution: Under no circumstances should these be employed as coverings for nitrate-nitrite salt baths.* Accidental contamination of austempering baths with accumulations of carbon black, which may build up at the discharge end of gas carburizing or carbonitriding furnaces, must also be avoided. Where work is to be austempered directly from such furnaces, an opening for frequent cleanout should be provided.

Introduction

INDUCTION HEATING is a method of heating electrically conductive materials by the application of a varying magnetic field whose lines of force enter the workpiece. In this process, the varying magnetic field induces an electric potential (voltage), which can then create an electric current depending on the shape and the electrical characteristics of the workpiece. These so-called eddy currents dissipate energy and produce heat by flowing against the resistance of an imperfect conductor.

Because all metals are fair electrical conductors, induction heating is applicable to several types of metal processing operations such as melting, welding, brazing, heat treating, stress inducement, zone refining, and heating prior to hot working (Table 1). The technique also lends itself to a variety of nonmetal applications including adhesive bonding, graphitizing carbon, drying, curing, and superheating glass. Of these applications, heat treating predominates in terms of the number of units used, with surface hardening of steel and cast iron being the most prevalent use. Compared to furnace techniques, induction heating can often provide energy savings and much higher heating rates than convection, radiation, conduction, or even flame-impingement processes. Other advantages of induction heat treating, which stem from this noncontact method and its generation of heat within the workpiece, are:

- Ease of automation and control
- Reduced floor space requirements
- Quiet and clean working conditions Suitability for integration in a production line or general work area due to the elimination of secondary or radiated heating

- Self-monitoring capability

Table 1 Induction heating applications and some typical products

Preheating prior to metalworking
Forging Gears Shafts Hand tools Ordnance
Extrusion Structural members Shafts
Heading Bolts Other fasteners
Rolling Slab Sheet (can, appliance, and automotive industries)
Heat Treating
Surface hardening, tempering Gears Shafts Valves Machine tools Hand tools
Through hardening, tempering Structural members Spring steel Chain links Tubular goods
Annealing Aluminum strip Steel strip
Welding
Seam Welding Oil-country tubular products Refrigeration tubing Line pipe
Melting
Air melting of steels

Ingots Billets Castings
Vacuum induction melting
Ingots Billets Castings "Clean" steels Nickel-base superalloys Titanium alloys

Acknowledgement

Much of the material presented in this article was adapted from *Elements of Induction Heating--Design, Control, and Applications,* ASM International, 1988 and from *Induction Heat Treatment of Steel,* ASM International, 1986.

Principles of Induction Heating

The basic components of an induction heating system are an induction coil, an alternating-current (ac) power supply, and the workpiece itself. The coil, which may take different shapes depending on the required heating pattern, is connected to the power supply so that a magnetic field is generated from the current flow (Fig. 1a). The magnitude of the field depends upon the strength of the current and the number of turns in the coil.

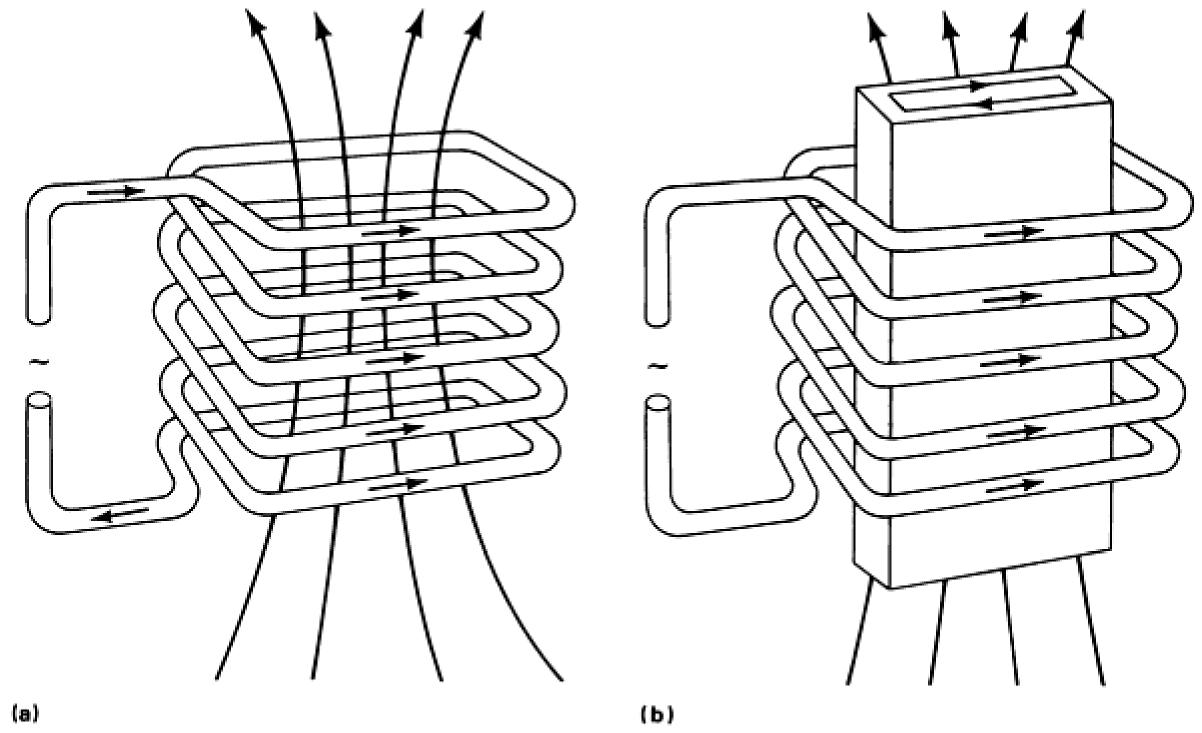


Fig. 1 Pattern of currents and the magnetic field in a solenoid coil (a). In (b), note that the induced eddy current in the specimen is opposite to that in the coil.

If an electrically conductive object is placed inside a coil with a varying current, the eddy currents are generated from the varying magnetic field within the object. These eddy currents are induced as a result of Faraday's law of electromagnetic induction:

$$e = -N\frac{d\Phi}{dt} \qquad \textbf{(Eq 1)}$$

which relates an induced voltage (e) to the time rate of change of the magnetic field (Φ) and the number of turns (N) in the coil. In effect, the coil acts in much the same manner as a primary winding of a transformer, with the workpiece acting as a single-turn (or short-circuited) secondary winding. Hence, the term "transformer action," which is sometimes used to describe the process (see the section "Coil Design" and the discussion of Fig. 31).

Eddy Current Characteristics. At any moment the direction of the induced current in the workpiece is approximately opposite to that in the inductor coil, and in general its flow pattern will describe a kind of "shadow image" of the coil conductors. The induced currents also generate their own magnetic fields, which are in opposition to the field generated by the coil and thereby prevent the field from penetrating to the center of the object (Fig. 1b). Therefore, the eddy currents are more concentrated at the surface and decrease in strength toward the center of the object (Fig. 2a). This phenomenon of the eddy currents travelling closer to the surface of a conductor is called the "skin effect."

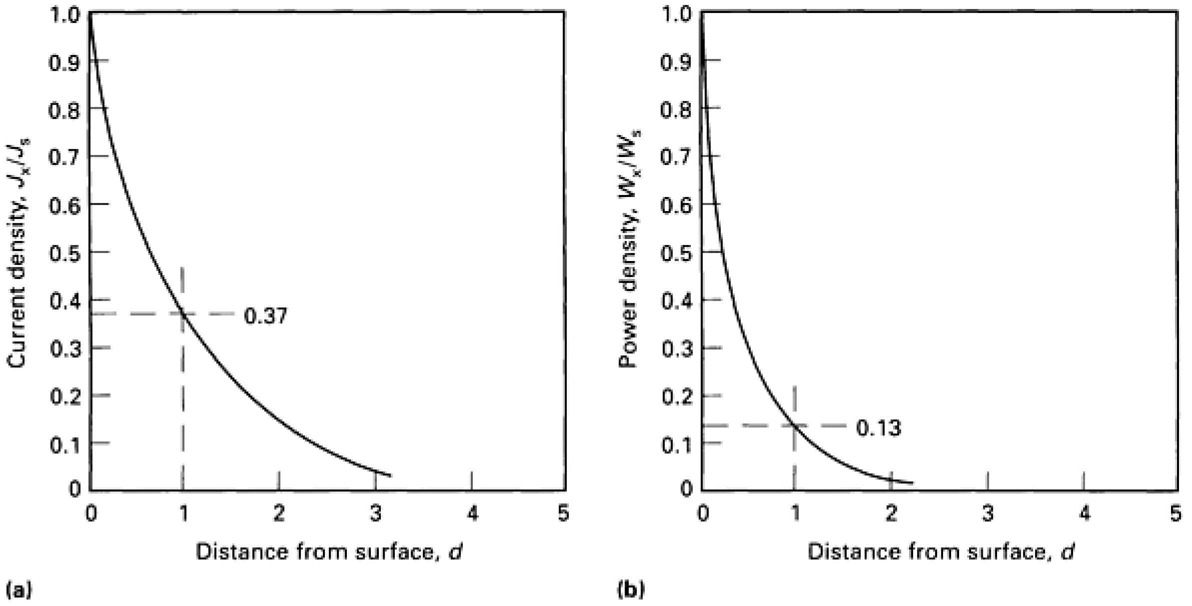


Fig. 2 Schematics showing current density (a) and power density (b) characteristics. In (a), $J_x = J_s\, e^{-x1d}$, where J_x is the current density at some distance, x, from the surface, J_s is the current density at the surface, and *d* is the reference depth as given in Eq 2. In (b) $W_x = W_s\, e^{-2x1d}$, where W_x and W_s represent the power density at some distance, x, from the surface and the surface power density, respectively.

Reference Depth. The mathematics needed to explain the skin effect involve a differential equation that has solutions in the form of Bessel functions. These solutions demonstrate that the induced current in a large planar object (that is, a plate much thicker than the expected eddy current penetration) decreases exponentially from the surface into the workpiece, or electrical load. This allows the definition of an "effective" depth of eddy currents known as the "reference depth" or "penetration depth," where the current density has dropped by 1/*e* (or 37%) of its surface value. The formula for this depth is given by:

$$d = \sqrt{\frac{r}{p m_0 m f}} \qquad \textbf{(Eq 2)}$$

where *d* is the reference depth; ρis the resistivity of the workpiece; μ_0 is the magnetic permeability of the vacuum; μ is the relative magnetic permeability of the workpiece (dimensionless); and *f* is the frequency of the alternating magnetic field of the work coil. If the current is squared, a curve that relates to the heating effect of the eddy currents (Fig. 2b) is obtained. At the depth of penetration, *d,* the heating effect therefore drops to $1/e^2$, or 14% of its value at the surface.

Figure 3(a) presents plots of penetration depth at various frequencies as a function of electrical resistivity. Figure 3(a) also illustrates different frequency requirements for a given penetration depth during various steel processing methods. These variations occur for any given material, because the resistivity of conductors varies with temperature. Furthermore, for ferromagnetic metals, the relative permeability varies with temperature, decreasing to a value of one (relative to free space) at the so-called Curie temperature. Also, as the power density is increased, steels may become magnetically saturated, leading to decreased permeability and hence increased reference depth (Fig. 3b). Because of these effects, the reference depth in nonmagnetic materials may vary by a factor of two or three over a heat-treatment temperature range, whereas for magnetic steels it can vary by a factor of 20.

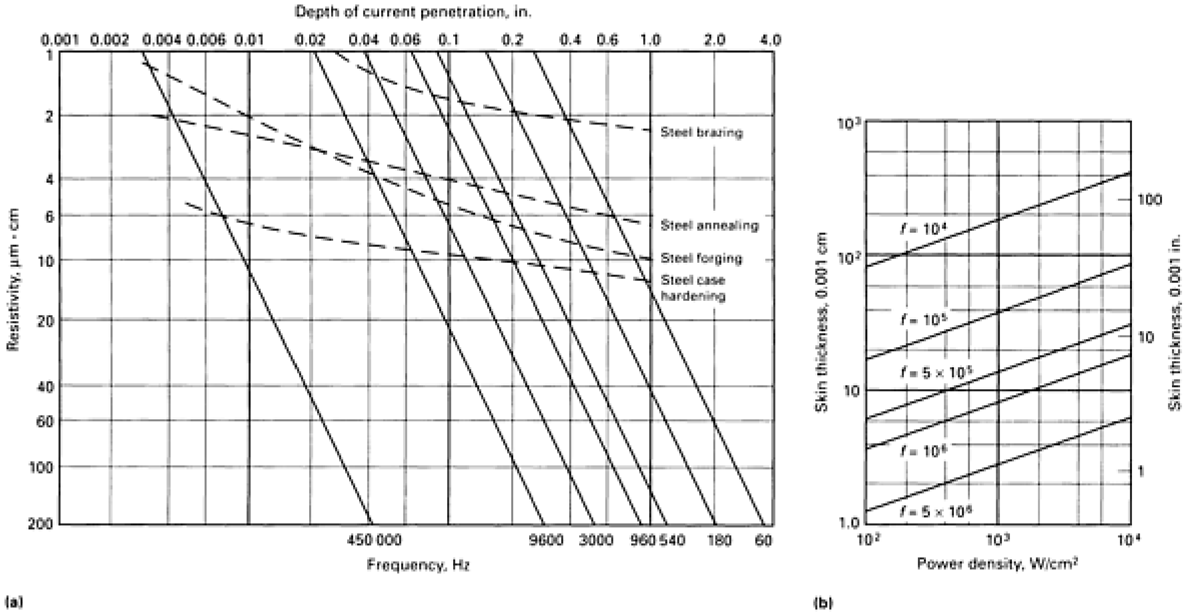


Fig. 3 Plots of penetration depth at various frequencies as a function of electrical resistivity. (a) Curves of current penetration versus frequency for induction heating with longitudinal flux. The dashed lines represent the reference depth for ferromagnetic steel below the Curie temperature for various operations. (b) Reference (skin) depth for magnetic steel as a function of power density

Current Cancellation. As previously noted, current density decreases exponentially (Fig. 2a) if the dimensions of the part are sufficiently large. However, if eddy currents in the inner regions of an object overlap each other, then the currents cancel each other. This effect is illustrated in Fig. 4(a) for various ratios of object thickness (*a*) and reference depth (*d*). The dashed lines show exponential decay from either side, while the solid line gives the net current from the summation of the two dashed lines. Net heating curves (Fig. 4b) are obtained by squaring the net current density.

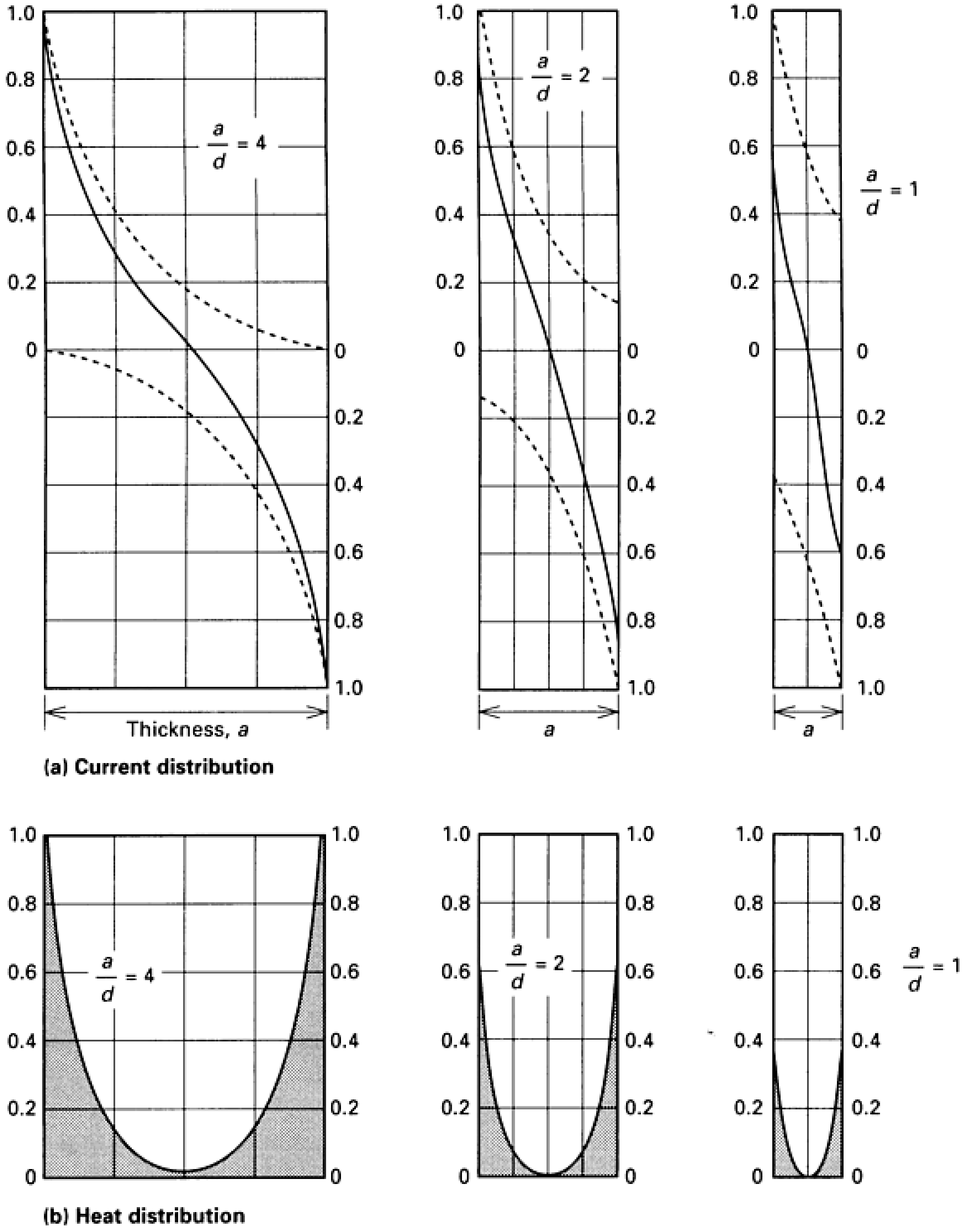


Fig. 4 Schematics showing current distribution (a) and heat distribution (b) for specimens of varying thicknesses. See the discussion of current cancellation for details.

Because current cancellations reduce the efficiency of heating, the rule of thumb for good efficiency is to have the reference dimension of the part at least 3 times greater than the reference depth (*d*). The reference dimension is the diameter of round objects or the thickness of rectangular objects such as strips or slabs.

Heat Generation. The primary mechanism of heat generation occurs from the flow of eddy currents in the workpiece. A second mechanism of heat generation occurs in ferromagnetic materials when energy is dissipated during the reversal of magnetic domains. This effect in ferromagnetic materials is usually ignored in induction heating calculations, because

the effect is small for the typical strength levels of magnetic fields for induction heating. Therefore, the rate of heating in units of power (watts) is largely a function of I^2R, or Joule heating.

The heating rate is affected by several variables such as:

- Field strength (expressed in units of ampere-turns of the work coil)
- Proximity of the workpiece to the coil conductors
- The electrical and magnetic properties of the material such as resistivity (ρ) and magnetic permeability (μ)

Heating rates are typically controlled by the coil voltage, because the field strength (or coil current) is roughly proportional to coil voltage.

The desired rate of heating varies with the application, and the mathematical analysis of induction heating processes can be quite complex for all but the simplest of workpiece geometries. This is because of the effects of nonuniform heat generation through the workpiece, heat transfer, and the fact that the electrical, thermal, and metallurgical properties of most materials exhibit a strong dependence on temperature. For this reason, quantitative solutions exist for the most part only for the heating of round bars or tubes and rectangular slabs and sheets. Nevertheless, such treatments, if properly applied, may provide useful insights into the effects of coil design and equipment characteristics on heating patterns in irregularly shaped parts. This information, coupled with knowledge generated through years of experimentation in both laboratory and production environments, serves as the basis for the practical design of induction heating processes.

Coupling and Flux Shaping. The degree of coupling between the workpiece and the magnetic field of the coil is determined by the number of magnetic flux lines that enter the workpiece. This flux density (number of lines of force) is proportional to the coil current, and the amount of energy transferred is proportional to the square of the number of flux lines intercepted by the workpiece. The frequency of coil currents also influences the pattern of induced currents, because flux lines tend to stay closer to the coil conductors as frequency is increased.

Flux leakage refers to the flux that does not thread through the heated material. The degree of flux leakage depends, in part, upon the electrical gap between the coil conductors and the workpiece. This so-called air gap is of greater concern as frequency increases, because flux lines tend to stay closer to the surface of coil conductors as frequency is increased. The factors influencing the air gap distance are discussed in the section "Coil Design" in this article (see the discussion on coupling distance).

Flux leakage can also be influenced by the use of flux concentrators, which are ferromagnetic materials purposely placed on or near the coil assembly. These devices, which are described in the section "Coil Design" in this article, provide a path of low magnetic reluctance and facilitate the concentration of flux lines in desired regions.

Induction Heat-Treating Equipment

An induction heating system typically consists of a power supply, a workstation, an inductor (heating) coil, controls, and workpiece handling units. When a steel or cast iron is being hardened, the system may also include a quenching system, depending on the hardenability of the particular grade.Some annealing practices may also be enhanced by accelerated cooling. It is common practice to include other auxiliary equipment such as line starters, electrical disconnects, and equipment cooling systems as part of an induction heating package.

The basic architecture of an induction heating system includes a workstation (or heat station), which contains load matching components such as output transformers and capacitors, plus high-frequency contactors, protective devices, cooling-water manifolds, and quench valves. The principal function of the workstation is to provide the proper electrical impedance match between the output of the power supply and the inductor (induction heating coil) for optimum power transfer into the heated load. The coil is normally mounted on the front of and close to the workstation. Workstation components may sometimes be installed in the power supply enclosure, as is often the case in small solid-state, medium-frequency heaters, and in many of the vacuum-tube oscillator units. Here the only external component that may be needed for load matching is an output transformer that may be positioned up to several feet from the power supply.

Power Supplies

Besides the induction coil and workpiece, the power supply is probably the most important component of an overall induction heating system. The function of the power supply is to accept power from a line at 60 Hz (50 Hz or other utility frequency in other parts of the world) and to deliver ac electrical energy through the load matching circuit to the inductor coil circuit at a useful voltage and frequency. Over the years, three basic frequency ranges have evolved for the classification of ac induction heating systems:

- Low-frequency systems (50 or 60 Hz line-frequency systems)
- Medium-frequency systems (150 or 180 Hz triplers or converters up to about 10 kHz)
- High-frequency systems (10 kHz and up)

Medium- and high-frequency power supplies suggest the need for conversion of line-frequency power, preferably three phase, to a single phase of higher frequency. Typical power ratings as a function of frequency are shown in Fig. 5.

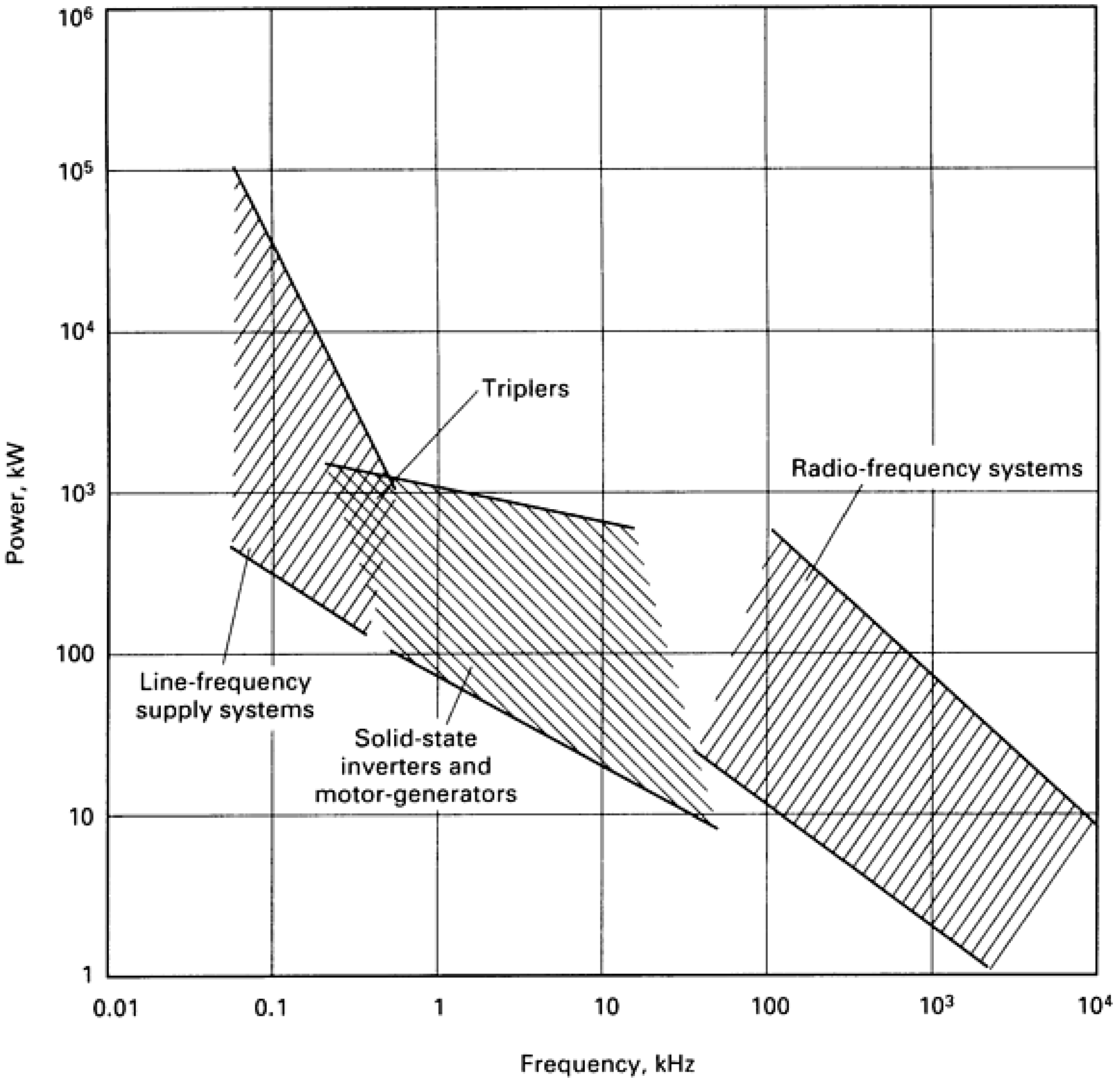


Fig. 5 Ranges of power ratings and frequencies for various induction power systems

There are essentially six different types of power supplies for ac induction heating applications, each designed to supply ac power within a given frequency range. These six types are line-frequency systems, frequency multipliers, solid-state (static) inverters, motor-generators, spark-gap converters, and radio-frequency (RF) power supplies. At the present time, the spark-gap oscillator is no longer manufactured, and the static, solid-state power supply has all but replaced rotating

machines or motor-generators. Table 2 gives the frequency and power ranges, approximate efficiencies, and other features of four major induction heating power sources.

Table 2 Characteristics of the four major power sources for induction heating

Power source	Frequency range	Power range	Efficiency %	Features
Line frequency	60 Hz	100 kW to 100 MW	90-95	High efficiency; low cost; no complex equipment; deep current penetration
Motor-generator	500 Hz to 10 kHz	10 kW to 1 MW	75-85	Low sensitivity to ambient heat; low sensitivity to line surges; fixed frequency; low maintenance cost; spares not needed
Solid state	180 Hz to 50 kHz	1 kW to 2 MW	75-95	No standby current; high efficiency; no moving parts; needs protection outdoors; no warmup time; impedance matches changing loads
Vacuum tube	50 kHz to 10 MHz	1 kW to 500 kW	50-75	Shallow heating depth; localized heating; highest cost; impedance matches changing loads; lowest efficiency

Choice of a power source depends primarily on the desired frequency, although there is often considerable overlap of application capability for any given unit in its frequency range. The frequency required for efficient induction heating is determined by the material properties (that is, resistivity and relative magnetic permeability) and the workpiece cross-sectional size and shape (see, for example, the previous discussions of Fig. 4). In a great many cases, a suitable frequency may also be impacted by the application requirements such as case depth in surface hardening of steels or the allowable temperature gradient for through hardening. In general, however, equipment cost per kilowatt increases with frequency, so a power supply of the lowest possible frequency that will accomplish the job efficiently is usually the best place to start when considering equipment. However, there is a trend away from 60 Hz even where they can be used, because they may not always be the most economical in initial cost when compared to solid-state supplies. Typical frequency selections for a number of specific applications are summarized in the section "Frequency Selection" in this article.

Power requirements for induction heating are also dependent on the specific application. For through heating applications, the power needed is generally based upon the amount of material processed per unit of time, the peak average temperature, and the material's heat capacity at this temperature. A power determination for localized heating and other operations, such as surface hardening of steel, is not as simple because of the effects of heat conduction to the adjacent metal and/or unhardened core. Nevertheless, guidelines in such situations are available (see the section "Power Density and Heating Time" in this article).

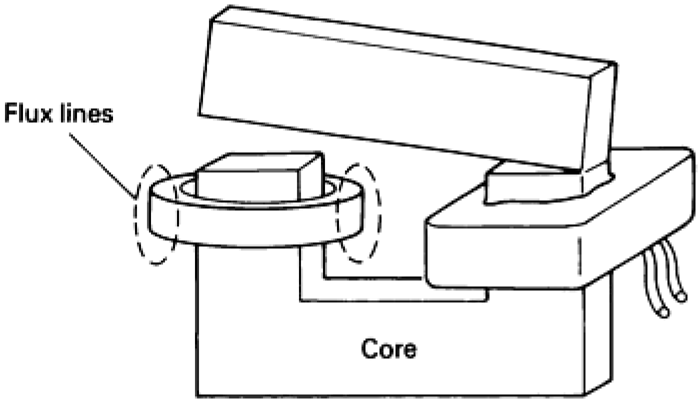
Line-frequency power supplies are considered low-frequency (50/60 Hz) and apply the local utility frequency to the coil, so no frequency conversion is needed. From an application viewpoint, the primary use for line-frequency induction equipment is through heating or very deep heat treating. Because most requirements in through heating applications call for some reasonable degree of surface-to-core temperature uniformity, these frequencies are more applicable than the higher ones. Line-frequency heating also works well for deep hardening large-diameter parts such as mill rolls. A line voltage of 220 or 440 V is acceptable for supplies rated to about 300 kW, whereas ratings to 1000 kW might operate from a 2300 or 4160 volt line, depending on how the electric utility services the plant and the internal power distribution system. Primary voltages of 6 kV or more are used with solid-state switching in higher power ratings up to 20 MW.

A major advantage of this type of system is the fact that there is no frequency conversion. Power losses and maintenance costs are therefore low because of the absence of rotating machinery or complex electronic equipment. Switchgear, power-factor correction capacitors, control components, and so forth, may often be standard catalog items. Equipment cost is generally less than that of medium- or radio-frequency units, although sometimes a standard medium-frequency solid-state power supply will prove the exception. Low-frequency induction heating with conventional water cooled longitudinal coils have been limited to deep case hardening and to quench-and-temper operations for steel cross section thickness of 125 mm (5 in.) and larger. It may be somewhat difficult to apply because of high mechanical forces and stray field effects, but it can provide more uniform temperatures from the surface to the required depth.

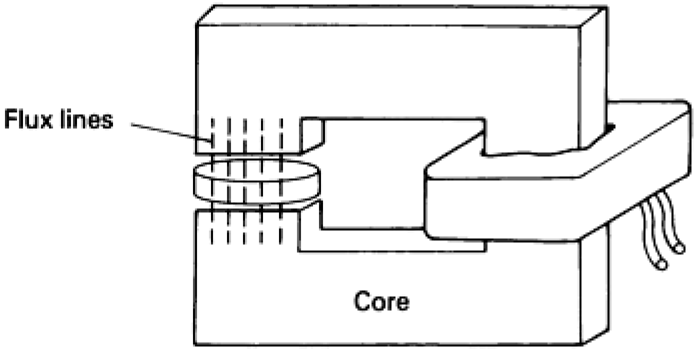
When high power levels are involved, balanced three-phase systems are often required to meet the electric utility or the plant requirements for power distribution. These may be achieved by the use of a three-phase coil or three separate coils, with each part energized by a different phase. Such arrangements yield a reasonably balanced load, provided that the coils are filled with a workpiece. If one coil or coil section is only partly filled, one phase becomes out of balance. For this reason, it is good practice to avoid a neutral wire in the supply line, which could carry an excessive current. Another option is to use a three-to-single-phase load balancer. Sometimes, the higher temperatures required for heating steel above the Curie temperature (at which $\mu = 1$) are more efficiently achieved with medium frequencies; so in a dual-frequency progressive heating system, a number of 60-Hz coils can be used such that each can be energized separately by a single phase. This produces a well balanced three-phase load to the line. Thus, three or any multiples of three small single-phase coils can be loaded on a three-phase supply.

Portable line-frequency power supplies designed specifically for pipe preheating and postheating are available in single-phase ratings to 150 kVA (150 kW with a power factor of 1). These consist of movable transformer modules, generally supplied with a temperature sensing thermocouple and control instrument, and with insulated cables to be wrapped around the work and connected to the secondary winding output. Portable units used in the field on construction sites may obtain power from a diesel generator.

Core-Type Induction Heater. Another type of self-contained line-frequency power supply is the core-type heater. In this device, the workpiece is placed in or around the core of a power transformer instead of being heated in a coil. Air or water cooled primary windings are placed around a laminated silicon-steel transformer core, 75 mm × 75 mm (3 × 3 in.) or larger cross section. A ring-shaped workpiece such as a ring gear, bearing, or wheel may be placed around a movable section of the core in which case the part becomes a short-circuited single-turn secondary winding of a true core-type transformer (Fig. 6a). If a solid workpiece is sandwiched between a split section of core (Fig. 6b), the metal will be inductively heated through transverse flux. Heaters of this type are used extensively to preheat parts, to stress relieve, and they may be capable of heating some parts to supercritical temperatures. In general, however, standard core-type heaters and those using coils made of thermally insulated cable wrapped around a cylindrical load are limited to preheating, stress relieving, and post-welding treatments.



(a)



(b)

Fig. 6 Core-type inductor heater arrangements. (a) Split-yoke arrangement for heating a ring with longitudinal flux lines. (b) Arrangement for heating a solid object with transverse flux lines

Single-phase line-frequency heaters may be acceptable to a utility up to some power level, particularly if other single-phase loads are available to balance the incoming three-phase system. Three-phase power may be considered for any line-frequency heater where three, or multiple of three, heating coils are employed, or where two coils can be energized from a Scott-connected transformer.

Balancing the load on a three-phase line when connected to a single winding coil may also be accomplished with a phase-balancing network using an inductive reactor and capacitors. These are commonly applied to induction melting furnaces up to several thousand kilowatts, but use in heat treating is quite limited.

Load matching apparatus for a line-frequency heater starts at the power transformer which may be equipped with primary and/or secondary voltage-adjusting taps, plus power factor correction capacitors to supply leading reactive current to offset the lagging inductive reactance of the load. To meet most electric utility requirements and/or to minimize rate penalties for low power factor, the heater should be corrected to a 0.85 power factor or better.

Heating Coils for Low-Frequency (50/60 Hz) Heaters. Because low-frequency induction heaters operate with low volts-per-turn and high current, the electromagnetic forces are greater than at higher frequencies. At high power and current levels, forces in the coil must be considered in determining the rigidity of coil construction. For some low-power-density coils used in heating ferromagnetic metals, forces in the coil may not be a serious concern. Core heater coils are somewhat typical and may have fiberglass wrapped turns with varnish or epoxy as a binder. Stud board construction may be used for high-power coils with spaced turns, and turn-to-turn insulation with the entire assembly clamped under pressure is appropriate for close wound coils.

Work Handling Equipment for Low-Frequency (50/60 Hz) Heaters. Because electromagnetic forces exist between the coil and the load, low frequencies also have a greater tendency to physically move parts and cause vibration. Positive clamping or containment may be needed in fixtures, and greater driving force may be required to enter an energized low-frequency coil.

Controls and auxiliary equipment for low-frequency (50/60 Hz) induction heaters will be similar to those used in higher-frequency systems. Voltage regulation and/or power control may come from a line-side saturable core reactor, a rotary induction regulator, an on-load tap switch, or from a solid-state thyristor switching system. Simple on-off cycles can be initiated and terminated by an electromechanical line contactor or a solid-state switch. When power-factor correction capacitors are used, one should be cautious of high inrush currents and potential problems with harmonics of thyristor switching. Auxiliary devices for line-frequency systems might also include a three-to-single-phase balancer and some electrical protection devices such as a fused disconnect and/or a circuit breaker.

Frequency multipliers are used to obtain multiples of the line supply, most often 180 and 540 Hz. Like line-supply installations, they are used primarily for large heating and melting applications.

The 180 Hz supply, also known as a tripler because it is derived directly from 60 Hz line current, is composed of three saturable reactors, each of which is connected between one leg of a Y-connected secondary and a single-phase load. The voltages from the secondaries are 120° apart. Passing them through a single-phase output, therefore, produces three pulses in the same time period as that in which a normal 60 Hz system would produce one waveform. Accordingly, the frequency is essentially tripled. The 180 Hz system is similar to the 60 Hz heater in that the circuit containing the load must be turned to the frequency of the power supply--namely, 180 Hz. Systems may be cascaded to produce other multiples of the line frequency, such as 540 Hz.

Solid-State Systems. Medium-frequency power supplies using solid-state frequency conversions make up the vast majority of induction heating and melting power supplies in use today. These systems, which utilize high-power silicon-controlled rectifiers (SCRs) having rapid turn-on/turn-off times, have largely replaced motor-generator sets for medium-frequency conversion. As compared with motor-generator sets, the basic advantages of solid-state power supplies are their improved efficiency (Fig. 7), low initial cost and maintenance, and availability in a multitude of sizes and frequencies.

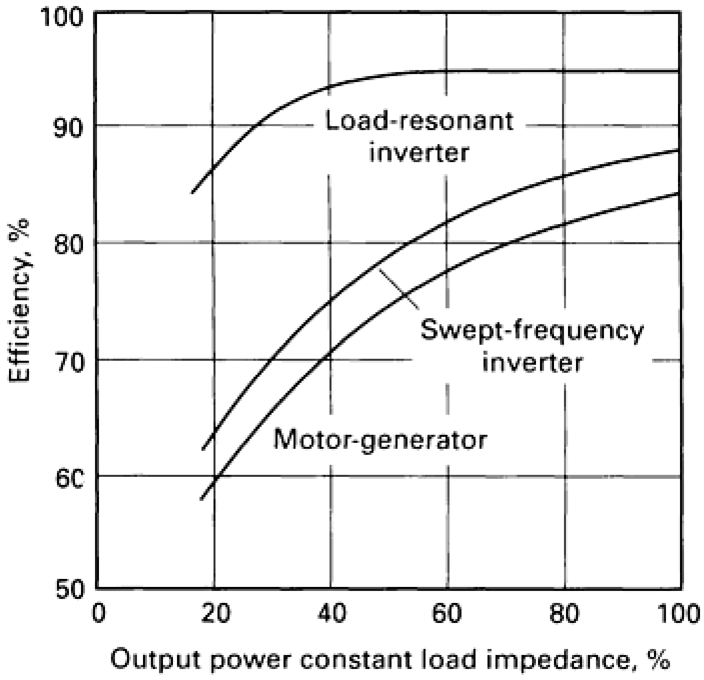


Fig. 7 Comparison of the overall system efficiency of a typical motor-generator, swept-frequency inverter, and load-resonant (constant-current) inverter

With the exception of an ac-to-ac solid-state converter, which does not have wide usage in heat-treating applications, all of the commercial medium-frequency solid-state inverters for induction heating use a two-step conversion in which 60 Hz ac is changed to dc and the dc changed back to ac at the desired frequency. Diodes or thyristors first rectify three-phase line frequency to produce direct current, and solid-state logic then converts dc into ac by one of the two methods discussed below. In both types of solid-state inverters, the system frequency is tuned to the load, whereas in motor-generator circuits the load is tuned to the fixed frequency of the generator. This greatly simplifies load matching when the electrical characteristics of the load change during a heating cycle.

Constant-Voltage (Swept-Frequency) Inverter. The first development in solid-state frequency conversion for induction heaters was based on the swept- (or variable-) frequency inverter. With this system (Fig. 8a), line voltage is converted to direct current and then is applied by means of a capacitive voltage divider to an SCR (dc-to-ac) inverter circuit. The system utilizes internal commutation to turn off the SCR's in the inverter circuit. A feedback circuit from the resonant tank, together with power- and voltage-control signals, is fed to a local oscillator whose output signal then controls the inverter firing rate. The system then operates at a frequency along the straight portion of the tank's resonant-frequency curve, but not at the resonant frequency.

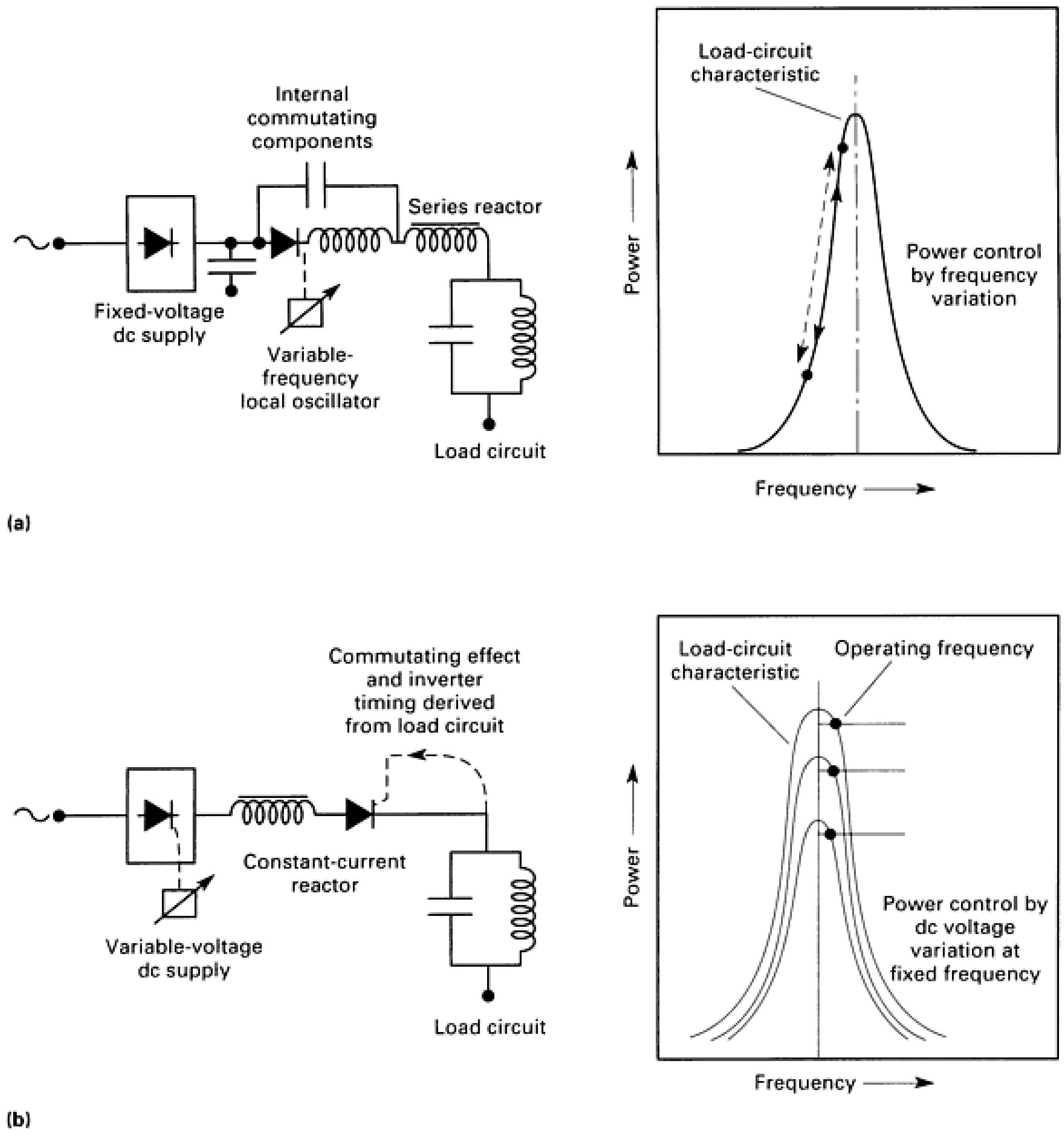


Fig. 8 Circuit schematics for (a) a swept-frequency inverter and (b) a load-resonant or constant-current solid-state inverter

By offsetting the firing rate of the oscillator from the resonant frequency of the tank, the unit can be made to operate along the power curve (Fig. 8a). The frequency from the local oscillator can thus be shifted by the resonant frequency of the tank circuit (or heat station), and the power supply (if set for constant output at the load) can shift its frequency as the load is heated. Nevertheless, it is necessary first to tune the system so that the tank frequency is within the frequency band of the local oscillator. Once the tank is tuned within the range of the local oscillator, it too will provide a constant output as the resonant frequency of the tank shifts, especially when the temperature passes through the Curie point during heating of magnetic steels.

Constant-Current (Load-Resonant) Inverter. The other common solid-state inverter, known as the load-resonant or current-fed inverter (Fig. 8b), also utilizes a dc power source. However, this inverter is provided with an SCR for voltage control. The SCR inverter uses no local oscillator but derives its commutating effect directly from the resonant tank circuit. Thus, it is load-resonant. In actuality, for reasons based on the operational characteristics of the SCR's, the system is usually operated with a slightly leading power factor and thus an operating frequency slightly higher than the load-resonant frequency (Fig. 8b).

Because the frequency is dependent on the tank-resonant conditions, changes in the coil inductance (such as when a magnetic material passes through the Curie temperature) will shift the frequency of operation without any change in power output. If it is desired to select a specific frequency, depending on the application, capacitor taps can be adjusted to meet this requirement. Because the system always operates at the resonant frequency of the tank circuit, its power factor is usually close to unity, and therefore impedance matching by means of a transformer-tap change is the only routine adjustment that need be made to secure optimum power output. This procedure is the same as that for tuning a fixed-frequency motor-generator system.

Ratings. Solid-state power supply ratings vary with design. Output power ratings vary with frequency (Fig. 5), and conversion efficiencies can be higher than 90%. Except for power output above 500 kw, most power ratings are based on a three-phase, 480 V line-frequency input. Above 500 kw, higher nonstandard input voltages may be appropriate, and a special input transformer may be used.

Because solid-state inverters were initially designed to replace motor-generators, the frequency and power ratings of these systems were based on standard motor-generator rating techniques with power rated at the terminals neglecting the losses in the heat station, coil, and so forth. However, solid-state power supplies are really not frequency limited, because they are either load-resonant or the frequency is controlled by a local oscillator. Thus, a frequency can be selected which is optimum for the application. In effect, all solid-state generators are actually variable-frequency inverters, generally designed to operate within some reasonable frequency range.

Motor-Generator Sets. As the name implies, a motor-generator set is a rotating machine in which a driven generator uses electromagnetic induction to produce higher-frequency current. The motor and the generator can be individual units with a mechanical coupling and a common base, or they can be constructed on a single shaft in a common housing. Both horizontal and vertical types have been used. A cooling system is used to remove the heat dissipated by the current flowing in the windings and the hysteresis losses that develop in the structure and motor laminations. Early motor-generator systems utilized forced air cooling, but later water-cooled, finned copper tubing heat exchangers were built within the unit shell and have since become standard. Frequencies generated by motor-generators are determined by rotational speed (usually 3600 rpm) and the number of poles in the generator. Frequencies that are low multiples of a supply frequency (such as 180 Hz from 60 Hz) can be produced with motor-generator sets using a standard induction or synchronous motor driving an ac generator.

A more widely used subclass of motor-generator is the inductor-alternator with no windings on the rotor. In this instance, both the field (or excitation) winding and the output windings are on the stator; therefore, no centrifugal forces act on the output windings, and the rotor can be an extremely robust package of silicon steel punchings. Such designs permit higher frequencies and higher power capacity to be obtained from the motor-generator class of equipment. Inductor-alternators are available with output frequencies of 180 Hz, 360 Hz, 400 Hz, 1 kHz, 2 kHz, 3 kHz, 10 kHz, 12 kHz (European) and 20 kHz. Kilovolt-ampere ratings range from $7\frac{1}{2}$ to 1800 kVA with output voltages of 220, 400, or 800 volts. Conversion efficiencies are 75 to 85%, with lower efficiencies at the higher frequencies. Because the power needed to spin the heavy rotor is the same at light load or full power, system efficiency (Fig. 7) is low when the generator is loaded lightly (that is, when only a fraction of its rated power is drawn). Moreover, some power is consumed when the load is completely removed.

Radio-Frequency (RF) Power Supplies. For frequencies above 150 kHz, frequency conversion can be performed by either vacuum-tube or solid-state systems. Vacuum-tube systems are the most widely used type at the present time, and they can attain frequencies up to about 2 MHz for induction heating. Solid-state systems presently produce RF heating energy in the frequency range 20 to 200 kHz. Frequencies higher than 2 MHz are used for dielectric heating (of nonconductors) instead of induction heating.

Vacuum-tube radio-frequency induction heaters, like most solid-state inverters, use ac/dc/ac conversion stages. Radio-frequency energy is similarly developed in tuned tank circuit and then transferred to the workpiece. The work coil can be placed in series with the tank coil (Fig. 9a) or connected to the secondary of an RF output transformer (Fig. 9b). The series-connected system, usually utilizing a tapped tank coil, is often referred to as a DTL (direct tank loaded) technique, simply because the work coil becomes a functioning part of the tank-circuit inductance. On the other hand, in transformer coupled output circuits, the primary winding is a part of the tank, and the work coil is isolated from both the transformer primary and the tank circuit. The work coil may be center or midpoint grounded to minimize voltage potential and, therefore, arcing from coil to ground.

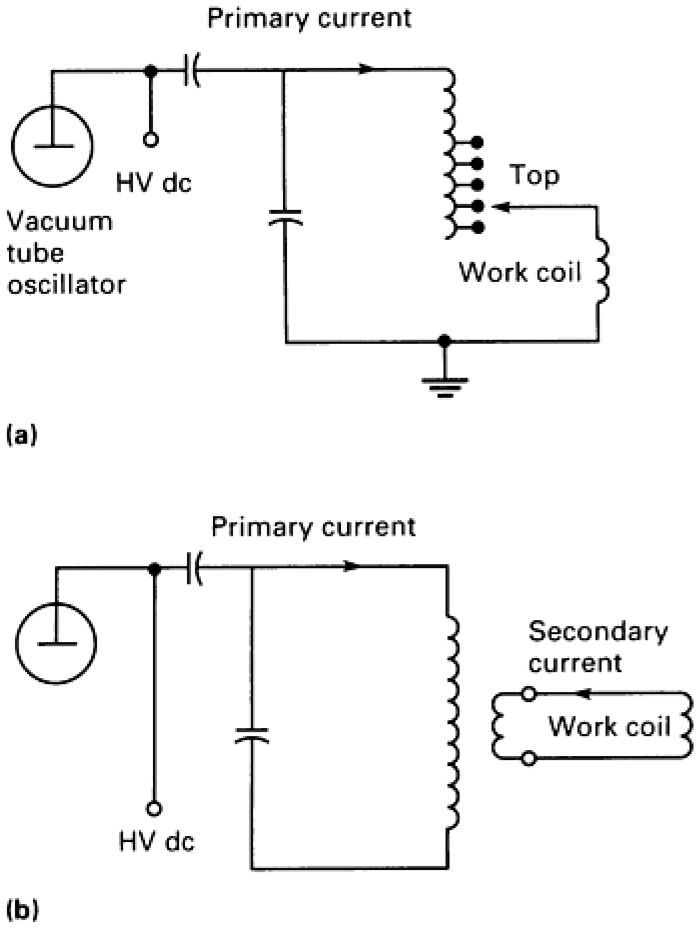


Fig. 9 Output tank circuits of common high-frequency inductor generators (a) direct tank loaded and (b) transformer coupled

It is also possible to locate the entire tank circuit (capacitance and inductance) remotely in a way similar to heat stations running off low- or medium-frequency power supplies. In this case, the remote tank and work coil (either DTL or transformer circuit) is connected to the oscillator by means of semiflexible coaxial cable. Moving the tank circuit itself rather than the coil involves much lower current at impedance levels that are more forgiving. The feedback necessary for oscillation is generally obtained from the tank circuit with a pick-up coil. An RF output transformer can be used a short distance from the power-supply enclosure, but if a fairly low-impedance heating coil is used some distance from the generator, significant power losses can occur. To minimize voltage drop, RF should be designed for low impedance. This is particularly true for leads from a transformer to a coil. Moreover, in the case of a remote output station or a DTL system, personnel must be protected from the high voltages from these lines. Radio-frequency interference can also develop from unshielded high-voltage leads. Grounded aluminum or shielded coaxial cable should be used for energy transmission. According to FCC regulations, all RF generators (10 kHz and above) must be type certified to be below allowable radiation levels.

Vacuum-Tube RF Generators. The first methods used to generate radio frequencies for induction heating utilized spark gap and vacuum-tube oscillators. In general, vacuum tube frequency conversion process starts with one-phase (to 5 kW) or three-phase line current being changed to direct current (dc). The dc is then almost universally applied to a class C oscillator, which produces RF energy for heating. Rectifiers for the initial ac-to-dc conversion can be mercury vapor two-element or three-element tubes (the latter for variable dc voltage and power control). In recent years, solid-state diodes or thyristors are being used for the same purpose. Oscillator tubes are forced air cooled up to 10 kW maximum, while larger oscillator tubes have water-cooled anodes. Guaranteed life is in the range of 5000 to 10 000 h. Tube output ratings vary from 1 to 200 kW with effective overall conversion efficiency of 60 to 75%. Tank circuits and other losses account for conversion efficiency of 50 to 60%.

Solid-state RF power supplies also now operate at 20 to 200 kHz in a wide range of power outputs. Unlike the inverters used at 20 kHz and below, these units do not have SCR's, but are instead powered by MOSFET (metal-oxide semiconductor field-effect transistor) output devices.

A solid-state RF power supply is similar to an SCR inverter in that line voltage enters the system through an isolation transformer and is then changed to a dc voltage, the level of which is adjustable through thyristor rectifiers. This filtered dc output is the input for the solid-state RF supply's power boards. The MOSFETs on each board and the boards themselves are connected in parallel. Frequency sensing from the tank circuit feeds the tank resonant-frequency signal back to the microprocessor. The MOSFETs in turn are driven at this frequency by the microprocessor. The software will also change the system operating frequency in response to changes in tank resonant frequency. As does the load-resonant inverter, the solid-state RF system operates at the peak of the resonant curve, and its efficiency is therefore similar.

Similarly, the software for these microprocessor-driven systems can be modified to provide constant current, constant power, or constant voltage, depending on the conditions required for the particular application. The software also permits interrogation of the system through a computer-keyboard interface.

Spark-Gap Converters. Although no longer produced commercially, the spark-gap converter was one of the earliest means of providing high-frequency ac power in the radio-frequency region. It was initially developed for metal melting, but has been used in a wide variety of heat-treating applications. It is almost obsolete because of high maintenance, difficulty in maintaining repetitive application of power, and the potential for RF interference.

In its simplest form, the spark-gap converter includes a step-up transformer to increase the line voltage to a few thousand volts, which is impressed across the spark gap. In operation, as the voltage rises in each half-swing of the 60-Hz line current, the voltage across the gap also rises until it discharges at the breakdown level, thus firing the tuned load. Frequencies generated by this system are generally in the range of 20 to 40 Hz for the quenched gap type and 80 to 200 kHz for the mercury hydrogen type. However, many frequency components are produced simultaneously so that the output is not purely sinusoidal, and a damped wave output has the disadvantage of a high peak voltage for a much lower average voltage. Efficiency of these systems is rather low--on the order of 15 to 50% line-to-load.

Induction Heat Treating of Steel

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Inductor Coils

The inductor (or heating) coil is the device that shapes the electromagnetic field around and into the part or material being heated. The resulting magnetic flux achieved by an inductor can be classified as one of two modes:

- Longitudinal flux
- Transverse flux (sometimes called proximity heating)

Longitudinal flux induction heating is by far the most widely used mode of application, typified by the coil turns surrounding the load with flux lines flowing longitudinally in the direction of part movement (Fig. 1b). When the air gap between the coil and workpiece is reasonable for the frequency and load conditions involved, heating can be quite efficient because the flux lines tend to be confined, with a large percentage of them coupled to the workpiece. However, because eddy current cancellation occurs when the thickness of the object becomes small in comparison with the reference signal (Fig. 4), longitudinal flux heating of thinner parts requires higher frequencies than transverse flux.

Transverse flux heating means the field flux is applied at right angles to the axis or movement of the part. Because current flows at right angles to the flux (right hand rule), it will then produce an image pattern of the coil on one face of the part. The term proximity heating implies that the coil is only placed in proximity to the work, rather than surrounding it. Additional information on transverse flux heating can be found later in this article (see the section "Coil Design").

Coil Design

Coil design is influenced by many factors including the dimensions and configuration of the workpiece, the number of parts to be heated, the temperature required, the pattern of heat desired, and whether the workpiece is to be heated at one time or progressively. The applied frequency and the level of power also enter into coil design.

In a sense, coil design for induction heating is built upon a large store of empirical data whose development has sprung from theoretical analyses of several rather simple inductor geometries such as the classical solenoidal coil. Because of this, coil design is generally based on experience. In this section, the fundamental electrical considerations in design of inductors are reviewed and some of the most common coils in use are described. The actual construction of coils and the selection of power-supply leads are also discussed.

Design Considerations. In many texts on induction heating as well as in the section "Principles of Induction Heating" in this article, an analogy between a transformer and an inductor/workpiece combination has been described. The inductor is similar to the transformer primary, and the workpiece is equivalent to the secondary (Fig. 10). Therefore, several of the characteristics of transformers are useful in the development of guidelines for coil design.

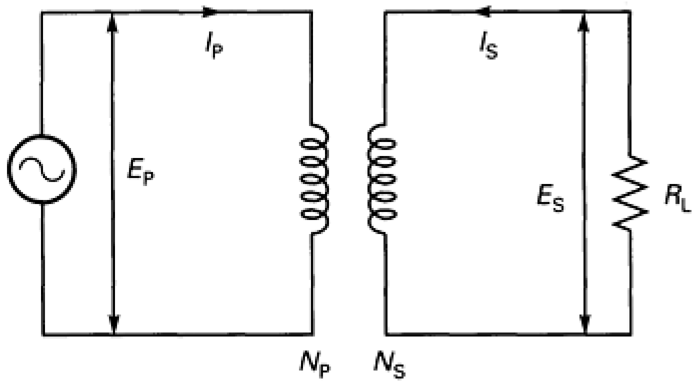


Fig. 10 Electrical circuit illustrating the analogy between induction heating and the transformer principle. E_p = primary voltage (V); I_p = primary current (A); N_p = number of primary turns; I_s = secondary current (A); N_s = number of secondary turns; E_s = secondary voltage (V); R_L = load resistance (Ω)

One of the most important features of transformers lies in the fact that the efficiency of coupling between the windings is inversely proportional to the square of the distance between them. In addition, the current in the primary of the transformer multiplied by the number of primary turns is equal to the current in the secondary multiplied by the number of secondary turns. Because of these relationships, there are several conditions that should be kept in mind when designing any coil for induction heating:

- The coil should be coupled to the part as closely as feasible for maximum energy transfer. It is desirable that the largest possible number of flux lines intersect the workpiece at the area to be heated. The denser the flux at this point, the higher will be the current generated in the part
- The greatest number of flux lines in a solenoid coil are toward the center of the coil. The flux lines are concentrated inside the coil, providing the maximum heating rate there
- Because the flux is most concentrated close to the coil turns themselves and decreases farther from them, the geometric center of the coil is a weak flux path. Thus, if a part were to be placed off center in a coil, the area closer to the coil turns would intersect a greater number of flux lines and would therefore be heated at a higher rate, whereas the area of the part with less coupling would be heated at a lower rate; the resulting pattern is shown schematically in Fig. 11. This effect is more pronounced in high-frequency induction heating
- At the point where the leads and coil join, the magnetic field is weaker; therefore, the magnetic center of the inductor (along the axial direction) is not necessarily the geometric center. This effect is most apparent in single-turn coils. As the number of coil turns increases and the flux from each turn is added to that from the previous turns, this condition becomes less important. Due to this phenomenon and the impracticability of always centering the part in the work coil, the part should be offset slightly toward this area. In addition, the part should be rotated, if practical, to provide uniform exposure
- The coil must be designed to prevent cancellation of the field of magnetic induction by opposite sides of the

inductor (Fig. 12)

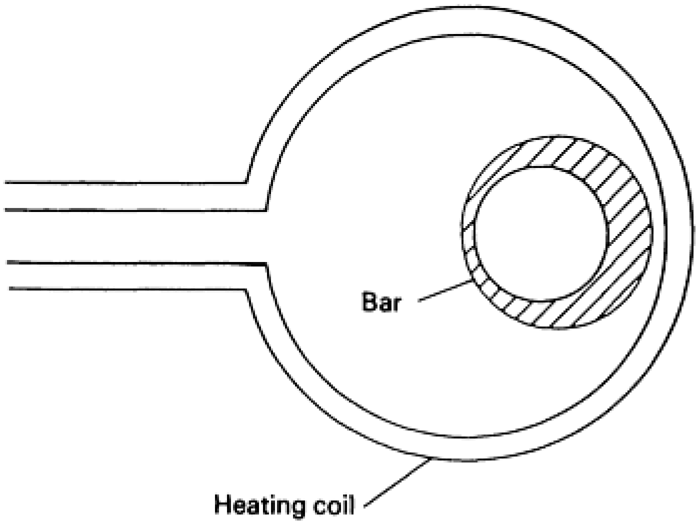


Fig. 11 Induction heating pattern produced in a round bar placed off center in a round induction coil

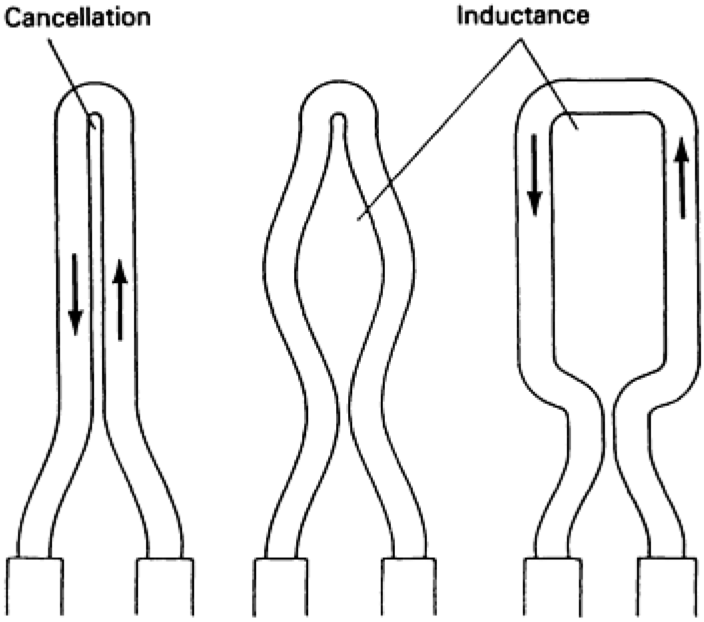


Fig. 12 Effect of coil design on inductance. The coil on the left has no inductance because the opposite sides of the inductor are too close to each other. Putting a loop in the inductor (center coil) will provide some induction. The coil will then heat a conducting material inserted in the opening. The design at the right provides added inductance and is more representative of good coil design.

Because of the above principles, some coils can transfer power more readily to a load because of their ability to concentrate magnetic flux in the area to be heated. For example, three coils which provide a range of heating behaviors are the following:

- A helical solenoid with the part or area to be heated located within the coil and thus in the area of greatest magnetic flux
- A pancake coil where the flux from only one surface intersects the workpiece

- An internal coil for bore heating, where only the flux on the outside of the coil is utilized

In general, helical coils used to heat round workpieces have the highest values of coil efficiency and internal coils have the lowest values.

Besides coil efficiency, design considerations with regard to heating pattern, part motion relative to the coil, and production rate are also important. Because the heating pattern reflects the coil geometry, inductor shape is probably the most important of these factors. Quite often, the method by which the part is moved into or out of the coil can necessitate large modifications of the optimum design. The type of power supply and the production rate must also be kept in mind. If one part is needed every 30 s but a 50-s heating time is required, it is necessary to heat parts in multiples to meet the desired production rate. Keeping these concurrent needs in mind, it is important to look at a wide range of coil techniques to find the most appropriate one.

Low-Frequency Heating Coils. Low-frequency induction heating is generally desired for through heating of metals, particularly those with large and relatively simple cross sections. Typical applications are round or round-cornered square (RCS) stock for forging or extrusion and slabs for hot rolling. In these cases, coil design is often quite simple, usually consisting of a solenoid coil or a variation of it that matches the basic workpiece cross-sectional shape (for example, square, rectangular, trapezoidal, and so forth).

Low-frequency coils often have many turns. Accordingly, the coil usually forms the total tank inductance, and an autotransformer may be used to match the coil impedance to that of the induction generator. In any case, the coil or transformer inductance must be high in order to reduce the number of tank capacitors needed to tune the resonant circuit at the operating frequency. Generally, the lower the frequency, the larger the coil or the greater number of turns. When low-inductance coils are occasionally required, isolation transformers can be used to match the coil impedance to that of the induction generator. However, these occasions are considerably fewer at the lower frequencies. In a practical sense, coils of this nature are generally purchased as part of an overall system, with total responsibility for operation resting with the system supplier.

Medium-to-High-Frequency Coils. Simple solenoid coils, as well as variations of them, are also often relied on in medium-to-high-frequency applications such as heat treatment. These include single- and multiple-turn types. Figure 13 illustrates a few of the more common types based on the solenoid design. Figure 13(a) is a multiturn, single-place coil, so called because it is generally used for heating a single part at a time. A single-turn, single-place coil is illustrated in Fig. 13(b). Figure 13(c) shows a single-turn, multiplace coil. In this design, a single turn interacts with the workpiece at each part-heating location. Figure 13(d) shows a multiturn, multiplace coil.

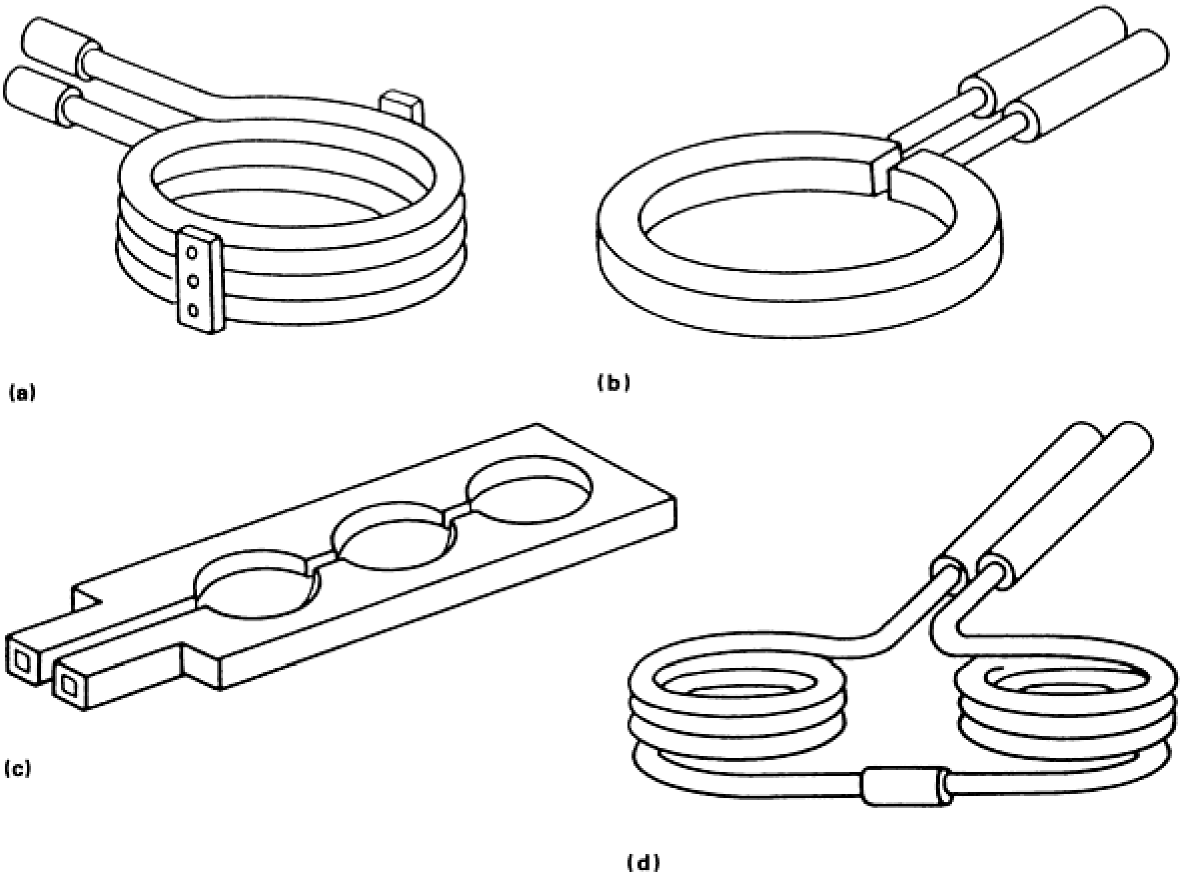


Fig. 13 Typical configurations for induction coils. (a) Multiturn, single-place. (b) Single-turn, single-place. (c) Single-turn, multiplace. (d) Multiturn, multiplace

More often than not, medium-to-high-frequency applications require specifically configured or contoured coils with the coupling adjusted for heat uniformity. In the simplest cases, coils are bent or formed to the contours of the part (Fig. 14). They may be round (Fig. 14a), rectangular (Fig. 14b), or formed to meet a specific shape such as the cam coil (Fig. 14c). Pancake coils (Fig. 14d) are generally utilized when it is necessary to heat from one side only or where it is not possible to surround the part. Spiral coils (Fig. 14e) are generally used for heating bevel gears or tapered punches. Internal bores can be heated in some cases with multiturn inductors (Fig. 14f). It is important to note that, with the exception of the pancake and internal coils, the heated part is always in the center of the flux field.

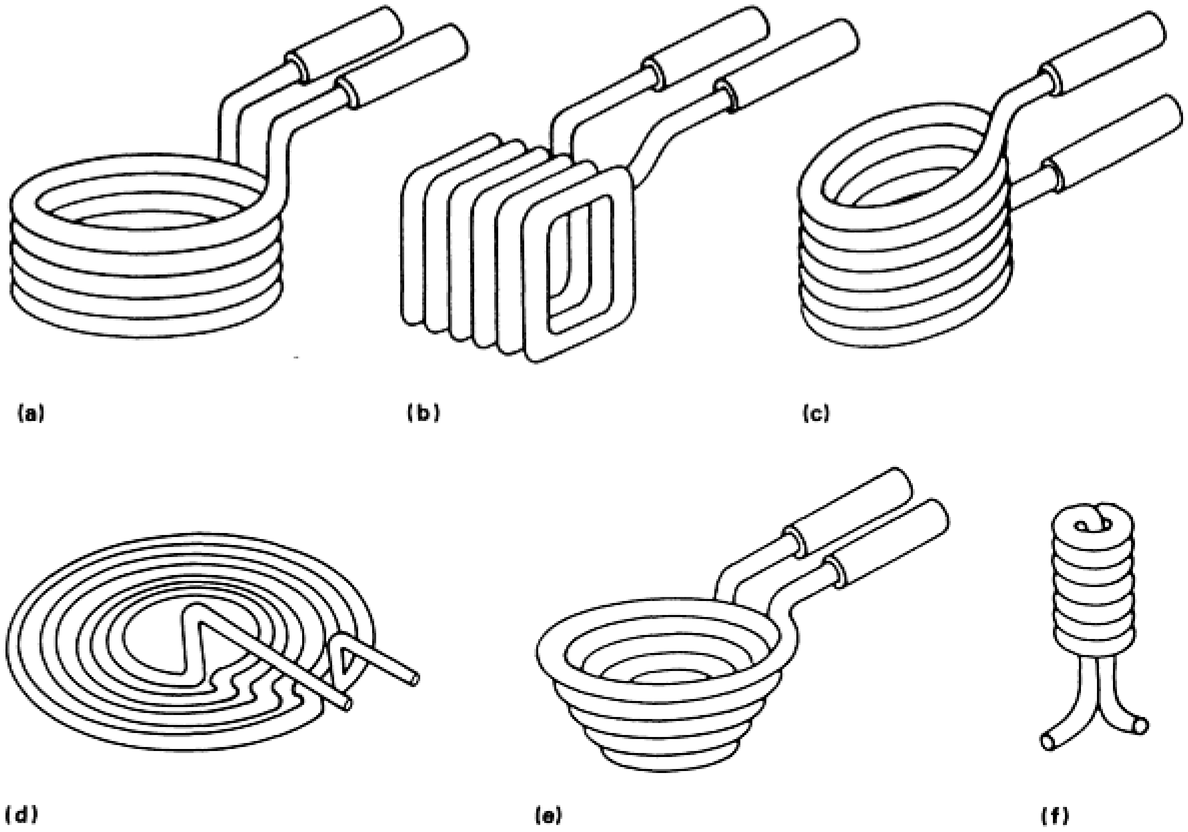


Fig. 14 Multiturn coils designed for heating parts of various shapes. (a) Round. (b) Rectangular. (c) Formed. (d) Pancake. (e) Spiral-helical. (f) Internal

Regardless of the final part contour, the most efficient coils are essentially modifications of the standard, round coil. A conveyor or channel coil, for example, can be looked at as a rectangular coil whose ends are bent to form "bridges" in order to permit parts to pass through on a continuous basis. The parts, however, always remain "inside" the channels where the flux is concentrated. Figure 15 illustrates similar situations in which the areas to be hardened are beside the center of the coil turns and thus are kept in the area of heaviest flux.

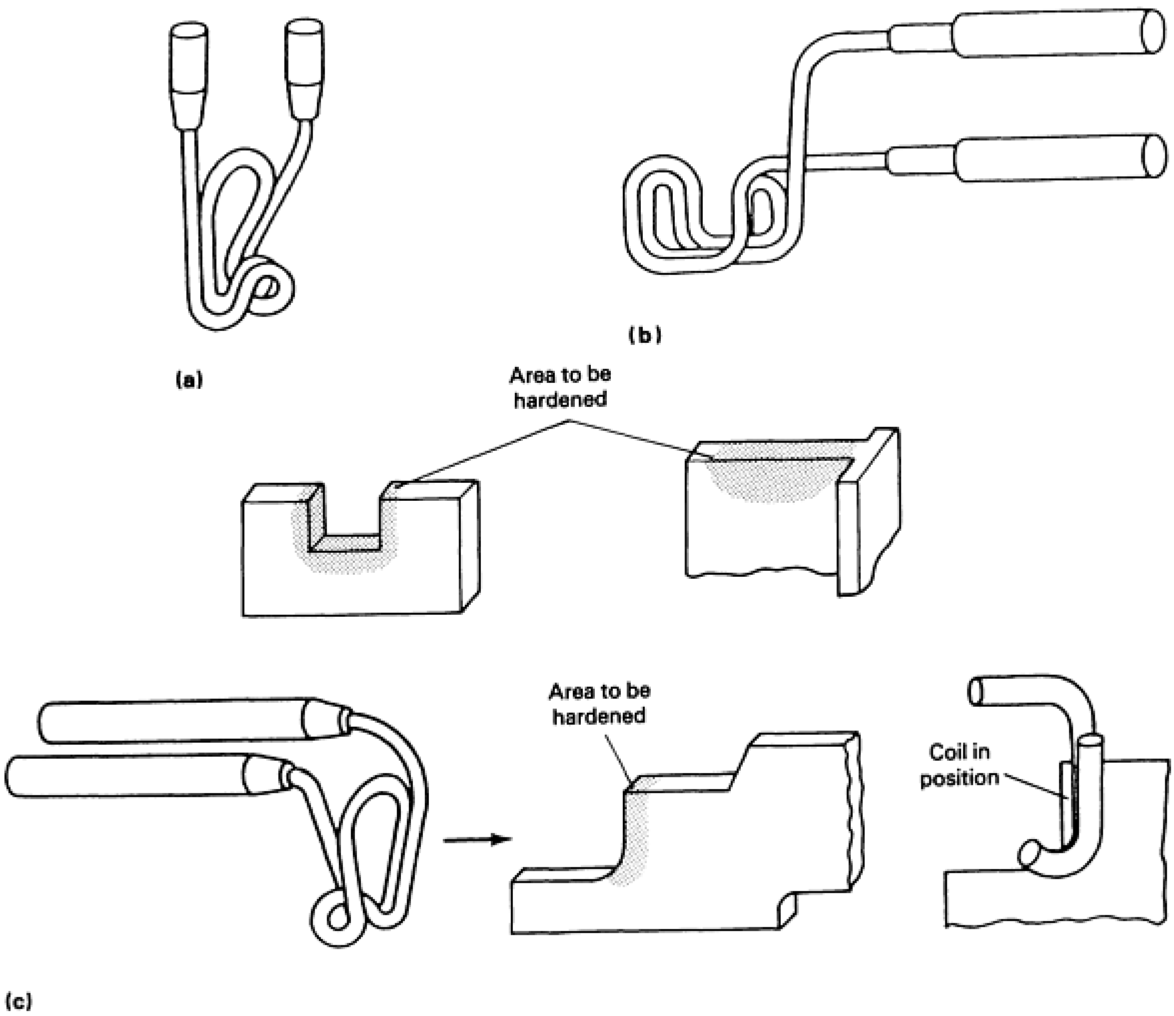


Fig. 15 Coil modifications for localized heating of three different parts

Internal Coils. Heating of internal bores, whether for hardening, tempering, or shrink fitting, is one of the major problems most commonly confronted. For all practical purposes, a bore with an approximately 10 mm (0.45 in.) internal diameter is the smallest that can be heated with a 450-kHz power supply. At 10 kHz, the practical minimum inside diameter is 25 mm (1 in.).

Tubing for internal coils should be made as thin as possible, and the bore should be located as close to the surface of the coil as is feasible. Because the current in the coil travels on the inside of the inductor, the true coupling of the maximum flux is from the inside diameter of the coil to the bore of the part. Thus, the conductor cross section should be minimal, and the distance from the coil outside diameter to the part (at 450 kHz) should approach about 1.5 mm (0.062 in.).

Internal coils, of necessity, utilize very small tubing or require restricted cooling paths. Further, due to their comparatively low efficiency, they may need very high generator power to produce shallow heating depths. Because of the high currents utilized during the heating cycle as well as the heat radiated from the workpiece surface, more cooling than can be obtained using the normal coil water supply is required here. It is best to provide a separate, high-pressure water supply for the coil to achieve a satisfactory flow rate.

Coil Characterization

Because magnetic flux tends to concentrate toward the center of the length of a solenoid work coil, the heating rate produced in this area is generally greater than that produced toward the ends. Further, if the part being heated is long, conduction and radiation remove heat from the ends at a greater rate. To achieve uniform heating along the part length,

the coil must thus be modified to provide better uniformity. The technique of adjusting the coil turns, spacing, or coupling with the workpiece to achieve a uniform heating pattern is known as coil characterization.

There are several ways to modify the flux field. The coil can be decoupled in its center, increasing the distance from the part and reducing the flux in this area. Secondly, and more commonly, the number of turns in the center (turn density) can be reduced, producing the same effect. A similar approach--altering a solid single-turn inductor by increasing its bore diameter at the center--achieves the same result. Each of these techniques is described and illustrated in this section.

In Fig. 16(a), the coil turns have been modified to produce an even heating pattern on a tapered shaft. The closer turn spacing toward the end compensates for the decrease in coupling caused by the taper. This technique also permits "through the coil" loading or unloading to facilitate fixturing. A similar requirement in the heat treatment of a bevel gear is shown in Fig. 16(b). Here, because of the greater part taper, a spiral-helical coil is used. With a pancake coil, decoupling of the center turns provides a similar approach for uniformity.

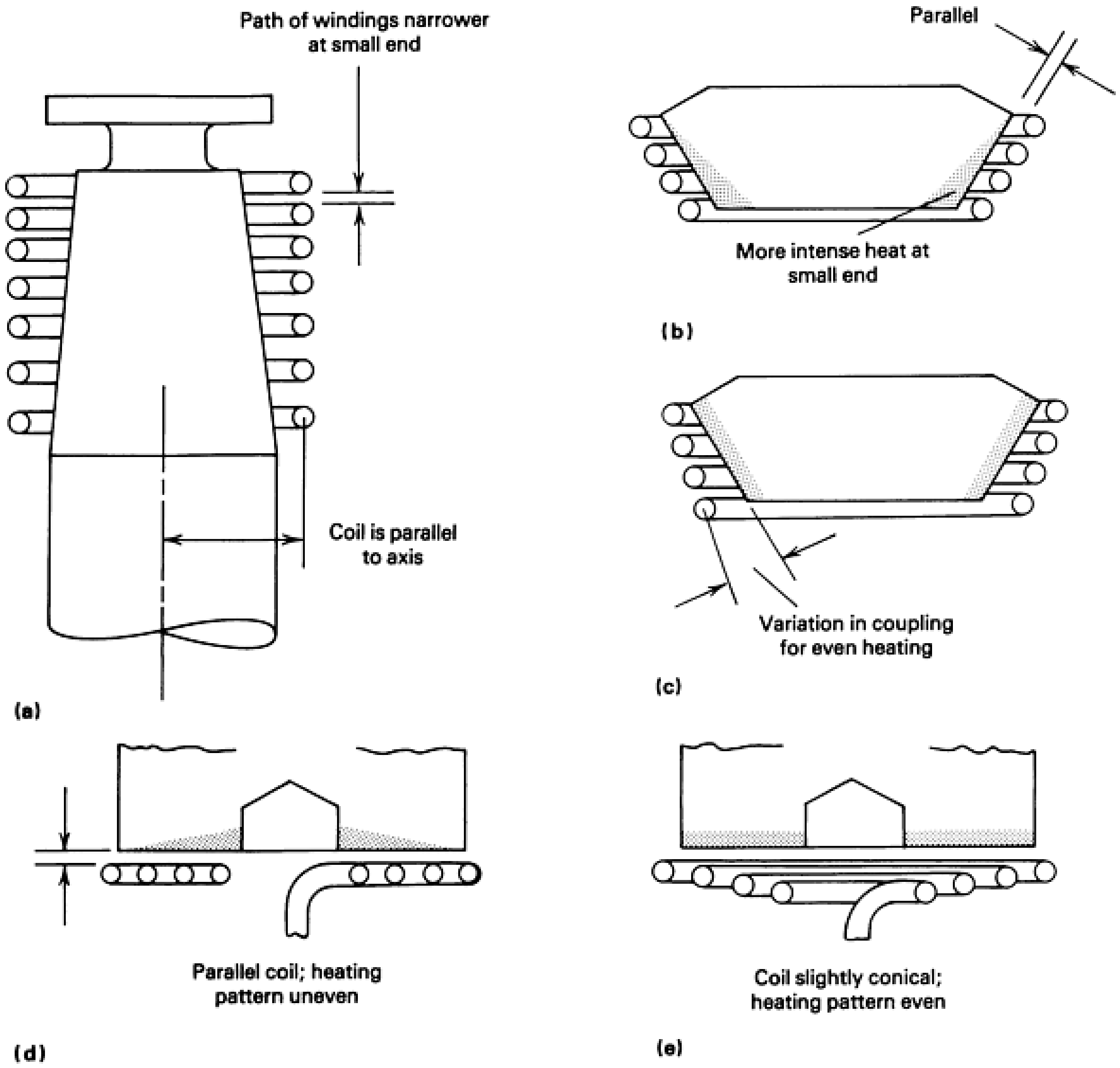


Fig. 16 Adjustment (coil characterization) of induction heating patterns for several parts by varying the coupling distance or turn spacing

Selection of Multiturn versus Single-Turn Coils. Heating-pattern uniformity requirements and workpiece length are the two main considerations with regard to the selection of a multiturn versus a single-turn induction coil. A fine-pitch, multiturn coil, which is closely coupled to the workpiece develops a very uniform heating pattern. Similar uniformity can be achieved by opening up the coupling between the part and the coil so that the magnetic flux pattern

intersecting the heated area is more uniform. However, this also decreases energy transfer. Where low heating rates are required, as in through heating for forging, this is acceptable. When high heating rates are needed, however, it is sometimes necessary to maintain close coupling. The pitch of the coil must be opened to prevent overloading of the generator.

Because the heating pattern is a mirror image of the coil, the high flux field adjacent to the coil turns will produce a spiral pattern on the part. This is called "barber poling" and can be eliminated by rotating the workpiece during heating. For most hardening operations, which are of short duration, rotational speeds producing not less than ten revolutions during the heating cycle should be used.

If part rotation is not feasible, heating uniformity can be increased by using flattened tubing, by putting an offset in the coil, or by attaching a liner to the coil. Flattened tubing should be placed so that its larger dimension is adjacent to the workpiece. The offsetting of coil turns (Fig. 17) provides an even horizontal heating pattern. Offsetting is most easily accomplished by annealing the coil after winding and pressing it between two boards in a vise. A coil liner is a sheet of copper that is soldered or brazed to the inside face of the coil. This liner expands the area over which the current travels. Thus, a wide field per turn can be created. The height (that is, axial length) of this field can be modified to suit the application by controlling the dimensions of the liner.

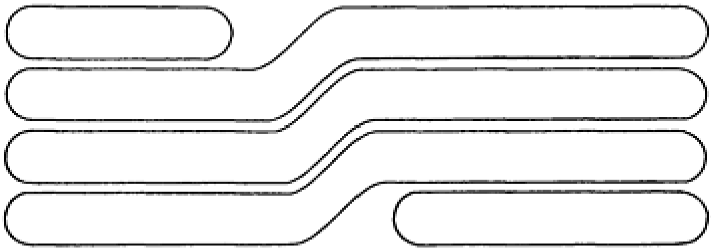


Fig. 17 Induction coil with an offset used to provide heating uniformity

When the length of the coil exceeds four to eight times its diameter, uniform heating at high power densities becomes difficult. In these instances, scanning the part with either a single-turn or multiturn coil is usually preferable. Multiturn coils generally improve the efficiency, and therefore the scanning rate, when a power source of a given rating is used. Single-turn coils are also effective for heating of bands which are narrow with respect to the part diameter, particularly for ferrous materials.

The relationship between diameter and optimum height (that is, axial thickness) of a single-turn coil varies somewhat with size. A small coil can be made with a height equal to its diameter because the current is concentrated in a comparatively small area. With a larger coil, the height should not exceed one-half the diameter. As the coil opening increases, the ratio is reduced--that is, a 50 mm (2 in.) inside diameter coil should have a 19 mm (0.75 in.) maximum height, and a 100 mm (4 in.) inside diameter coil should have a 25 mm (1.0 in.) height.

Single-Shot versus Scanning Techniques. When only one part at a time is placed in the coil and heated, the process is referred to as a *single-shot* process. Although handling of parts and conversion of the system for treatment of parts of different sizes are easy with this arrangement, such systems frequently are not economical to operate because the induction generator is not operated continuously at its rated power output. This type of system is not commonly used for long-time heating for through-heating, but it can be useful in surface hardening of gears (see the discussion of Fig. 48 later in this article). Modifications of single-shot techniques may also be employed for preferential hardening of only certain portions of gear teeth, such as tooth tips or flank regions.

The other class of technique, which allows high output in production environments (particularly for through-heating applications), is referred to as *induction scanning.* In this method, the workpiece is moved through a solenoid coil. Alternatively, a short coil may be moved along the workpiece length once (or several times), a common procedure when the workpiece is large and not easily moved. In this manner, the generator is operated continuously and, if its power output is low, smaller areas can still be heat treated, leading to progressive processing of the part.

For continuous or scan heat treating, the heating time is a function of scan rate so it must be accurately controlled through the drive system. Speed of travel may be sensed through a tachometer feedback system or some other sensing means so power can be adjusted to produce a desired heating result at varying speeds. Likewise, in continuous processing lines, material size (diameter, width, and so forth) can be sensed and the output power adjusted to suit the product. These are all possibilities and the response to changes by external control is rapid because as an electromagnetic process, induction heating has almost zero time lag and changes take place immediately within the product rather than at the surface.

Coupling distance refers to the space between the coil conductors and the workpiece, and the amount of this gap influences the degree of coupling and flux leakage (flux which does not thread through the workpiece). Although the coupling distance should be as small as possible to reduce flux leakage, the air gap dimensions are often dictated by process conditions, material handling requirements, and perhaps mechanical clearance for the electrical and/or thermal insulation of the coil.

Frequency is a major process condition that influences coupling distance. Because flux lines tend to stay closer to the coil conductor at higher frequencies, a larger air gap becomes more critical and less tolerable when frequency is increased. Coil current (and thus applied power) is also related to frequency. Coil currents at higher frequencies are lower, and thus coupling must be increased by a reduction in coupling distance or the use of flux shapers. With low and medium frequencies, coil currents are considerably higher, which thus allows a larger air gap and decreased coupling.

Preferred coupling distance also depends on the type of heating (single-shot or scanning) and the type of material (ferrous or nonferrous). In static surface heating, in which the part can be rotated but is not moved through the coil, a coupling distance of 1.5 mm (0.060 in.) from part to coil is recommended. For progressive heating or scanning, a coupling distance of 2 mm (0.075 in.) is usually necessary to allow for variations in workpiece straightness. For through heating of magnetic materials, multiturn inductors and slow power transfer are utilized. Coupling distances can be looser in these cases--on the order of 6.5 to 9.5 mm (0.25 to 0.38 in.). For nonferrous materials, coupling should be somewhat closer, usually between 1.5 and 3 mm (0.06 and 0.12 in.).

Coupling can also be influenced by the insulation around the coil. Heating coils used to austenitize tubulars in a continuous quench and temper operation, for example, are exposed to radiated heat from a high-temperature load for long periods of time and may serve better with thermal insulation at the hot face. This will add to the electrical gap because air space is still needed to accommodate expansion and distortion of the load, and still allow free movement. Hot face thermal insulation is used in coils up to about 3 kHz where sufficient electrical gap can be tolerated. More gap can be tolerated at lower frequencies, such as in the through heating of billet stock (prior to hot working). In this low-frequency application, coupling distance must be increased significantly because thick refractory materials, as well as electrical insulation, must be incorporated into the inductor design. In most cases, the distance increases with the diameter of the billet, typical values being 19, 32, and 45 mm (0.75, 1.25, and 1.75 in.) for billet-stock diameters of approximately 38, 100, and 150 mm (1.5, 4, and 6 in.), respectively.

To secure consistent results, constant coupling is necessary in induction hardening. For a given part and coil, the coupling will be determined primarily by the ability of the fixture to position the part consistently to provide a constant air gap between the coil and the part. Some variation in coupling can be tolerated when the inductor completely surrounds the workpiece by one or more turns. For face heating with a pancake-type coil or modifications thereof, the coupling is critical, and should be maintained within 0.4 mm ($\frac{1}{64}$ in.) if a highly restricted hardness pattern is required.

Effects of Part Irregularities on Heating Patterns. With all coils, flux patterns are affected by changes in the cross section or mass of the part. As shown in Fig. 18, when the coil extends over the end of a shaftlike part, a deeper pattern is produced on the end. To reduce this effect, the coil must be brought to a point even with or slightly lower than the end of the shaft. The same condition exists in heating of a disk or a wheel. The depth of heating will be greater at the ends than in the middle if the coil overlaps the part. The coil can be shortened, or the diameter at the ends of the coil can be made greater than at the middle, thereby reducing the coupling at the former location.

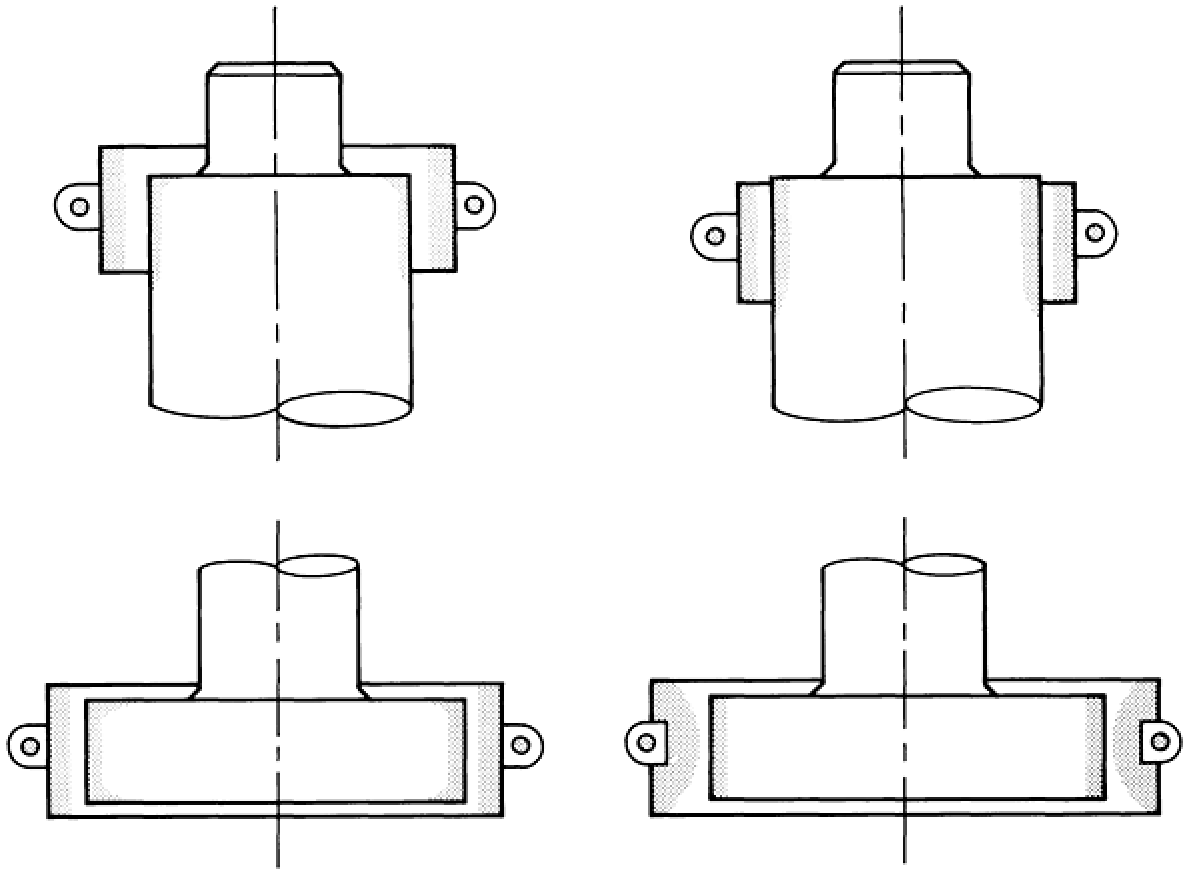


Fig. 18 Effect of coil placement on the heating pattern at the end of a workpiece. When the coil overlaps the edge (left), overheating will occur on the end surface. Coil placement should be slightly below the edge (right) for a more uniform heating pattern.

Just as flux tends to couple heat to a greater depth at the end of a shaft, it will do the same at holes, long slots, or projections (Fig. 19). If the part contains a circular hole, an additional eddy-current path is produced which will cause heating at a rate considerably higher than that in the rest of the part. The addition of a copper slug to the hole can be used to effectively correct or eliminate this problem. The position of the slug (Fig. 20) can control the resultant heating pattern. In addition, the slug will minimize hole distortion if the part must be quenched following heating. For slotted parts heated with solenoid coils, the continuous current path is interrupted by the slot, and the current must then travel on the inside of the part to provide a closed circuit. This is the basis for concentrator coils, which are discussed below. It is of interest to note, however, that with the slot closed, the applied voltage of the work coil causes a higher current to flow. This is due to the fact that the resistive path, now around the periphery of the part, is considerably shorter. The increase in current then produces a considerably higher heating rate with the same coil.

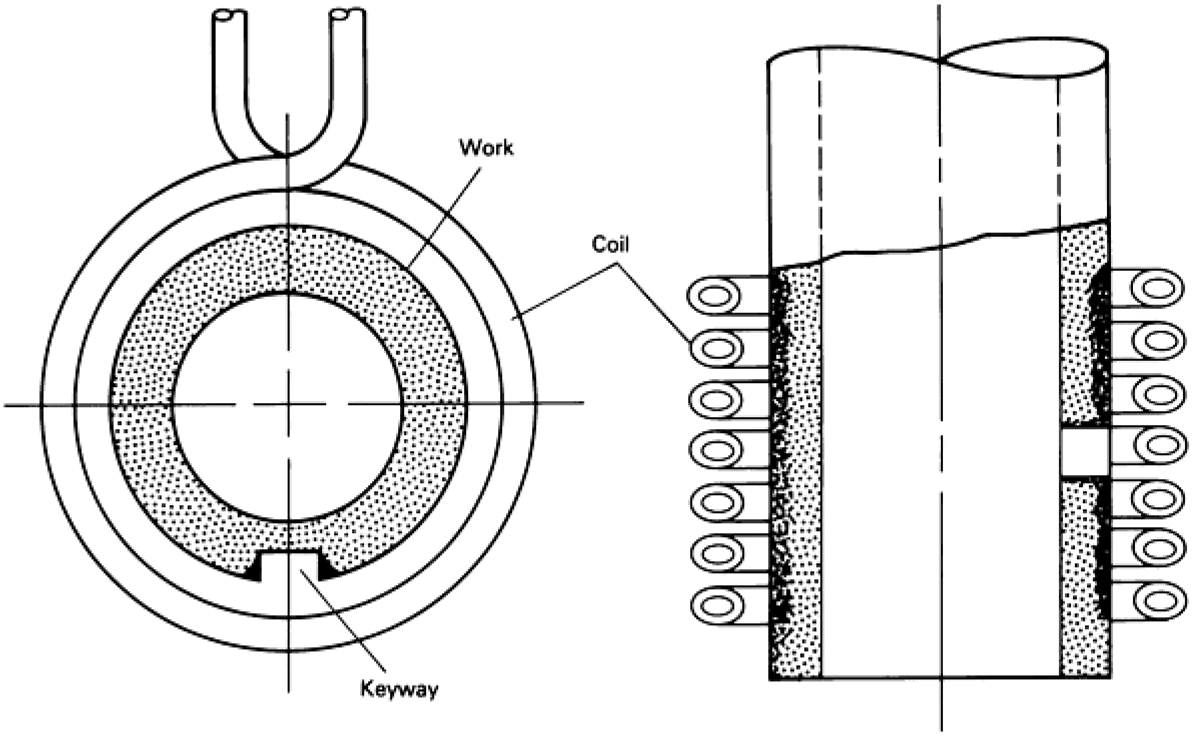


Fig. 19 Localized overheating of sharp corners, keyways, and holes most prevalent in high-frequency induction heating

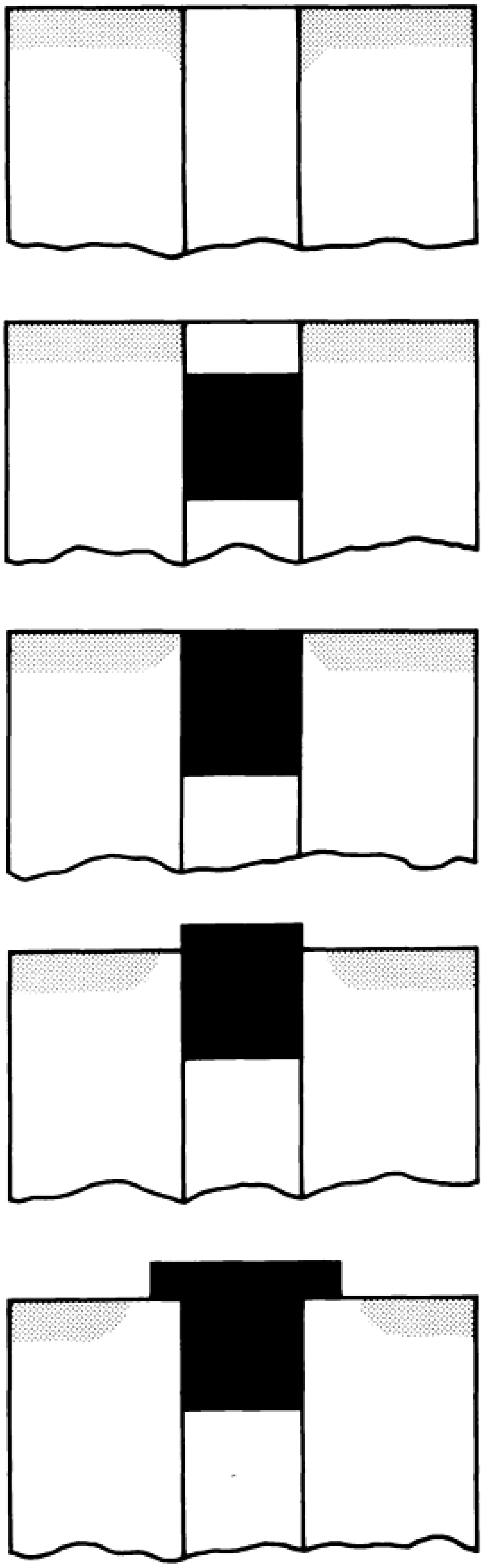


Fig. 20 Control of heating pattern at a hole through the use of copper slugs

Flux Diverters. When two separate regions of a workpiece are to be heated, but are close together (Fig. 21), it is possible that the magnetic fields of adjacent coil turns will overlap, causing the entire bar to be heated. To avoid this problem, successive turns can be wound in opposite directions. By this means, the intermediate fields will cancel, and the fields that remain will be restricted. It should be noted that, as shown in Fig. 21, lead placement is critical. Having the return inductor spaced far from the coil leads would add unneeded losses to the system.

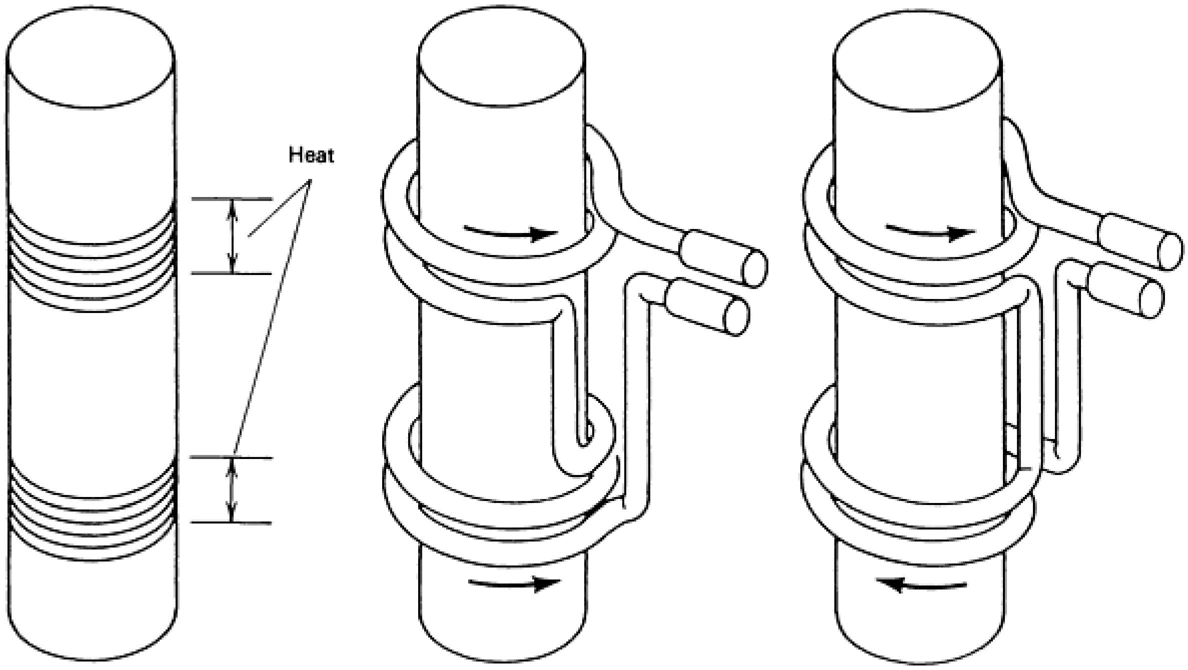


Fig. 21 Control of heating patterns in two different regions of a workpiece by winding the turns in opposite direction

Another technique that can be utilized in the above circumstances involves the construction of a shorted turn or "robber" placed between the active coil turns. In this case, the shorted loop acts as an easy alternative path for concentration of the excess flux, absorbing the stray field. It is therefore sometimes called a flux diverter. As for the active coil turns, the robber must be water cooled to dissipate its own heat (Fig. 22).

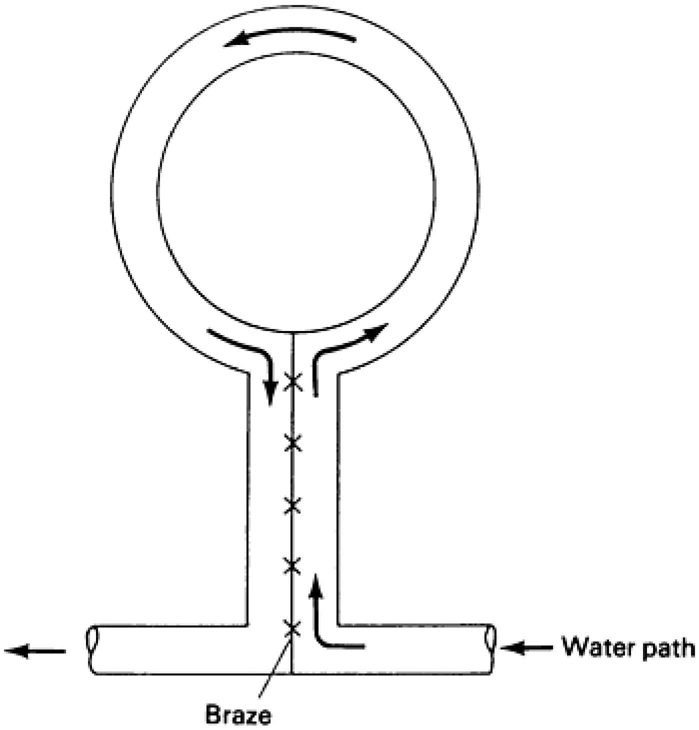


Fig. 22 Typical construction of a water-cooled flux robber

Flux robbers or flux diverters can also be used in fabricating test coils when it is desired to determine the optimum number of turns empirically. In these situations, a few additional turns are provided that can be added or removed as required.

Specialty Coils

As mentioned above, coil designs are based on the heating-pattern requirements of the application, the frequency, and the power-density requirements. In addition, the material-handling techniques to be used for production also determine to a large extent the coil to be used. If a part is to be inserted in a coil, moved on a conveyor, or pushed end to end, or if the coil/heat station combination is to move onto the part, the coil design must take the appropriate handling requirements into consideration. Accordingly, a variety of specialty coil designs have evolved for specific applications.

Master Work Coils and Coil Inserts. When production requirements necessitate small batches (as in job-shop applications) and a single-turn coil can be used, master work coils provide a simple, rapid means of changing coil diameters or shapes to match a variety of parts. In its basic form, a master work coil consists of copper tubing that provides both an electrical connection to the power supply and a water-cooled contact surface for connection to a coil insert. A typical design, shown in Fig. 23, consists of a copper tube that is bent into the form of a single-turn coil and soldered to a copper band which conforms to the slope of the coil insert and is recessed. Holes in the inserts which match tapped holes in the master coil securely clamp the inserts to the master coil, providing good transfer of electrical energy and heat removal. Inserts are machined from copper with a thickness that matches the required heating pattern and should be somewhat greater in thickness than the depth of the recess for easy removal. Special coil shapes are easily configured. It is important to note that, because of the less-than-optimal cooling technique, coil inserts are particularly well-adapted to processes requiring short heating times or those in which they are also cooled by the quenching medium.

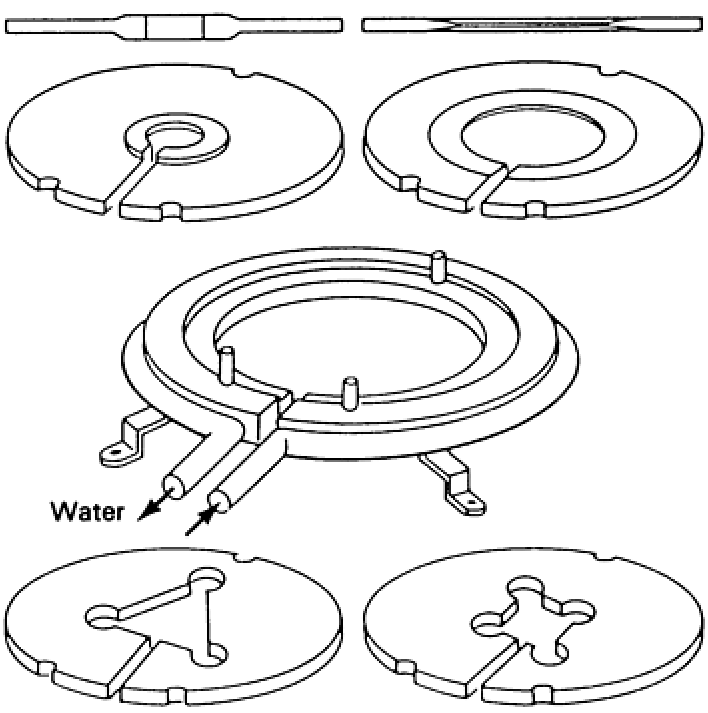


Fig. 23 The design of a master coil with interchangeable inserts

Coils for progressive hardening (scanning) are built using two techniques. The simpler of the two employs a simple single-turn or multiturn coil with a separate quench ring which can be mounted on the scanner (Fig. 24). For larger production runs, on the other hand, a double-chamber coil which incorporates both coil cooling and quenching capabilities is often the preferred choice. The scanning inductor shown in Fig. 24(b) is typical of the latter type of design. Cooling water flows through the upper, or inductor, chamber to keep the copper resistivity low. The quenchant is sprayed from perforations in the beveled face onto the workpiece as it exits from the inductor. The beveled face normally is at an angle of 30 ° to the vertical so that there is some soaking time between the end of induction heating and the quenching operation. This delay time helps to increase uniformity. Proper choice of the spray direction also reduces the amount of fluid runback on the shaft, which could cause variation in bar temperature and result in uneven hardness. Well-directed quench spray holes are required inasmuch as "barber poling" can occur due to erratic or misdirected quenchant that precools the part ahead of the main quench stream.

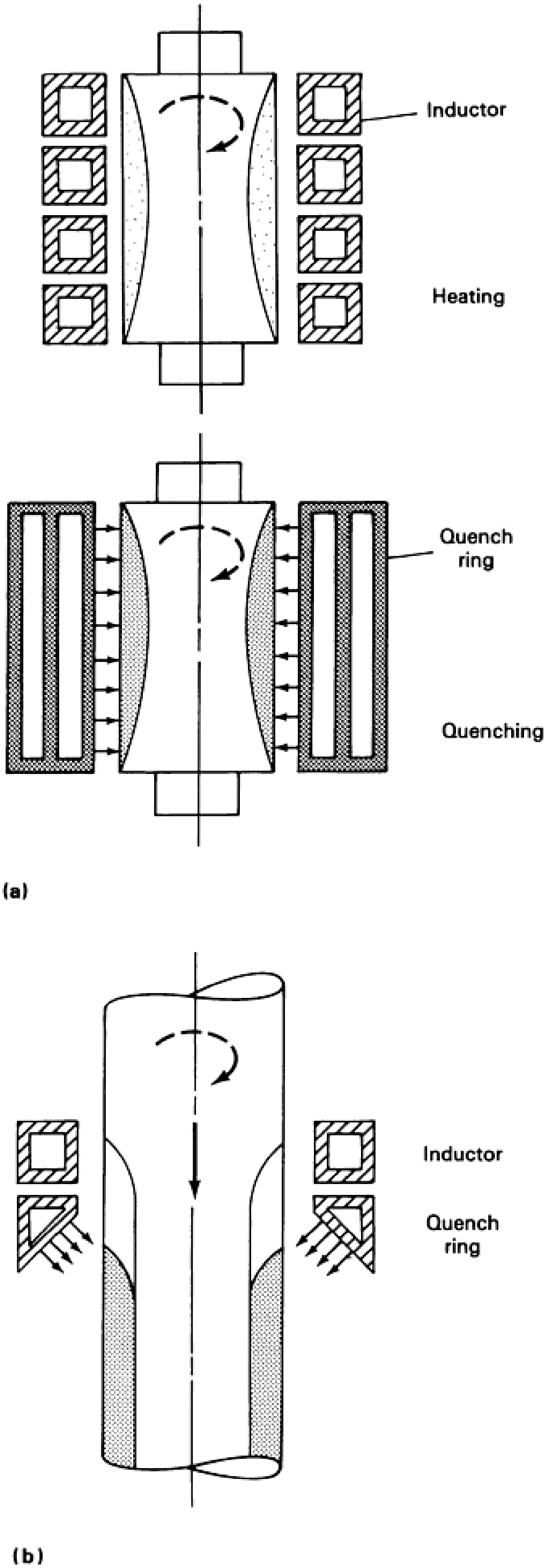

Inductor
Heating
Quench
ring
Quenching
(a)
Inductor
Quench
ring
(b)

Fig. 24 Inductor/quench designs for induction scanning. (a) Separate coil and quench. (b) Two-chamber, integral coil and quench

Split coils are generally utilized as a last resort for applications in which it is difficult to provide a high enough power density to the area to be heated without very close coupling and where part insertion or removal would then become impossible. Typical examples of such situations include hardening of journals and shoulders in crankshafts. In these cases, the split-coil design would also include the ability to quench through the face of the inductor.

It should be noted that with a split inductor good surface-to-surface contact must be made between the faces of the hinged and fixed portions of the coil. Generally, these surfaces are faced with silver or special alloy contacts that are matched to provide good surface contact. Clamps are used to ensure closure during heating. Often, high currents at high frequency pass through this interface, and the life of the contact is generally limited to both wear and arcing. Figure 25 illustrates a hinged split inductor.

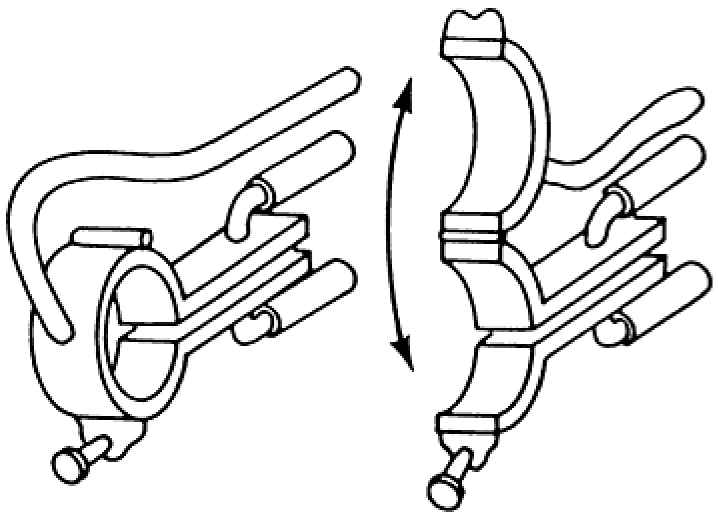


Fig. 25 A split inductor used for heating crankshaft journals

Coolant for the coil chamber of a split inductor is carried by flexible hoses that bypass the hinge so that excessive heating does not occur in the movable section during the cycle. The quench chamber is fed by a separate hose arrangement. The face of the quench chamber is closest to the work during heating and therefore carries most of the current. Accordingly, it must be sufficiently thick to preclude either melting or distortion during the heating cycle.

With split coils it is also frequently necessary to provide some means of locating the part in the coil to maintain the proper coupling distance. Ceramic pins or buttons are frequently secured to the face of the inductor. These pins contact the part during the heating cycle and establish rigid relative positioning between part and coil. However, they are subject to thermal shock during the heating and quenching cycles and suffer mechanical abuse as well. Therefore, they should be designed for simple replacement as required.

Butterfly Coils. One of the most difficult heating challenges is the creation of an even heating pattern at the end of a bar or shaft. Patterns developed with a pancake inductor produce a dead spot at the center due to field cancellation in this area.

The butterfly coil (Fig. 26), so named because of its appearance, utilizes two specially formed pancake coils. The current paths of the adjacent sides are aligned so that they are additive. The "wings" of the butterfly may be bent up to decouple their fields from the shaft, or if heat is required in this location, they may be coupled with the shaft itself. In winding this coil, it is important that all center turns be wound in the same direction so that they are additive. Further, only these turns should couple directly with the part to produce the desired pattern; part rotation is required to provide uniform heating on the end of the part.

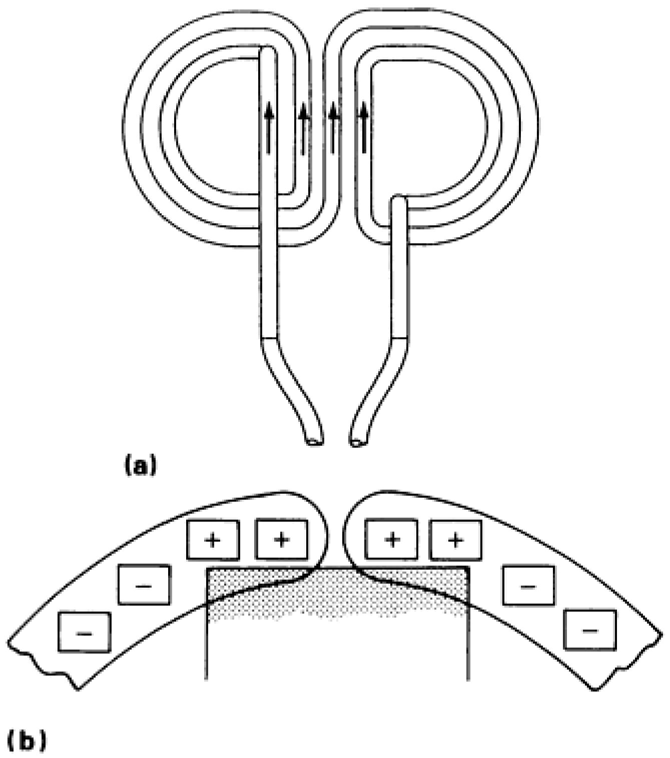


Fig. 26 Schematic of a butterfly coil. (a) Coil construction (arrows indicate reinforcing type of current flow in coil. (b) Coupling between the turns of the coil and the end of the workpiece to produce a uniform heating pattern

Split-Return Inductors. If a narrow band of heat is required and heating must be accomplished from one surface only as in weld-seam annealing, the split-return inductor offers distinct advantages (Fig. 27). With this design, the center runner of the work coil carries twice the current of each of the return legs. The pattern on the workpiece, being a mirror image of the coil, produces four times as much heat under the center leg as in each of the return loops. With proper balancing, the high-heat path can then be extremely narrow while the heat produced in each of the return legs is insufficient to affect the remainder of the part.

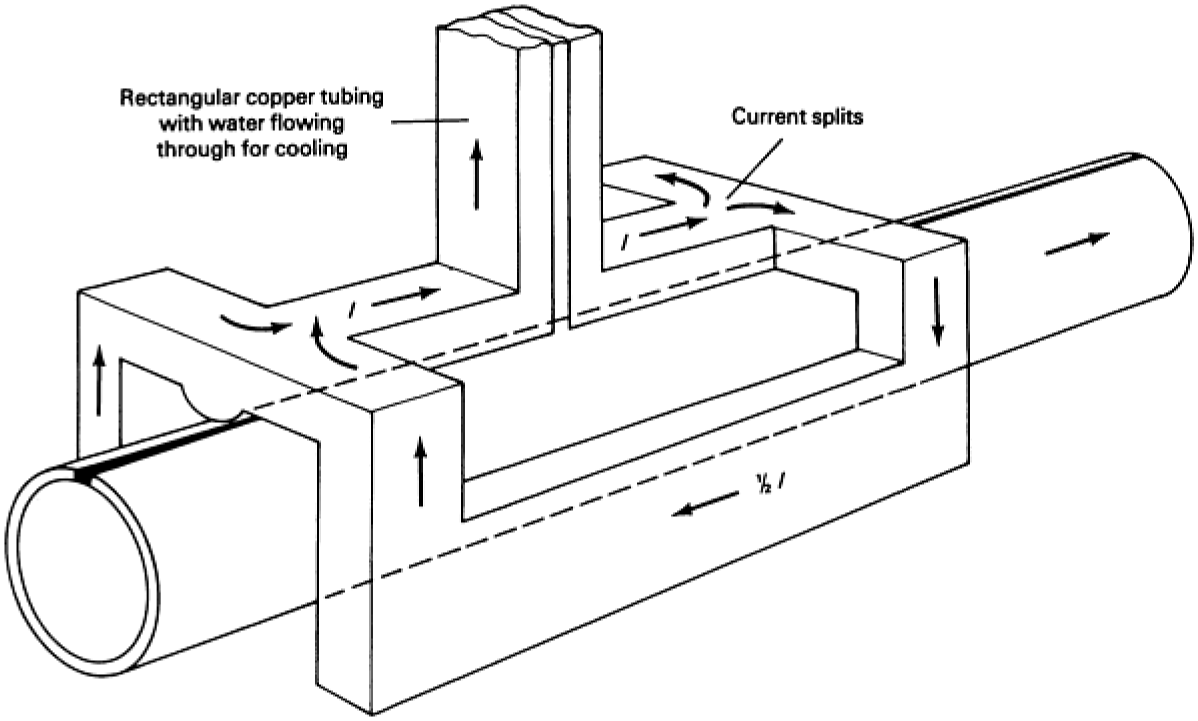


Fig. 27 Split-return coil for annealing of seam welds in pipe or tubing

Transverse-Flux Coils. In heating of parts that have a long longitudinal axis and a thin cross section, a circular coil wrapped around the workpiece produces a heating pattern (Fig. 28) that, due to coupling distances, is effective only at the edges. In transverse-flux heating, however, the coil is designed to set up a flux field which is perpendicular to the sheet or similar part. In this way, the path of the eddy currents is changed so that it is parallel to the major axis of the work. For example, in the manufacture of items such as hacksaw blades, the steel moves between the turns of the coil and the eddy-current path is a circular one across the flat of the blade. For heating of wide sheet materials, specially designed transverse-flux inductors have become available in recent years.

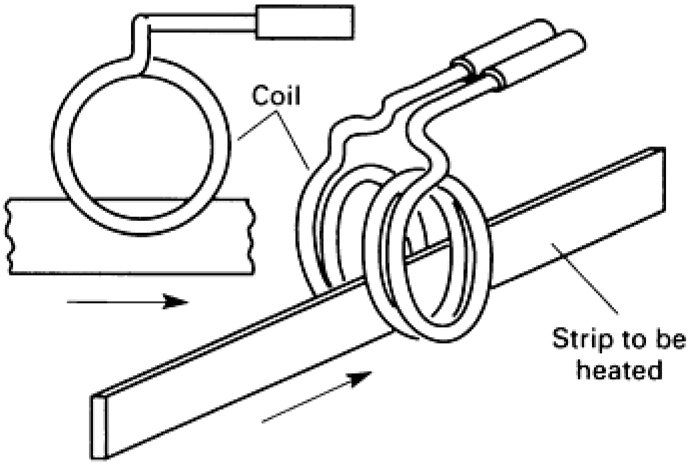


Fig. 28 Transverse-flux coil for heating thin sections

These inductors usually contain laminated iron cores with a series of windings along the length of the strip which induces a circulating current that flows across the width of the strip and returns on itself along the edges under adjacent pole faces. In this type of arrangement, coil sections are placed on both sides of the strip to force the magnetic flux to pass

transversely through the strip as opposed to the typical longitudinal flux pattern developed with a coil that encircles the strip.

Series/Parallel Coil Construction. It is sometimes desirable to have long work coils or coils with many turns connected in series. The current through each turn is identical and it is simple to balance the heating pattern. Furthermore, if an imbalance occurs in any one turn (for example, it is suddenly loaded more heavily), the other turns are affected equally. Thus, if a slow-down occurs in one location of a conveyor, the power along the whole line can be adjusted proportionally. In some situations, however, as the number of coil turns and resultant length increases, the voltage must also be increased to drive the current through the coil turns. This means that on long coils, the voltage between the workpiece and the coil can be extremely high, and arcing can occur. This may be a problem, for example, in the heating of continuous strip, in which speeds are high, and coils are therefore very long. In these situations, it becomes advantageous to use parallel coils, thereby reducing the applied voltage.

With parallel coils, the voltage required is limited to that needed to drive current through a single inductor. However, coil resistance and inductance in parallel inductors are such that extreme care must be taken to preclude all the current going through the inductor closest to the power supply.

The best method for parallel coil construction makes use of a wide bus arrangement. With identical coils mounted to the bus, this method permits rapid, simple replacement of individual sections as required, and fabrication of the individual sections is easily accomplished. A second technique which assures an even current distribution comprises the interwinding of several coils. An even current distribution is assured in that each coil receives its current from the same point in the bus.

Conveyor/Channel Coils. When power densities are low and heating cycles not extremely short, parts can be processed by means of a turntable or conveyor in a continuous or indexing mode. The coil must then be designed to permit easy entry and exit of the part. The simplest conveyor or channel coil used in these situations is a modification of the hairpin inductor. With the indexing technique, in which the part is at rest in the coil during the heating cycle, the ends of the hairpin can be decoupled to prevent overheating of the ends. The raised portions or bridges also facilitate the passage of the part through the coil. When a wide heat zone is to be produced on the part, coupling over a greater area can be effected through the addition of a liner to the coil turn, or more ampere turns can also be produced with a multiturn channel inductor. Channel coil liners may also be configured to produce specialized heat patterns where greater heat densities are required in specific areas.

During design of heating operations utilizing channel coils, there is a "fill factor" which must be considered from an efficiency standpoint. The unused portion of the coil appears as lead losses. Therefore, parts must be as close as possible to each other, without touching, to utilize the full capabilities of the inductor. Another important consideration when using a channel coil is the fact that those areas of the workpiece closest to the coil receive the greatest portion of the flux and therefore heat the fastest. If conduction through the part is slow, the part should be rotated while passing through the coil. Sufficient time (in an indexing conveyor or turntable) or speed variation (in a continuous motion device) must be provided to allow heat uniformity to occur in part areas furthest from the coil turns.

Flux Concentrators. If a ferromagnetic material with incomplete current paths is introduced into the coil field, it will provide a low-reluctance path for the flux (without dissipating energy). This low-reluctance path reduces the stray flux and tends to gather flux lines, thereby concentrating the field. This use of flux concentrators improves the load power factor and may thus reduce coil current requirements.

Flux concentrators can play a very important role in enhancing the induction heating process when they are properly applied in and around the induction coil. The major uses of flux concentrators are:

- Improve heating at coil ends
- Improve heating effect of internal coils
- Improve the heating effect of proximity or stray field coils
- Improve the general efficiency of any coil

For example, flux concentrators applied at coil ends will tend to make the heat pattern more uniform along the coil length. The performance from coils used to heat the inside or bore of a part also can be improved by placing the flux concentrator

or core inside the coil. Transverse flux coils can heat more effectively when a flux concentrator is placed on the face opposite the heating face.

The material chosen for a flux concentrator depends on the applied frequency, the kind of service, and the degree of exposure to radiated heat. Commonly used materials include stacks of silicon-steel laminations used at frequencies below 10 kHz or ferrites for higher frequencies, including those in the RF range. Figure 29 shows the effect of a flux concentrator on heating a shaft.

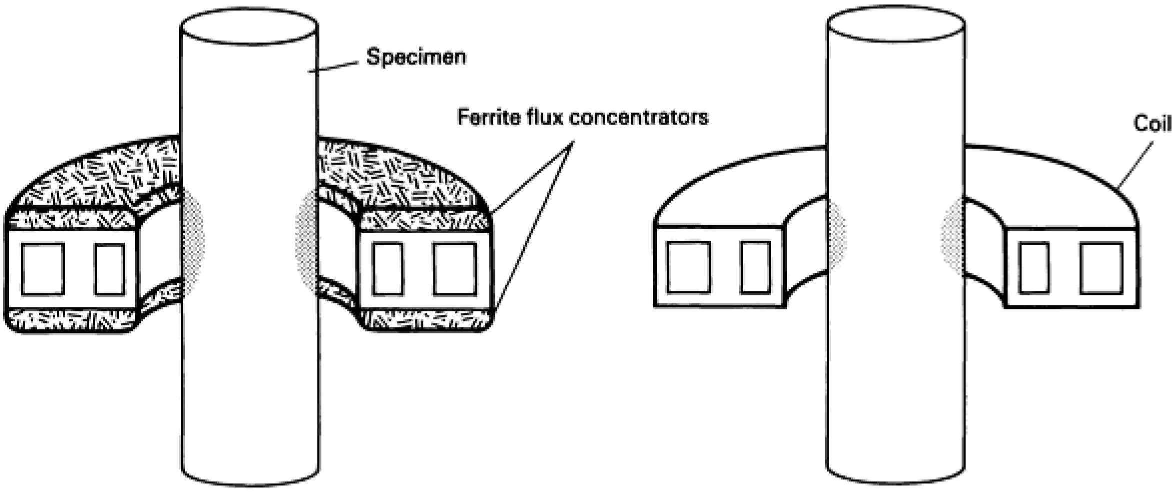


Fig. 29 The effect of using a flux concentrator on the heating of a shaft

Coil Construction and Cooling

Coil Construction. The most widely used material for coil construction is oxygen-free high-conductivity (OFHC) copper. Many high-frequency coils are made of standard round refrigeration tubing (which can be flattened) or special drawn tubing with square and rectangular cross sections. The coil conductor should be thicker as frequency is decreased, because the skin effect is less pronounced. To minimize coil losses, the current-carrying wall should not be much less than the depth of current penetration in copper. The various types of coil conductors used for lower frequencies include:

- Heavy-wall copper tubing
- Copper bar brazed to tubing
- Specially extruded tubing with a heavier wall at the hot face

Machined inductor coils are used primarily as single-turn inductors, and special heavy-wall shapes are primarily for 60 Hz coils. For brazed joints, both phosphorus copper and silver brazing alloys are used, the latter being preferred for electrical conducting joints and ones where ductility is needed.

Mechanical Design Considerations. When electrical currents travel in adjacent conductors, the two conductors are either attracted or repelled by a force that is proportional to the square of current flowing. Currents traveling in opposite directions cause a repelling force between two adjacent conductors, whereas two currents traveling in the same direction tend to attract the two conductors. These forces, which occur at coil turns and in the coil leads or bus, must be considered in coil design.

At high frequencies and at comparatively low currents (except for high power densities), the forces are minimal and free-standing tubing may be used. Coil turns may be supported with studs and brazed to each turn and then fastened to an insulating board to reduce the potential for cyclic movement or to maintain turns spacing.

Medium-frequency coils, which experience greater electromechanical forces, require more attention to the coil support system and to the integrity of brazed joints. Again, the forces, which are a function of current, may not be of real concern at low power levels. Because the repelling forces relax when a coil is deenergized, cyclical applications of power may

tend to work harden braze metal or even the basic copper and can cause fatigue failure in parts of the coil, particularly where stresses are concentrated.

Coils energized by line frequency or from triplers (180/150 Hz) require attention to details of how the turns are supported and how they will resist damage from low-frequency vibration. Brazed or welded studs and insulating board of heavy construction may be used for coils with spaced turns. Close wound coils can be constricted by using mica or melamine insulating rings between turns of rectangular copper tubing with the entire assembly clamped between end boards of hard insulating material with nonmagnetic metal tie rods and clamped with pressure maintained through bellville washers. Slotted nonmagnetic metal endplates can back up the insulating board. Another possibility is to cast the entire assembly in refractory or epoxy, but a great deal of attention should be paid to the materials used and the technique.

Electrical Characteristics. Power can be conveyed to induction heating coils by copper bus bars, tubing, flexible stranded cable or coaxial cable. Some inductance exists in all power leads and it produces an inductive reactance (X_L) expressed by the following equation:

$$X_L = 2\pi fL \qquad \textbf{(Eq 3)}$$

where f is frequency in Hz, and L is the inductance in henrys. Inductive reactance (X_L) can be offset by capacitive reactance (X_C), but the energy from capacitors increases the circulating current and the I^2R losses in the system, so it is desirable to minimize unnecessary inductance anywhere in the system, particularly in leads that carry high current at low voltages. This is especially true for high-frequency systems for low-voltage coils. Ideally, the voltage drop in the leads due to X_L will be a small fraction of the voltage across the heating coil or inductor.

The inductance of the leads is a function of the electrical gap between conductors, and in general it is best to minimize the space between them (Fig. 30) and support them to increase the area of opposing faces. This is one reason for using wide rectangular tubing, flat face-to-face copper bus, or coaxial cable. When insulated varnished cambric or other insulated cable is used for conductors at medium to high frequencies, extra flexible fine strand cable should be used and taped every foot to maintain a low inductance close configuration. This array can be supported in nonconductive or open-loop metal hangers or laid in an expanded metal aluminum trough. Ratings for open air operation for some of the standard cable sizes at 1, 3, and 10 kHz are given in Table 3.

Table 3 Transmission lines for use from generator to station or between stations with sine-wave output

Input ratings		**Single-conductor cable[b]**					
		+ - One per leg Maximum run			**+ - Two per leg Maximum run**		
A	**kW[a]**	**Size**	**m**	**ft**	**Size**	**m**	**ft**
10 kHz, 220 V							
34	7.5	10	38.7	127	14	93.6	307
68	15	6	19.2	63	10	39.0	128
136	30	4/0	12.8	42	6	23.8	78
227	50	. . .	. . .	. . .	4/0	19.8	65

10 kHz, 400 V							
375	150	. . .	. . .	. . .	500 MCM	24.4	80
10 kHz, 440 V							
68	30	6	37.8	124	10	77.7	255
114	50	1/0	30.2	99	6	57.3	188
227	100	. . .	. . .	. . .	4/0	39.0	128
10 kHz, 800 V							
188	150	350 MCM	38.7	127	1/0	83.2	273
219	175	. . .	. . .	. . .	4/0	71.6	235
313	250	. . .	. . .	. . .	350 MCM	57.6	189
3 kHz, 400 V							
75	30	6	116.1	381	10	179.8	590
250	100	500 MCM	52.1	171	1/0	112.8	370
375	150	. . .	. . .	. . .	250 MCM	80.2	263
500	200	. . .	. . .	. . .	500 MCM	65.2	214
3 kHz, 800 V							
125	100	2	164.6	540	6	350.5	1150
188	150	4/0	109.1	358	4	247.5	812
250	200	500 MCM	104.9	344	1/0	226.8	744
375	300	. . .	. . .	. . .	250 MCM	160.0	525
1 kHz, 800 V							

313	250	500 MCM	243.8	800	1/0	356.6	1170
438	350	. . .	. . .	. . .	250 MCM	585.2	1920

(a) The power-carrying ability indicated is for motor-generator sets, typically from the generator to the control and/or the heat station. For most solid state converters the recommended power levels will be about 25% less because they operate with a slightly leading power factor and some additional reactive current must be carried. Manufacturers' recommendations should be followed.

(b) Cable sizes are designated by American Wire Gage (AWG) number where applicable or by actual size in thousands of circular mils (MCM). The size listed is the smallest cable that will carry the rated current. This cable is varnished cambric insulated, single braid, and standard strand. The maximum length listed was calculated for the following conditions: The voltage across the condensers is ≤ 1.1 times the generator terminal voltage, and the generator output power factor is 0.9 leading.

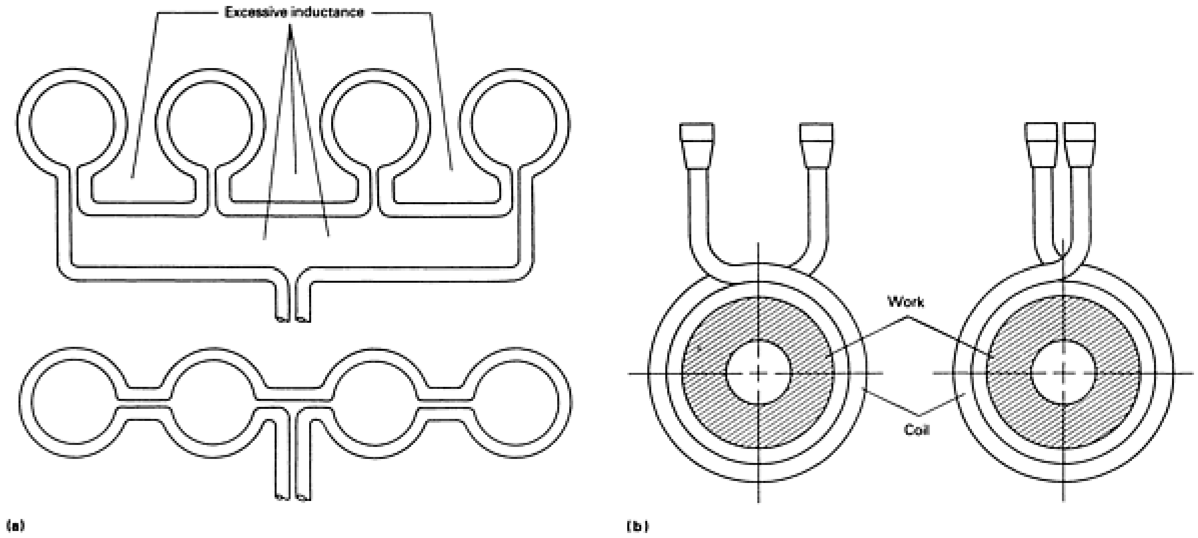


Fig. 30 Effect of coil-lead spacing on inductance of (a) multiplace inductors and (b) a single-turn coil. In both cases, closer spacing of conductors reduces lead inductance and thus power losses.

Water cooling, as described below, can be judiciously applied when needed, and the amount of air space or electrical insulating material between conductors must be appropriate for the voltages applied. In open air systems, the conductors should be smooth and clean and protected from dirt, water, and metal particles. Personnel should also be protected from exposure to any harmful voltages by covers and warning signs.

Coil Insulation. When heating coils are exposed to a high-temperature load for long periods of time (such as those used to austenitize tubulars in continuous quench-and-temper operations), the heating coils may provide better service and be more efficient with thermal insulation at the hot face. Electrically, this insulation is the same as air, and any added electrical gap will increase the coil current required to heat the metal, as well as reduce coupling efficiency. Hot-face thermal insulation is primarily used in coils up to about 10 kHz where the added electrical gap can be tolerated. Higher frequency coils may use a liner, but the thickness should be limited. The basic kinds of coil insulation are:

- Entire coil potted in a castable refractory
- Self-supporting coil with cast-in liner, a precast liner, or a precast liner with a split stainless steel or Inconel sleeve

Coil Cooling. Although most induction heating coils are water cooled, some low-temperature, low-kVA heating coils will function with convection or forced air cooling. Air cooling has been used on the following:

- Line-frequency core heaters, which have low I^2R losses because of their high power factor and low reactive current
- Solenoid coils used for low-temperature heating of steel and cast iron

The suitability of air or water cooling depends on whether the copper conductors are kept cool enough to maintain their strength. Coil cooling is also needed to minimize electrical resistance of the coil and to reduce the level of oxidation.

Cooling water passages should be as close as possible to the current-carrying face, which is usually adjacent to the work. Copper tubing can act both as conductor and cooling passage, or it may be brazed to solid copper body to simply act as the cooling passage. As a cooling passage, it should not alter the heat pattern. As a conductor, it should provide enough copper to carry current at the applied frequency.

Water pressure should be adequate to provide full flow without voids or steam pockets forming; typically gage pressures of 140 to 415 kPa (20 to 60 psig) are used. Much higher pressures up to 1035 kPa (150 psig) have been used to cool coils with very small water passages such as those used to heat small spaces such as small bores. It is advisable to use a minimum but adequate pressure.

If hard water is used for coil cooling and the temperature exceeds 55 °C (130 °F), some scale may build up in the cooling passages. If not cleaned out periodically, the water passages may become coated and/or restricted, in which case, cooling is impaired and overheating of the work coil or other water-cooled components may occur. Cleaning with an acid must be done carefully because overexposure to acid may produce leaks, particularly where the copper has been cold worked.

Impedance Matching

In maximizing the delivery of power from the power supply to the load (coil-work-piece) circuit, it is necessary to match or tune the load impedance with the output impedance of the power supply. This may require the use of a tank circuit either in parallel or in series with the inductor coil. The parallel circuit is most commonly used because it permits remote mounting of the tank circuit (heat station) with minimum losses in the transmission lines. The transmission voltage used is limited to the power supply voltage, unless a transformer is applied at the power source. Because the inductance of the transmission line becomes part of the tank inductance in a series circuit, the distance from the power supply to the work coil is limited for reasons of efficiency.

The apparatus to electrically match the output impedance of the power supply with the load circuit can be built into the power supply or be housed in a separate cabinet called a heat station. Some power supplies (such as solid-state converters and spark-gap converters) have the ability to follow load changes which occur during a heating cycle, even when iron and steel pass through a magnetic transformation at the Curie temperature.

In contrast, the power from fixed-frequency sources (such as a motor-generator or a tripler) may decrease significantly because of radical changes in coil/part impedance when magnetic materials are heated above the Curie temperature. In the interest of maintaining a high level of power to the load, it may be necessary to retune the system as the load becomes nonmagnetic.

Tuning of Fixed-Frequency Systems. Line-frequency power supplies, frequency multipliers, and motor-generators each produce output power at a single specific frequency. In order to obtain maximum power from the work coil, it is important to provide a tank circuit tuned to that specific frequency whose impedance matches that of the power supply. A series reactance or a series capacitor may be used to drop the supply voltage for voltage matching, but transformers are preferable because standard units are available in a wide variety of frequencies.

The schematic diagrams in Fig. 31 show the circuitry for both a high-impedance system using an autotransformer and a low-impedance tank circuit using an isolation transformer. Both systems have tapped transformer windings to match coil impedance to generator impedance and some means of connecting capacitance, as required, to tune the system to resonance at or near the operating frequency of the power supply. Because the capacitors are connected incrementally, it is not always possible to tune the circuit close to the output frequency of a motor generator, and thus, full output power is not always achieved.

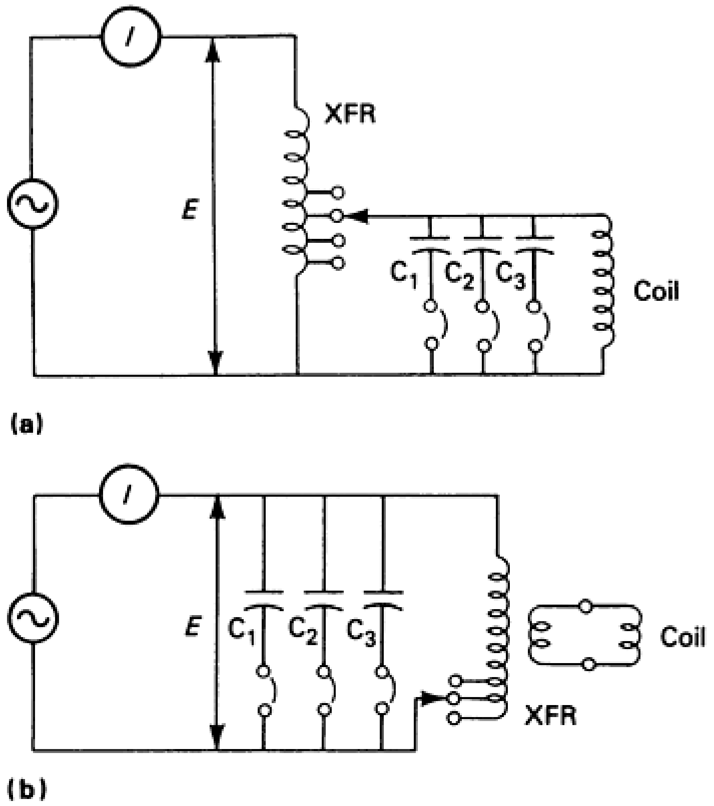


Fig. 31 Schematic circuit diagrams of low- to medium-frequency heat stations illustrating capacitor and transformer adjustments when using (a) an autotransformer for high-impedance induction coils and (b) an isolation transformer for low-impedance induction coils. Similar circuits are used in high-frequency systems (Fig. 9).

During the actual tuning operation, such as that for a motor-generator system, the field is slowly increased so that the meters begin to indicate. If the power factor is lagging, capacitance must be added in parallel to the tank circuit (assuming that a parallel tank circuit is used). If the power factor leads, capacitance might have to be removed. For set-up of a motor-generator and some solid-state converters, however, the tank circuit may be tuned to provide a slightly *leading* power factor. This helps to compensate for the internal inductive reactance and enables rated voltages to be established at the output terminals from the power supply. Operating with a slightly leading power factor also prevents exceeding the field-current rating when operating at rated voltage and power.

When the power factor has been corrected reasonably close to unity, power can be increased until either the voltage or the current reads the maximum permissible. Readings of all meters can then be taken. If the output voltage reaches a maximum before the current does, the coil voltage needs to be increased by reducing the primary-to-secondary ratio of the transformer. The ratio must be adjusted, or turns must be removed from the work coil based on the equation:

$$\text{Re}\,quired\ \text{turns} = \text{Present turns} \times \frac{\text{Amperes obtained at rated voltage}}{\text{Rated amperage}}$$

Should rated current be achieved before rated voltage, the primary-to-secondary ratio is too low. The ratio must be adjusted, or turns must be added to the work coil as follows:

$$\text{Re}\,quired\ \text{turns} = \text{Present turns} \times \frac{\text{Rated voltage}}{\text{Voltage obtained at rated amperage}}$$

When the work coil is modified, the circuit must be returned.

All fixed-frequency systems should be set up with the workpiece in the coil, because the impedance would differ dramatically if the part were not in place. Accordingly, balancing should be performed using short, low-power tests so that minimal heat is produced in the workpiece during setup and so that conditions for comparison therefore remain almost static. In tuning of a fixed-frequency system during progressive heating operations, readings and adjustments should be made with the part moving through the coil at its normal speed.

Tuning of Variable-Frequency Systems. Because the solid-state SCR-controlled power supplies generate frequencies determined by the tank circuit, these systems allow self-tuning. Nevertheless, it is first necessary to tune the system so the tank circuit is within the frequency band of the power supply. Once the tank is tuned to the frequency band of the supply, then the generator shifts frequency relative with changes in the tank circuit.

Transformers. As previously mentioned, transformers allow the change of output voltage from a power supply. Most transformers are water cooled. For frequencies up to about 10 to 25 kHz, the core is constructed of laminated silicon steel with lamination thickness ranging from 0.15 to 0.18 mm (0.006 to 0.007 in.) thick. For frequencies to 200 kHz, a ferrite core can be used. Above 200 kHz, no ferromagnetic core is used because significant losses can occur in ferrite at these higher frequencies.

Output transformers are only used when the output voltage of the supply differs from the voltage needed to energize the coil. At line frequencies (60 or 50 Hz) both air- and water-cooled transformers are used. At 180 or 150 Hz and above, water-cooled transformers are the norm. Tuning or resonating the load circuit can be achieved by maximizing the line or source current at a given voltage or by getting a close to unity indication on a reactive power (VAR) or power factor meter, if one is available. The object is to apply the desired power, which may be indicated by a kW meter at minimum voltage and minimum current.

An autotransformer (Fig. 31a) has a single winding, and it can be tapped to provide a variety of output voltages which are direct ratios of the turns and the primary voltage. This type of transformer is used where the primary/secondary turns ratio is no more than $2\frac{1}{2}$ to 1. It can be either water or air cooled depending upon frequency and power rating.

Isolated Winding Transformer. A typical two winding transformer can handle a wide range of ratios, well beyond the limited range of any autotransformer. The tapped variety (Fig. 31b) is a bit more expensive than the fixed ratio type, but it provides more load matching flexibility and is therefore more prevalent in commercial induction heating equipment. Taps can be either on the primary winding or the secondary winding, or both, but those in use with frequency converters almost invariably are tapped in the primary.

The typical medium- to high-frequency transformer uses a copper sheet wound as the secondary winding, mostly a single turn; some may be two or even three turns. Taps will be taken from the primary winding and brought to link-connected terminals. The windings are water cooled, and the core may have some water-cooled heat sinks stacked in the core. The high ratios are used to work into single-turn inductors or coils of only a very few turns, and ratios up to 32 to 1 are available in standard designs. Transformers in use up to 25 kHz have laminated silicon steel cores with the thickness of the individual laminations decreasing with increasing frequency.

Capacitors. Any induction heating load, by its very nature, reflects back to the power supply a great deal of inductive reactance, most of which should be corrected with capacitive reactance. Power factor correction capacitors then supply opposing reactive current to balance or resonate the circuit so the load appears to be almost entirely resistive. In this way energy transfer is maximized because the power supply does not have to furnish reactive current.

Because of their use in tuning, capacitors are usually rated in terms of reactive power (kVAR) for induction heating applications. The kVAR ability is an inverse square function of its applied voltage, and thus power factor correction (particularly at medium and high frequencies) is generally performed on the primary side of the load matching transformer, where the voltage is maximum. Because the transformer in this instance must carry full reactive current, and because its losses and current-carrying ability must be higher than with secondary correction, cooling becomes an important consideration. Should the coil voltage approach the rated operating voltages of standard capacitors, it may then be practical to consider capacitors on the secondary or coil side of the transformer. This condition occurs most often where autotransformers are used. The capacitor combination must have a high enough kVAR rating to match maximum output.

When a coil is changed or a new load introduced, the amount of capacitance to tune the circuit may need to be changed. As metal is heated, its resistivity increases, and this will have some limited effect on the load characteristics. However, it is the decreasing magnetic permeability (μ) and the loss of it above the Curie (magnetic transformation) temperature which requires some change to be made to the system, to maintain a reasonable level of power to the load. This may suggest the desirability for switching in additional capacitors, which is a practice often used in static deep-heating applications with motor-generator, line frequency, or tripler equipment.

Workhandling Equipment

Most manufacturers of induction heating equipment will offer mechanical handling apparatus to move the parts or material through the induction field. Vertical scanning units for hardening pins and shafts, and lift-rotate spindles designed to raise or lower parts into a coil and/or quench, may be available in standard packages. Most other workhandling systems will be specially engineered to meet the particular application requirements. Automated bar and tube-handling equipment is common for continuous annealing or the hardening and tempering of these product forms.

Special workhandling equipment can be almost anything from simple manually loaded holding fixtures to a completely automated materials-handling system. Automation is becoming more prevalent as induction heating is introduced. Hopperfeeders sort and orient a variety of parts such as fasteners of various types, cartridge cases, and small automobile engine parts. Because induction heating cycles are short, the process lends itself well to automated manufacturing. As such it eliminates carting parts to a separate heat-treating location, makes for a smooth flow of parts processed in an orderly fashion, and facilitates just-in-time delivery requirements.

Some of the basic requirements of a workhandling system for induction heating are:

- The material should be held without interfering with any part of the heat-treating process
- Parts or material processed must be positioned for each step of the process with the degree of accuracy required
- The part or material must be positioned properly and supported well enough to minimize distortion. In some cases, mechanical restraint may be used to accomplish this
- The part weight and/or the positioning devices should prevent it from moving when subjected to the electromechanical effects of the induction field (especially at lower frequencies)
- Electrical conducting materials used in construction of the fixture should be kept away from the heating field and stray induced currents avoided in drives, bearings, and moving parts

If the latter requirement is not entirely possible, fixture parts may be cut, slotted, electrically insulated from one another, or shielded by intercepting conductive material to reduce any induced heating effect. As a last resort they may be cooled by forced air, water, or even the quenchant. Nonfriction bearings should not be a part of any closed conducting loop through which induced current may flow.

Control Equipment

Induction heating power supplies should be equipped with meters to provide information needed for both initial tuning and for monitoring its performance during operation. Most of the electrical characteristics are measured from a current transformer (C/T) and a potential transformer (P/T) in the load circuit of the power supply.

Metering on fixed-frequency systems generally consists of a kilowatt meter, an ammeter, a voltmeter, and a kVAR or power-factor meter. These meters sometimes are read in percentages of their maximum ratings to simplify tuning. When the system is tuned properly, an increase in the output of the system will reflect increases in both current and voltage simultaneously. An increase in one and a decrease in the other are indicative of improper balance.

Solid state SCR converters use a system of logic to control firing of the SCR devices, and each manufacturer uses a logic system to provide the desired features of performance and control. Such a system may provide constant voltage, constant current, or constant power to the load, and it may allow the output frequency to float as it attempts to resonate with the changing characteristics of a metal being heated. Logic may also help a converter match a wide range of load conductance with very little frequency change.

Power Control. After the output circuit has been tuned to match the load, any needed power change is made by changing the voltage to the coil. The coil current (*I*) is essentially proportional to the impressed voltage (*E*), and so power ($E \cdot I$) delivered to the load is essentially a function of the voltage squared. The coil voltage, which can also be changed by transformer taps, thus determines the power level. If frequent tap changes are needed, no-load tap switches (manual or motorized types) can be used to make these voltage changes, either for set up or during an appropriate heating cycle.

On load, stepless voltage control is available through a number of different devices, the use of any one being appropriate only for certain kinds of equipment. Voltage control or stabilization on the line or primary side of a heater is available through:

- On-load motorized tap switch
- Motorized induction regulator
- Superior electric-type regulator
- Solid state (SCR) voltage controller (caution required for direct use on capacitance corrected loads)
- Saturable reactor
- Saturated transformer (voltage-regulating only)

Triplers and line-frequency induction heaters might use one of the line-side voltage controlling devices listed above. For a very limited range of output voltage control, a spark-gap converter may also use these devices. Most types of frequency converters can have a built-in system for stepless control or regulation of the output voltage:

- *Motor generator.* Output voltage is a function of the generator field current, so control of the generator voltage in the low-energy field controls the high-energy output of the generator
- *Solid state.* Output voltage can be controlled with solid state devices in the direct current (dc) supply, and/or by controlling the firing of dc to the output circuit
- *Vacuum tube oscillator.* Use of three-element rectifier tubes (thyrations) or solid state devices in the dc supply control voltage

By far most induction heat-treating operations are based upon a predetermined level of power applied for a given length of time. Repeatability of the treatment depends upon maintaining that cycle of power, which is a function of the applied coil voltage, and accurately timing the period it is applied. Timing a repeated *controlled* energy cycle is by far the most widely used process control technique.

Transformation Hardening of Steel

The difference between heat-treatment temperatures for induction heating and furnace heating is related to the inherent short heating times of the induction method and its effect on transformation temperatures. In this section, a number of key parameters that influence the hardening response of steels that have undergone induction heat treating are described. These include:

- Time-temperature relations for induction hardening and tempering
- Electrical and magnetic properties of steels
- Selection of induction frequency and power
- The effect of prior microstructure

Time-Temperature Relations

Induction Hardening. As with parts hardened by conventional heat-treating methods, the hardness and hardness profile of induction austenitized parts depend solely on the chemical composition of the steel and the quenching medium. Therefore, the primary metallurgical question that arises in induction hardening relates to austenitizing.

As with austenitizing by conventional furnace techniques, time and temperature are the two critical parameters that must be controlled. To completely austenitize a steel, a certain amount of time at or above the A_3 temperature is required. The

time to form a totally austenitic microstructure depends on the austenitizing temperature selected and the starting microstructure. In all cases, the speed with which austenite is formed is controlled by the diffusion of carbon, a process which can be accelerated a great deal by increasing temperature. For example, the time for complete austenitization in a plain carbon steel of eutectoid composition with an initial microstructure of pearlite is decreased from approximately 400 s at an austenitizing temperature of 730 °C (1345 °F) to about 30 s at an austenitizing temperature of 750 °C (1380 °F), as shown in Fig. 32. Each of these times is considerably increased if the starting microstructure is spheroidized with large carbide particles. This occurs because the diffusion distance for carbon, which must be transported from the carbon-rich carbide phase, is considerably larger than in pearlite, which has thin lamellae of ferrite and carbide. Conversely, the finer bainitic and martensitic microstructures tend to be reaustenitized more readily than pearlite.

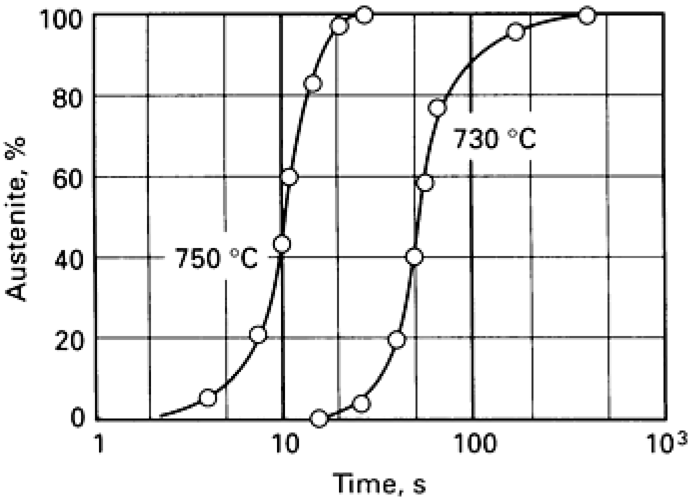


Fig. 32 Effect of austenitizing temperature on the rate of austenite formation from pearlite in a eutectoid steel

Data such as those in Fig. 32 suggest that at high enough temperatures, austenite forms in a fraction of a second. This fact is relied upon in induction surface hardening (very rapid heating rates) or induction through hardening (moderate heating rates) in which the workpiece surface or cross section is raised to a higher temperature than is normally used in much slower, furnace-based processes.

A tremendous amount of metallurgical research has been directed at the determination of the upper critical temperature (Ac_3) that signifies complete austenitization during continuous heating cycles such as those used in induction heating. Because the only "soaking" time available for phase transformation in these cases is that time after which the equilibrium critical temperatures (Ae_3 or Ae_{cm}) is exceeded, the continuous-heating critical temperatures are always above the equilibrium ones. This difference increases with heating rate, as might be expected, an effect shown in Fig. 33 for the Ac_3 temperature for 1042 carbon steel. Here the Ac_3 temperature is the one at which it has been estimated that the austenite reaction is complete. These data also show that the increase in critical temperature depends on the initial microstructure. The fine quenched-and-tempered, or martensite, microstructure revealed the least change in Ac_3 temperature as compared to the equilibrium Ae_3 temperature; whereas the same steel with annealed microstructure exhibits the largest difference in Ac_3 as compared to the Ae_3 obtained from very slow heating rates. Such a trend is readily explained by the fact that the diffusion distance to redistribute carbon is shorter in the former instance and longer in the latter microstructure in which carbides are much larger.

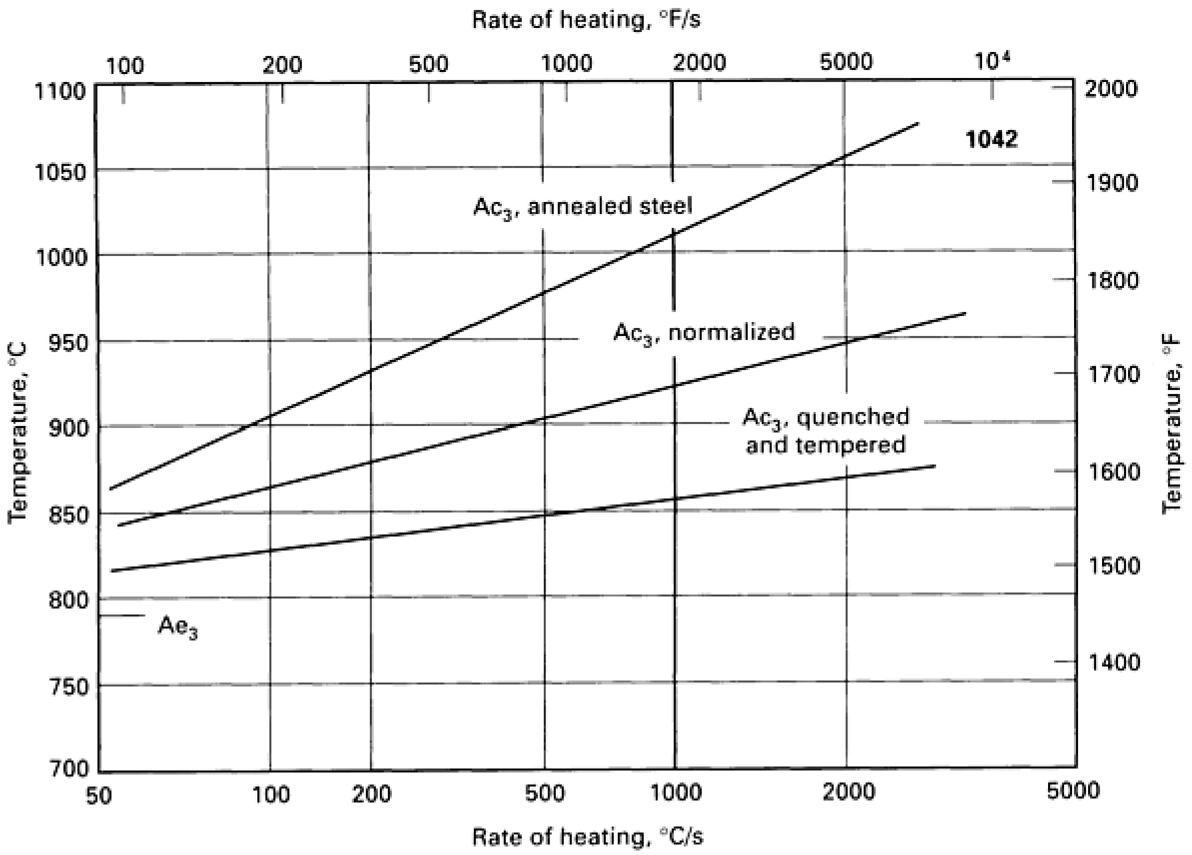


Fig. 33 Effect of prior structure and rate of heating on Ac_3 transformation temperature of 1042 steel

Data similar to those for 1042 steel are given in Fig. 34. For eutectoid 1080 carbon steel, the Ac_1 and Ac_3 temperatures nearly coincide during "slow" heat treatments. By contrast, they differ for rapid heating (Fig. 34). The lower critical temperature can be taken as one at which the reaction started, and the upper one as that at which transformation to austenite was completed. At the higher heating rates, the Ac_1 and Ac_3 are higher than at lower rates, an effect which offsets the shorter times at temperature.

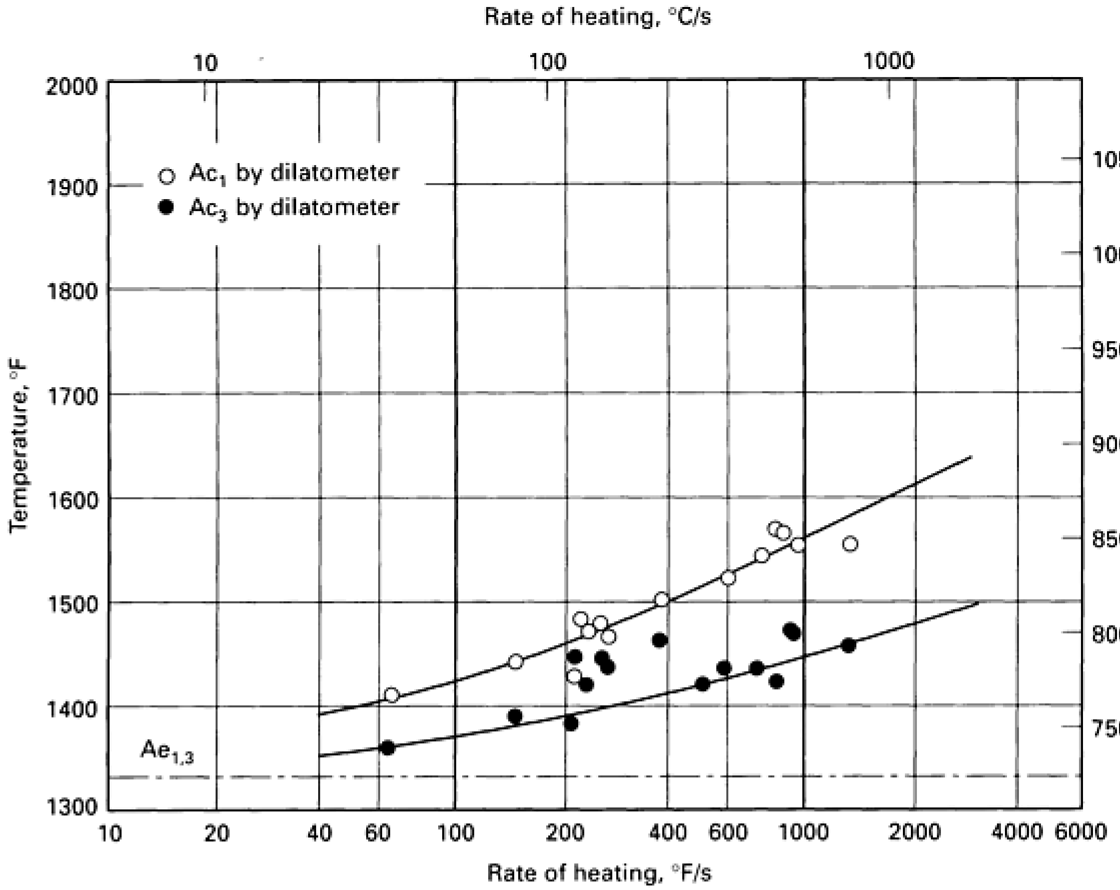


Fig. 34 Effect of heating rate on Ac_1 and Ac_3 temperatures for annealed 1080 steel

The above measurements are most useful when only the surface layers of a steel part are to be austenitized and hardened. In these cases, continuous rapid heating to the Ac_3 temperature is all that is needed. In other situations, in which deeper hardening or through-hardening is necessary, a certain amount of actual soaking time at temperature may be required.

Based on data such as those in Fig. 33 and 34, guidelines have been derived for the required austenitizing temperature for induction hardening of a wide range of steels (Table 4). Generally, the recommended temperatures increase with increasing A_3 temperature; they are approximately 100 °C (180 °F) above the equilibrium upper critical temperature primarily to reduce or eliminate totally the austenitizing time during continuous induction heating cycles. However, they are still below that at which undesirable austenite grain growth occurs in the short times characteristic of induction-based heating processes. The recommended austenitizing temperatures are at least another 100 °C (180 °F) higher in alloys with strong carbide-forming elements (for example, titanium, chromium, molybdenum, vanadium, niobium, or tungsten) than they are in carbon steels. These increases are a result of large increments in the critical temperatures of alloy steels.

Table 4 Approximate induction austenitizing temperatures for carbon and alloy steels

Carbon content, %	Temperature for furnace heating		Temperature for induction heating	
	°C	°F	°C	°F
0.30	845-870	1550-1600	900-925	1650-1700

0.35	830-855	1525-1575	900	1650
0.40	830-855	1525-1575	870-900	1600-1650
0.45	800-845	1475-1550	870-900	1600-1650
0.50	800-845	1475-1500	870	1600
0.60	800-845	1475-1550	845-870	1550-1600
>0.60	790-820	1450-1510	815-845	1500-1550

Note: Recommended austenitizing temperatures for a specific application will depend on heating rates and prior microstructure Free-machining and alloy grades are readily induction hardened. Alloy steels containing carbide-forming elements (for example, niobium. titanium. vanadium. chromium, molybdenum. and tungsten) should be austenitized at temperatures at least 55 to 100 °C (100 to 180 °F) higher than those indicated.

In addition to the increase in recommended austenitizing temperatures in alloy steels, induction austenitizing times may also need to be slightly increased. This is because of the kinetics of alloy carbide dissolution in austenite, which can be substantially slower than those of cementite dissolution, particularly when NbC, TiC, and VC are involved. Such increases in induction hardening temperature and time generally are not deleterious from the viewpoint of austenite grain growth, however, because of the effects of alloying.

The above recommendations for induction hardening temperatures should be used only as a guide. This is especially true for modern plain carbon steels, which are typically melted using a large percentage of scrap that may contain microalloyed high-strength low-alloy steels. Thus, the steel may still be considered to be nominally of the plain carbon type but may contain trace amounts of niobium, vanadium, and/or titanium, whose presence may greatly affect heat-treating response. For this reason, it is wise to obtain a complete chemistry on each lot of steel employed in induction hardening processes or to determine proper austenitizing temperatures experimentally.

Another important feature of induction hardening is its ability to impart as-quenched hardnesses somewhat higher than those of conventionally furnace-hardened steels. This trait is illustrated in Fig. 35 for plain carbon steels of various carbon contents. Data are presented for surface induction hardened (curve A), furnace through-hardened (curve B), and furnace-hardened (curve C) specimens given a low-temperature heat treatment consisting of cooling to liquid nitrogen temperatures and subsequently tempering at 100 °C (210 °F). The higher hardnesses of the induction hardened specimens may be attributable to three sources: residual stresses, smaller amounts of retained austenite, and carbon segregation. As to the first effect, compressive residual stresses are developed in surface-hardened steels because of the smaller density of martensite as compared with bainite or pearlite. During cooling following austenitizing, the higher-density inner layers shrink more than the surface layers, leading to such residual stresses (and thus increments in hardness). The second factor, smaller amounts of retained austenite in induction hardened steels, is a result of the finer martensite generally resulting from such steel heat treatments; the martensite may also be harder because it was formed from finer-grain, less-homogeneous austenite having a larger number of imperfections. The last factor, the increment in hardness due to carbon segregation, derives from the fact that induction austenitizing normally involves rapid heating and requires short holding times, which may lead to variation in carbon content within the austenite grains. Thus, a mixture of high-carbon and low-carbon martensite is formed during quenching. It is the high-carbon martensite which gives rise to higher hardnesses. This effect decreases in steels whose carbon contents exceed approximately 0.6 to 0.8 wt%, above which the hardness of martensite does not change.

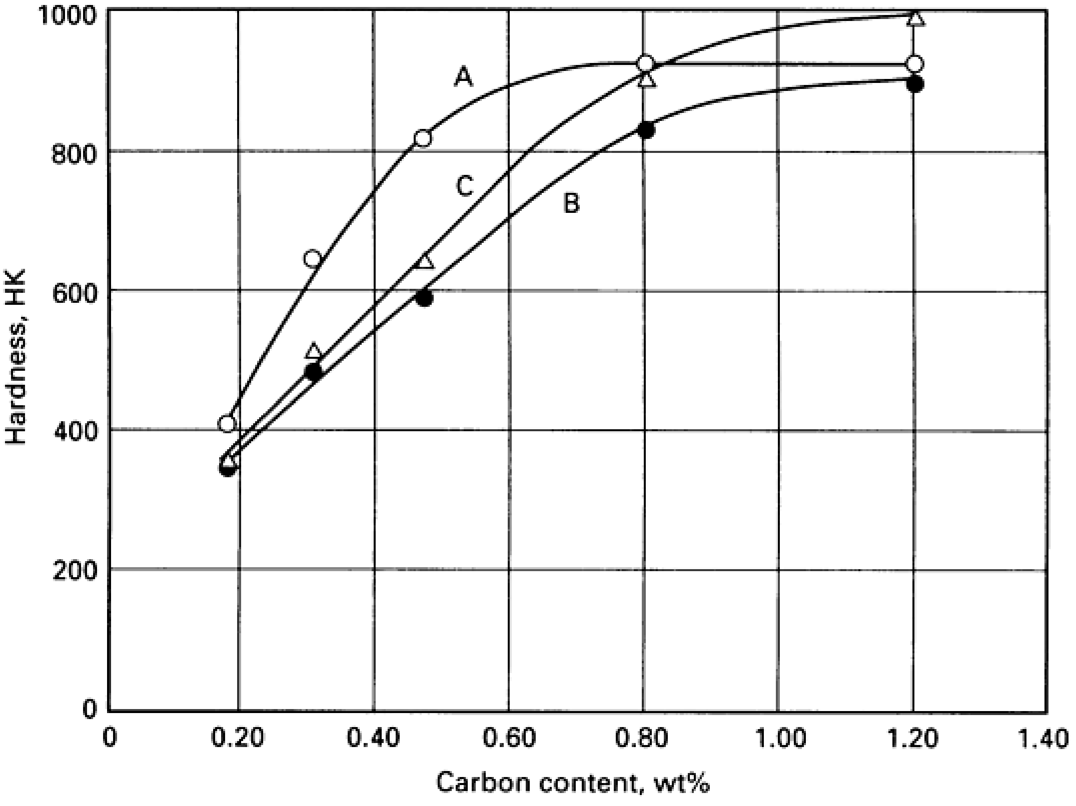


Fig. 35 Effect of carbon content on hardness in plain carbon steels. Curve A: induction hardened. Curve B: furnace hardened and water quenched. Curve C: furnace hardened, water quenched, and tempered. The quenched-and-tempered steels were treated in liquid nitrogen following water quenching prior to tempering at 100 °C (210 °F) for 2 h.

Induction Tempering. The major differences between induction and furnace tempering cycles lie in the times and temperatures involved. Tempering of hardened steel structures, such as martensite, involves diffusion of carbon atoms to form iron carbide (Fe_3C, or cementite). The extent of diffusion increases with both increasing temperatures and time. Thus, a short time/high-temperature treatment and a longer time/lower-temperature treatment will provide similar tempering responses. The former process would be typical of induction treatment and the latter of furnace treatment. The data in Fig. 36 illustrate this point. The results show the tempering response for a quench hardened 1050 steel that was tempered at a variety of temperatures between 150 and 650 °C (300 and 1200 °F). Consider, for example, the processing conditions to obtain a hardness of 40 HRC. Induction heat treatment at 540 °C (1000 °F) for 5 s gives this hardness, as does a much longer (1 h) furnace treatment at 425 °C (800 °F). Because other mechanical properties of quenched-and-tempered steels, such as yield and tensile strength, elongation, reduction in area, and fracture toughness, often correlate with hardness, these two different tempering treatments apparently yield a very similar product.

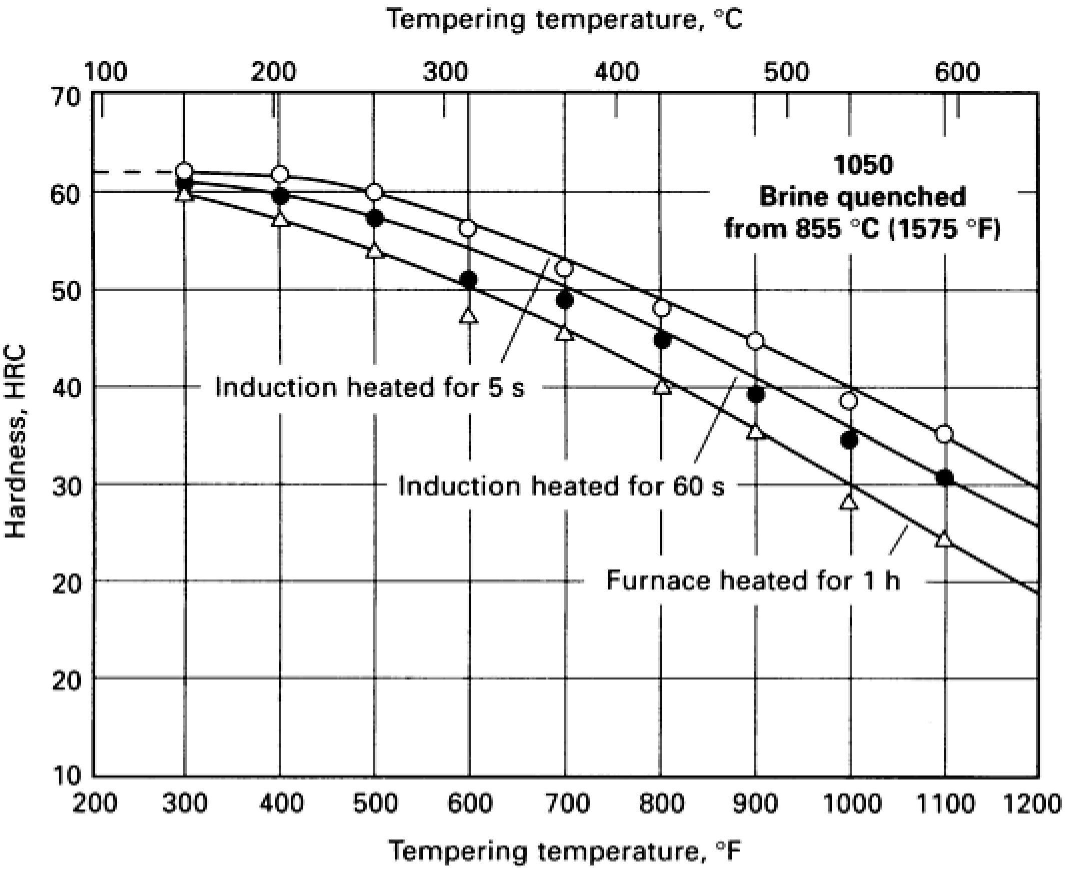


Fig. 36 Hardness as a function of tempering temperature and time for furnace and induction treated 1050 steel austenitized at 855 °C (1575 °F) and quenched in brine

Equivalent time/temperature cycles for tempering can be determined in several ways. For example, tempering experiments can be conducted at a variety of temperatures for a range of times; the hardness for each treatment is determined and then plotted, as in Fig. 36, to establish time-temperature relationships. This method, however, involves considerable time and effort.

A simpler technique uses a mathematical function known as the tempering parameter (T.P.). A number of researchers have found that the hardness of tempered martensite (as well as tempered bainite and pearlite) can be correlated to a certain function of the tempering time and tempering temperature. The formulation of the tempering parameter most widely used is that developed by Grange and Baughman:

$$\text{T.P.} = T(\text{C} + \log t)$$

where T is the absolute tempering temperature in degrees Rankine, C is a constant equal to 14.44, and t is tempering time in seconds.

To illustrate the application of the tempering parameter, consider the 40 HRC data discussed in Fig. 36. The tempering parameters for the two treatments are:

$$\text{T.P. furnace} = (800 + 460) \cdot (14.44 + \log 3600) = 22{,}675$$

$$\text{T.P. induction} = (1000 + 460) \cdot (14.44 + \log 5) = 22{,}105$$

Since the tempering parameters are almost identical, the hardness and other mechanical properties yielded by the two treatments should be nearly the same.

Electrical and Magnetic Properties of Steel

As described earlier in this article in the section "Principles of Induction Heating," the important material properties that determine the success of induction heating are the resistivity of the material, ρ, and relative magnetic permeability, μ. Both of these factors enter the equation for reference depth, *d* (see Eq 2). Since the values of ρ and μ are fixed once the material is selected, the only adjustable parameter is the frequency, *f*. Typically, higher frequencies are chosen for surface hardening and lower frequencies for through-hardening.

The resistivities of metals vary with temperature. Figure 37 shows this behavior for two ferrous alloys--electrolytic iron, an alloy with a negligible amount of carbon, and a 1% C steel. Both alloys have a similar dependence of resistivity on temperature. This can be attributed to the fact that both consist largely of ferrite at low temperatures and austenite at high temperatures. In fact, a change in slope of the curves occurs at temperatures between 700 and 800 °C (1290 and 1470 °F)--a region in which phase transformations occur.

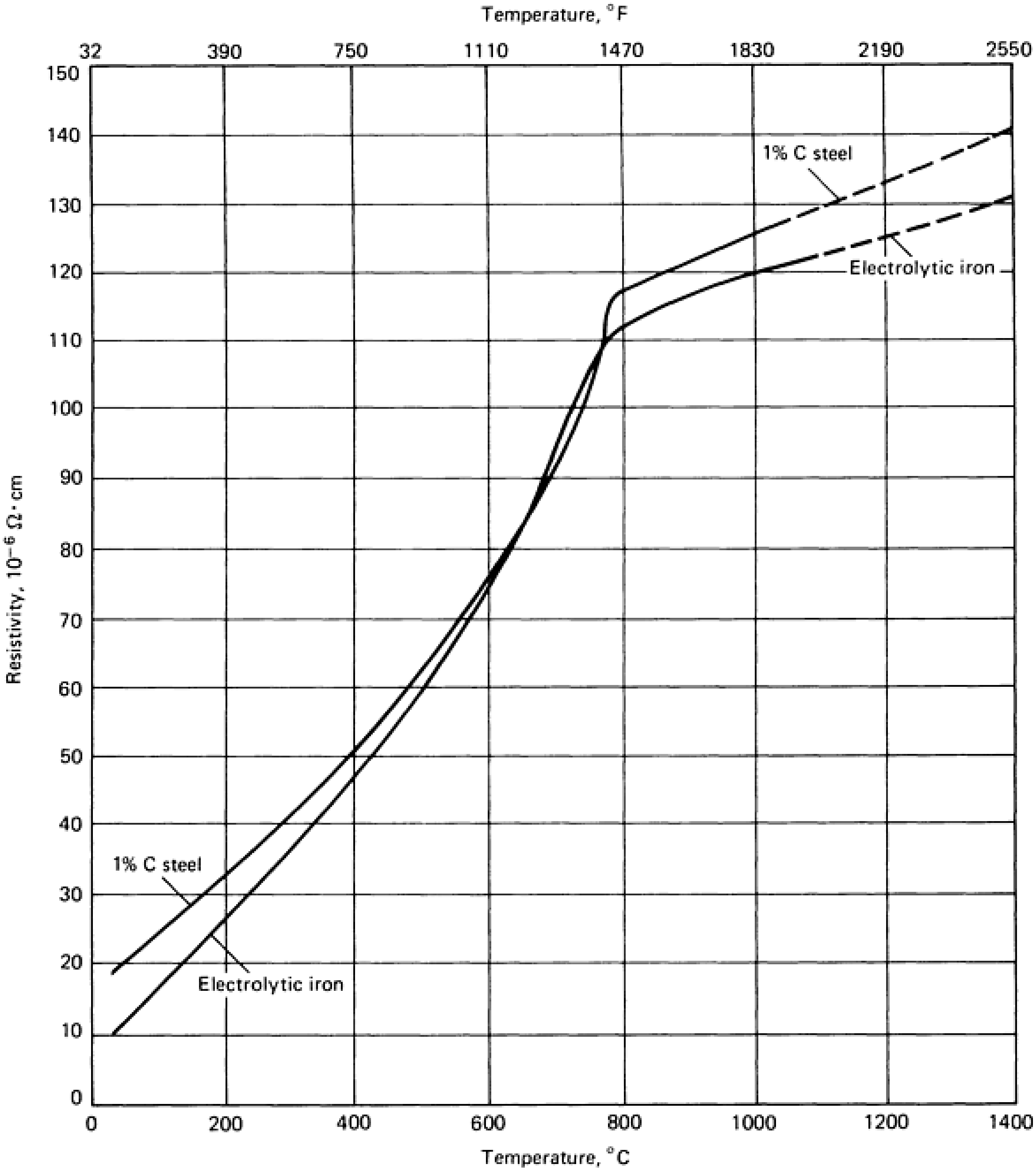


Fig. 37 Electrical resistivity versus temperature for electrolytic iron and a 1% C steel

The temperature at which the slope of the resistivity versus temperature plot for steel changes also coincides with that at which magnetic properties show a related effect. As the temperature is increased, the relative magnetic permeability of steels decreases until the Curie temperature is reached. Below this temperature, relative permeability varies with the intensity of the magnetic field and hence the current in carbon steels. For steels with less than 0.45% C, this temperature is 770 °C (1420 °F). In higher-carbon steels, the Curie temperature follows the A_3 line on the iron-carbon phase diagram to the eutectoid composition; thereafter, it coincides with the A_1 line. Alloying elements in steels change the Curie point by small amounts. Molybdenum and silicon increase it, and manganese and nickel decrease it.

In physical terms, the decrease in magnetic permeability with temperature in carbon steel signifies the loss of ferromagnetic properties and some of the ease with which these steels may be heated by induction. Below the Curie point, heating occurs as a result of both eddy-current losses and hysteresis losses. The latter are no longer present once the ferromagnetic property of steels is eliminated. Such a consideration is very important with regard to the austenitizing of steels in the hardening operation since this is done above the Curie temperature. Figure 38 illustrates this effect. Here it will be noticed that, below the Curie point, the amount of energy needed to heat a given mass of steel by induction is proportional to the temperature increase. Once the Curie temperature is reached, the required amount of energy per degree of temperature is substantially larger. Once the steel is above this point, however, the necessary electrical energy, although reduced, is still greater than that needed for low-temperature heating. When austenitizing temperatures only slightly above the Curie temperature are to be used, no adjustments in induction equipment are usually necessary. When the temperatures must be relatively high, on the other hand, devices such as load-matching circuits may be employed. These vary the impedance of the power source to compensate for the change in the magnetic properties of the steel.

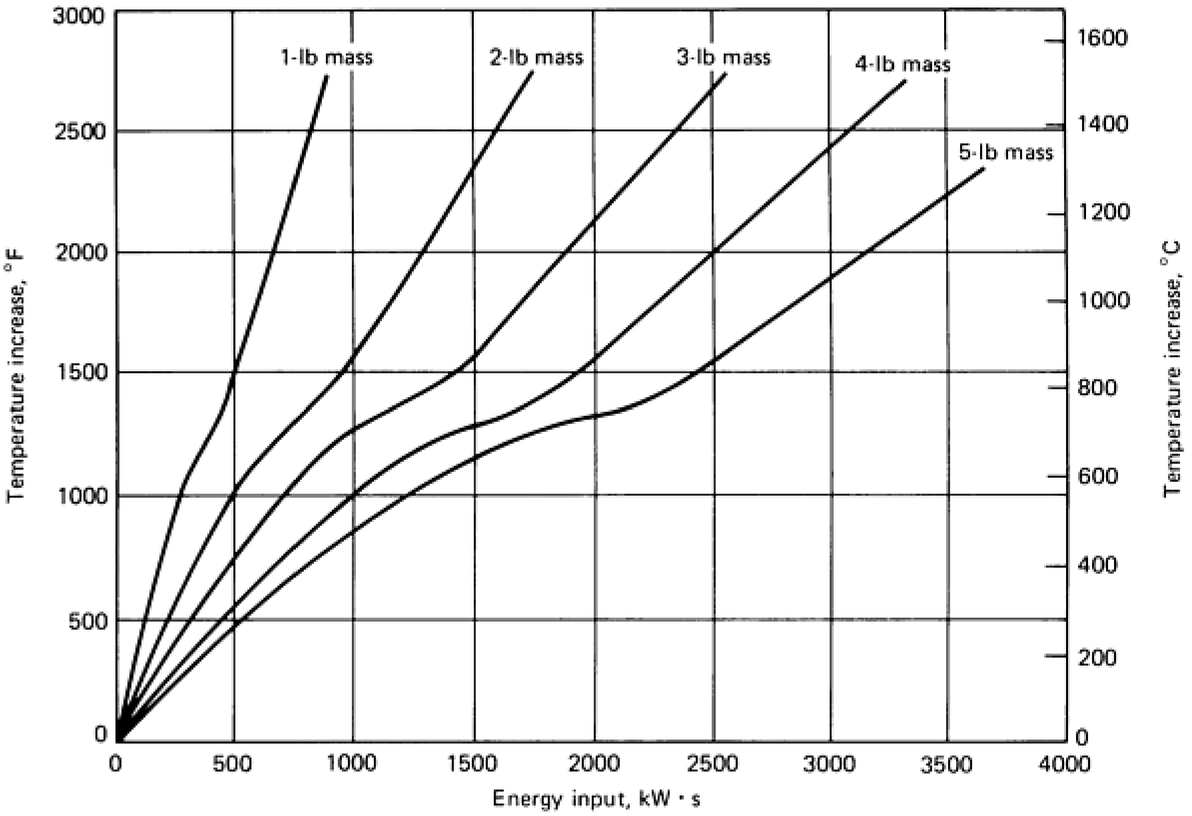


Fig. 38 Temperature increase as a function of energy input for induction heated carbon steel. Note the decrease in heating rate as the Curie temperature (770 °C, or 1420 °F) is approached and exceeded.

Heating Parameters

The temperature pattern generated by induction heating is influenced by such variables as:

- Workpiece characteristics (part geometry and electrical-magnetic properties)
- Coupling distance and coil design
- Frequency selection
- Power density (kilowatts per unit area exposed to the inductor)
- Heating time

The choice of suitable heating parameters is, to a large extent, determined by the temperature required and the depth of heating. Workpiece characteristics are also important. The distribution of induced current is influenced also by the magnetic and electrical characteristics of the part being heated, and because these properties change with temperature (see discussion above), the current distribution will change as the work is heated.

Optimum heating for a given workpiece and heat treatment requires detailed knowledge of the application and equipment. Initial guidance can come from charts or calculations for a specific set of conditions. Many induction heating equipment manufacturers have extensive computer programs based upon laboratory tests and production/operating data, which they use to recommend the proper apparatus and suggest application parameters. An estimate of what may be required for a new application can often be derived from results obtained on similar parts or by careful observation of the part itself as it is being heat treated. Final operating parameters are usually determined by experimentation.

Basic process control for most induction heating applications consists of applying power through a voltage-regulated power supply, for a measured period of time, and this has proved to be satisfactory for a wide variety of operations. Solid state inverters through their logic circuits can provide constant voltage, constant current, or constant power output and each in a particular way can help to ensure a repeatable heating effect with time under a wide variety of changing conditions. For a stationary hardening operation either an electronic or a synchronous timer can be used to control the heating time, any needed load-matching adjustments, and application of the quench. If energy input to the product is considered an appropriate measure of control, a kilowatt-second or kilowatt-hour energy monitor can be used to terminate a heating cycle. Typical heating and energy requirements for various induction processes are listed in Tables 5 and 6.

Table 5 Approximate induction heating temperatures required for typical metalworking processes

Process	**Required temperature, °C (°F), for processing of:**							
	Carbon steel	**Stainless steel**		**Nickel**	**Titanium**	**Copper**	**Brass**	**Aluminum**
		Magnetic	**Nonmagnetic**					
Hot forging	1230 (2250)	1095 (2000)	1150 (2100)	1095 (2000)	955 (1750)	900 (1650)	815 (1500)	540 (1000)
Hardening	925 (1700)	980 (1800)	. . .	760 (1400)	900 (1650)	815 (1500)	650 (1200)	480 (900)
Annealing/normalizing	870 (1600)	815 (1500)	1040 (1900)	925 (1700)	815 (1500)	540 (1000)	540 (1000)	370 (700)
Warm forging	760 (1400)	. . .	650 (1200)	650 (1200)	. . .	. . .	. . .	. . .
Stress relieving	595 (1100)	595 (1100)	595 (1100)	595 (1100)	595 (1100)	280 (500)	290 (550)	370 (700)

Tempering	315 (600)	315 (600)	315 (600)	315 (600)	315 (600)	. . .	. . .	. . .
Curing of coatings	230 (450)	230 (450)	230 (450)	230 (450)	230 (450)	230 (450)	230 (450)	230 (450)

Table 6 Average energy requirements for induction heating in typical metalworking processes

Process	**Required energy[(a)], kW · h/ton, for processing of:**							
	Carbon steel	**Stainless steel**		**Nickel**	**Titanium**	**Copper**	**Brass**	**Aluminum**
		Magnetic	**Nonmagnetic**					
Hot forging	400	375	430	450	375	700	400	300
Hardening/aging	250	260	. . .	300	325	600	325	275
Annealing/normalizing	225	210	375	400	300	425	375	210
Warm forming	175	. . .	250	240	. . .	. . .	. . .	. . .
Stress relieving	150	150	200	250	225	200	200	210
Tempering	70	70	100	120	110	. . .	. . .	. . .

(a) Based on in-line continuous process

Frequency Selection

Frequency is the first parameter considered for induction heating. Primary considerations in the selection of frequency are depth of heating, efficiency, type of heat treatment (such as surface hardening versus subcritical annealing), and the size and geometry of the part.

The frequencies and power supplies commonly used in the induction hardening of steel are compared in Table 7. As shown in this tabulation, the lower frequencies are more suitable as the size of the part and the case depth increase. However, because power density and heating time also have an important influence on the depth to which the part is heated, wide deviations from Table 7 may be made with successful results. This interrelationship is shown in Fig. 39 in terms of case depth for surface hardened steel. In some instances, the determining factor in selecting the frequency is the power required to provide power density sufficient for successful hardening, as lower-frequency induction equipment is available with higher power ratings.

Table 7 Selection of power source and frequency for various applications of induction hardening and tempering of steel

Heat-treatment criterion	**Section size**	**Power lines,**	**Frequency converter,**	**Solid state or motor**	**Vacuum tube,**

			50 or 60 Hz	180 Hz	generator			over 200 kHz
	mm.	in.			1000 Hz	3000 Hz	10,000 Hz	
Surface hardening depth			**Surface hardening ratings[a]**					
0.38-1.27 mm 0.015-0.050 in.	6.35-25.4	$\frac{1}{4}$-1	. . .	. . .	. . .	. . .	. . .	Good
1.29-2.54 mm 0.051-0.100 in.	11.11-15.88	$\frac{7}{16}$-$\frac{5}{8}$	. . .	. . .	. . .	. . .	Fair	Good
	15.88-25.4	$\frac{5}{8}$-1	. . .	. . .	. . .	. . .	Good	Good
	25.4-50.8	1-2	. . .	. . .	. . .	Fair	Good	Fair
	>50.8	>2	. . .	. . .	Fair	Good	Good	Poor
2.56-5.08 mm 0.101-0.200 in.	19.05-50.8	$\frac{3}{4}$-2	. . .	. . .	. . .	Good	Good	Poor
	50.8-101.6	2-4	. . .	. . .	Good	Good	Fair	. . .
	>101.6	>4	. . .	. . .	Good	Fair	Poor	. . .
Through hardening			**Through hardening ratings[b]**					
Through hardening based on heating rate of carbon steel in Fig. 40[b]	1.59-6.35	$\frac{1}{16}$-$\frac{1}{4}$	. . .	. . .	. . .	. . .	. . .	Good
	6.35-12.7	$\frac{1}{4}$-$\frac{1}{2}$	. . .	. . .	. . .	. . .	Fair	Good
	12.7-25.4	$\frac{1}{2}$-1	. . .	. . .	. . .	Fair	Good	Fair

	25.4-50.8	1-2	. . .	. . .	Fair	Good	Fair	. . .
	50.8-76.2	2-3	. . .	. . .	Good	Good	Poor	. . .
	76.2-152.4	3-6	Fair	Good	Good	Poor	Poor	. . .
	>152.4	>6	Good	Fair	Poor	Poor	Poor	. . .
Maximum tempering temperature			**Tempering ratings**[(c)]					
705 °C 1300 °F	0.32-0.64	$\frac{1}{8}$-$\frac{1}{4}$	. . .	. . .	. . .	. . .	. . .	Good
705 °C 1300 °F	0.64-1.27	$\frac{1}{4}$-$\frac{1}{2}$	. . .	. . .	. . .	. . .	Good	Good
425 °C 800 °F	1.27-2.54	$\frac{1}{2}$-1	. . .	Fair	Good	Good	Good	Fair
705 °C 1300 °F			. . .	Poor	Fair	Good	Good	Fair
425 °C 800 °F	2.54-5.08	1-2	Fair	Fair	Good	Good	Fair	Poor
705 °C 1300 °F			. . .	Fair	Good	Good	Fair	Poor
425 °C 800 °C	5.08-15.24	2-6	Good	Good	Good	Fair	. . .	. . .
705 °C 1300 °F			Good	Good	Good	Fair	. . .	. . .
705 °C 1300 °F	>15.24	>6	Good	Good	Good	Fair	. . .	. . .

(a) **Surface hardening ratings:** *Good* indicates frequency that will most efficiently heat the material to austenitizing temperature for the specified depth. *Fair* indicates a frequency that is lower than optimum but high enough to heat the material to austenitizing temperature for the specified depth. With this frequency, the current penetration relative to the section size causes current cancellation and lowered efficiency. *Poor* indicates a frequency that will overheat the surface unless low-energy input is used. Efficiency and production are low, and capital cost of converters per kilowatt-hour is high.

(b) **Through hardening ratings:** *Good* based on heating rates in Fig. 40(b). *Fair* is based on a smaller heating rate, but fair may also indicate a frequency higher than optimum that can overheat the surface at high-energy inputs. Converters cost more per kilowatt-hour than the converters

of optimum frequency. With some equipment, the efficiency may be lower. *Poor* indicates a frequency that will overheat the surface unless low-energy input is used. Efficiency and production are low and capital cost of converters per kilowatt-hour is high.

(c) **Tempering ratings** are based on efficiency, capital cost, and uniformity of heating. *Good* indicates optimum frequency. *Fair* indicates a frequency higher than optimum that increases capital cost and reduces uniformity of heating, thus requiring lower heat inputs. *Poor* indicates a frequency substantially higher than optimum that substantially increases capital cost and reduces uniformity of heating, thus requiring substantially lower heat inputs.

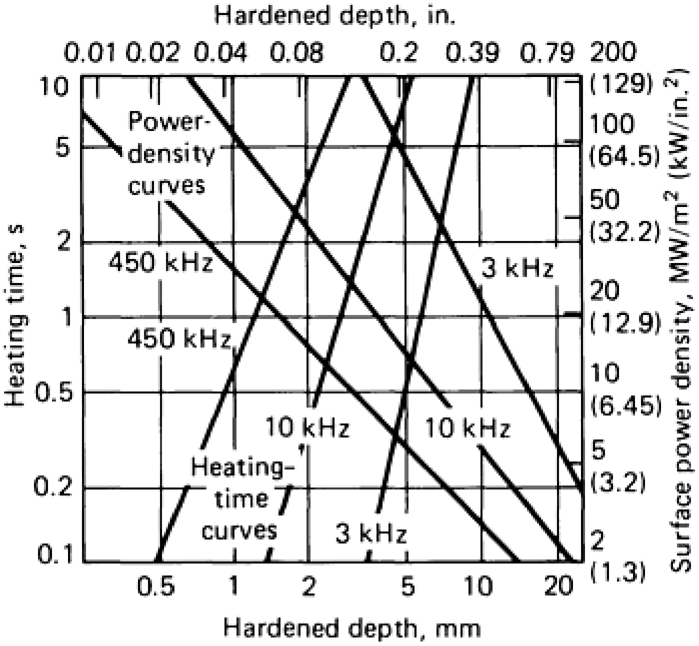


Fig. 39 Interrelationship among heating time, surface power density, and hardened depth for various induction generator frequencies

The equation given earlier in this article for reference depth, *d*, can be used to estimate the optimal generator frequency for induction hardening of steel . For surface hardening, the desired case depth is typically taken to be equal to about one-half the reference depth when selecting frequency. By contrast, when through-hardening is desired, the frequency is usually chosen such that the reference depth is a fraction of the bar radius (or an equivalent dimension for parts which are not round). This is necessary in order to maintain adequate "skin effect" and to enable induction to take place at all. If the reference depth is chosen to be comparable to or larger than the bar radius, there will be two sets of eddy currents near the center of the bar induced from diametrically opposed surfaces of the bar. These will tend to go in two different directions and thus cancel each other. To avoid this, frequencies for through-hardening are often chosen so that the reference depth does not exceed approximately one-fourth of the diameter for round parts or one-half the thickness for plates and slabs when using solenoid coils. When the bar diameter is less than four reference depths, or slab thickness less than two reference depths, the electrical efficiency drops sharply. By contrast, little increase in efficiency is obtained when the bar diameter or slab thickness is many times more than the reference depth.

Typical frequency selections for induction hardening of steel parts are listed in Table 7 and Fig. 40. Those for surface hardening will be examined first. For very thin cases such as 0.40 to 1.25 mm (0.015 to 0.050 in.) on small-diameter bars, which are easily quenched to martensite, relatively high frequencies are optimal. If the reference depth is equated to the case depth, the best frequency for a 0.75 mm (0.030 in.) deep case on a 13 mm (0.5 in.) diameter bar is found to be around 550 kHz. When the surface of a larger-diameter bar is hardened, particularly when the case is to be deep, the frequency is often chosen so that the reference depth is several times the desired case depth. This is because the large amount of metal below the surface layer to be hardened represents a large thermal mass which draws heat from the surface. Unless very high power densities are employed, it is difficult to heat only the required depth totally to the austenitizing temperature. As an example, consider the recommended frequency for imparting a 3.8 mm (0.15 in.) hardened case to a bar 75 mm (3 in.) in diameter. If the reference depth were equated to the case depth, a frequency of about 20 kHz would be selected, which would provide only "fair" results. If a frequency of 3 kHz were chosen, however, the reference depth would be

about 10 mm (0.41 in.), or about $2\frac{1}{2}$ times the required case depth. However, it is unlikely that the entire reference depth would ever reach austenitizing temperatures for the reason mentioned above.

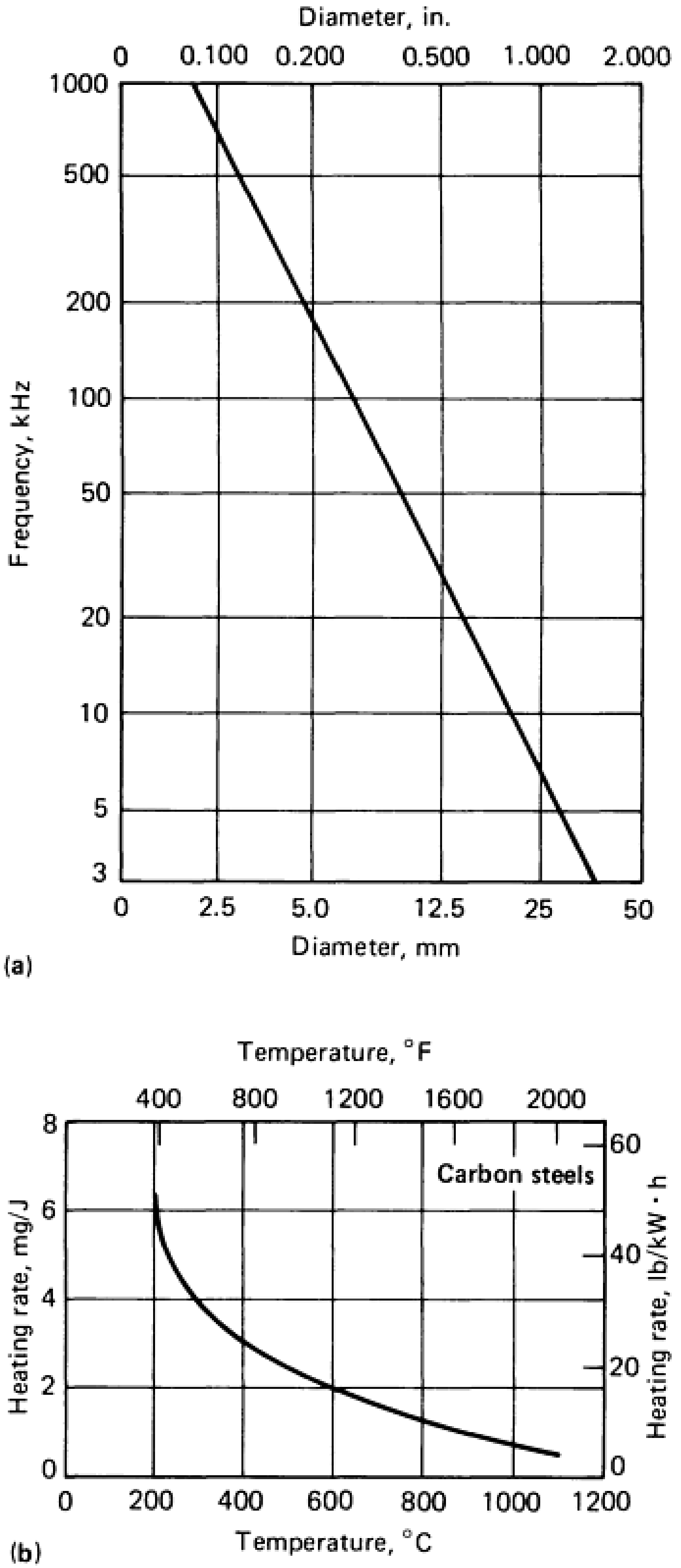


Fig. 40 Typical frequency selections and heating rates for induction hardening of steel parts. (a) Relationship between diameter of round steel bars and minimum generator frequency for efficient austenitizing using induction heating. (b) Heating rate for through heating of carbon steels by induction. For converted frequencies, the total power transmitted by the inductor to the work is less than the power input to the machine because of

converter losses. See also Table 7.

For through-hardening of a steel bar or section, the optimal frequency is often based on producing a reference depth about one-fourth of the bar diameter or section size. For instance, through-heating and through-hardening of a 64 mm (2.5 in.) diameter bar would entail using a generator with a frequency of about 1 kHz. If much lower frequencies were employed, inadequate skin effect (current cancellation) and lower efficiency would result. On the other hand, higher frequencies might be used. In these cases, however, the generator power output would have to be low enough to allow conduction of heat from outer regions of the steel part to the inner ones. Otherwise, the surface may be overheated, leading to possible austenite grain growth or even melting.

Power Density and Heating Time

Once the frequency has been selected, a wide range of temperature profiles can be produced by varying the power density and heating time. Selection of these two heating parameters depends on the inherent heat losses of the workpiece (from either radiation or convection losses) and the desired heat conduction patterns of a particular application.

In through-heating applications, the power needed is generally based on the amount of material that is processed per unit time, the peak temperature, and the material`s heat capacity at this temperature. Power specification for other operations, such as surface hardening of steel, is not as simple because of the effects of starting material condition and the desired case depth.

Surface heating is used primarily in the surface hardening of steel parts such as shafts and gears. In this type of application, high power densities and short heating times are used when thin case depths are desired.

Typical power ratings for surface hardening of steel are given in Table 8. These are based on the need to heat to austenitizing temperature (Table 4) very rapidly and have proven to be appropriate through the years of experience. When using these or other fixed ratings, however, the effect of heating time on case depth (Fig. 39) must be considered.

Table 8 Power densities required for surface hardening of steel

Frequency, kHz	Depth of hardening[a]		Input[b][c]					
			Low[d]		Optimum[e]		High[f]	
	mm	in.	kW/cm^2	$kW/in.^2$	kW/cm^2	$kW/in.^2$	kW/cm^2	$kW/in.^2$
500	0.381-1.143	0.015-0.045	1.08	7	1.55	10	1.86	12
	1.143-2.286	0.045-0.090	0.46	3	0.78	5	1.24	8
10	1.524-2.286	0.060-0.090	1.24	8	1.55	10	2.48	16
	2.286-3.048	0.090-0.120	0.78	5	1.55	10	2.33	15
	3.048-4.064	0.120-0.160	0.78	5	1.55	10	2.17	14
3	2.286-3.048	0.090-0.120	1.55	10	2.33	15	2.64	17
	3.048-4.064	0.120-0.160	0.78	5	2.17	14	2.48	16

	4.064-5.080	0.160-0.200	0.78	5	1.55	10	2.17	14
1	5.080-7.112	0.200-0.280	0.78	5	1.55	10	1.86	12
	7.112-8.890	0.280-0.350	0.78	5	1.55	10	1.86	12

(a) For greater depths of hardening, lower kilowatt inputs are used.

(b) These values arc based on use of proper frequency and normal overall operating efficiency of equipment. These values may be used for both static and progressive methods of heating; however, for some applications, higher inputs can be used for progressive hardening.

(c) Kilowattage is read as maximum during heat cycle.

(d) Low kilowatt input may be used when generator capacity is limited. These kilowatt values may be used to calculate largest part hardened (single-shot method) with a given generator.

(e) For best metallurgical results.

(f) For higher production when generator capacity is available

Through Heating. Power ratings for through hardening of steel are much lower than those for surface hardening to allow time for the heat to be conducted to the center of the workpiece. After awhile, the rates of increase of the surface and center temperatures become comparable due to conduction, and a fixed temperature differential persists during further heating. Using methods described by Tudbury (see the Selected References at the end of this article), the allowable temperature differential permits the generator power ratings to be selected. The basic steps in selecting the power rating are as follows:

- Select the frequency and calculate the ratio of bar diameter (or section size) to reference depth, a/d. For most through-heating applications, this ratio will vary from around four to six
- Using the values of the thermal conductivity (in W/in. · °F) and a/d, estimate the induction thermal factor, K_T (Fig. 41)
- The power per unit length is calculated as the product of K_T and the allowable temperature differential (in °F) between the surface and center, T_s - T_c. Multiplying this by the length of the bar yields the net power required in kilowatts

In addition to these estimates, radiation heat loss must also be considered when determining power ratings. The upper limit of radiation losses, which is defined by the emission characteristics of a blackbody, is shown in Fig. 42 as a function of temperature. Actual workpiece materials will exhibit less radiation loss than in Fig. 36 because they do not have the broad spectral range of blackbodies.

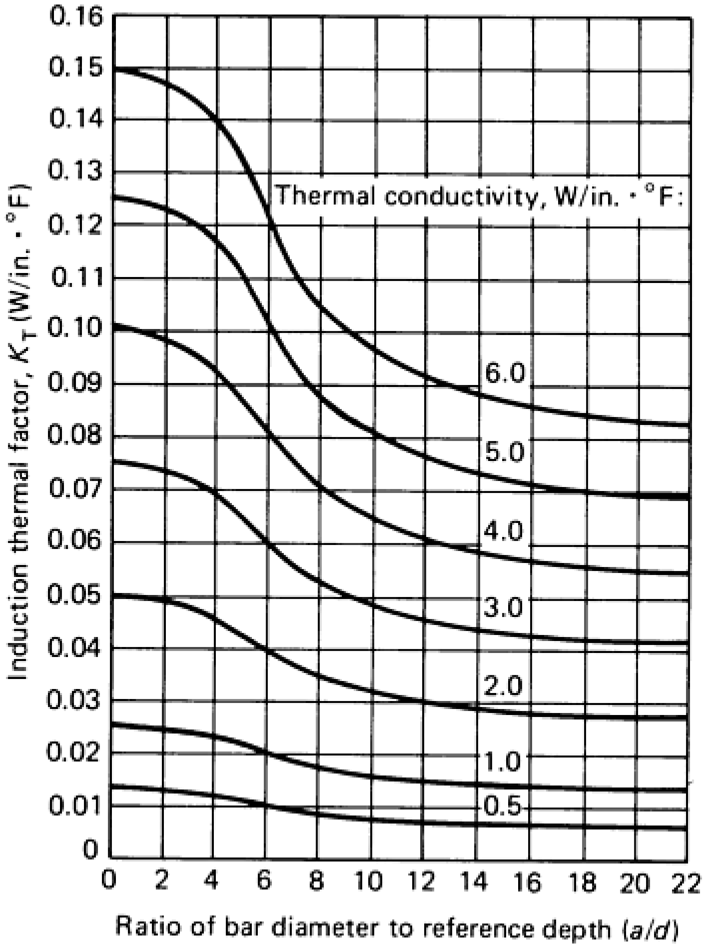


Fig. 41 Induction thermal factor for round bars as a function of the ratio of bar diameter to reference depth (*a*/*d*) and the thermal conductivity

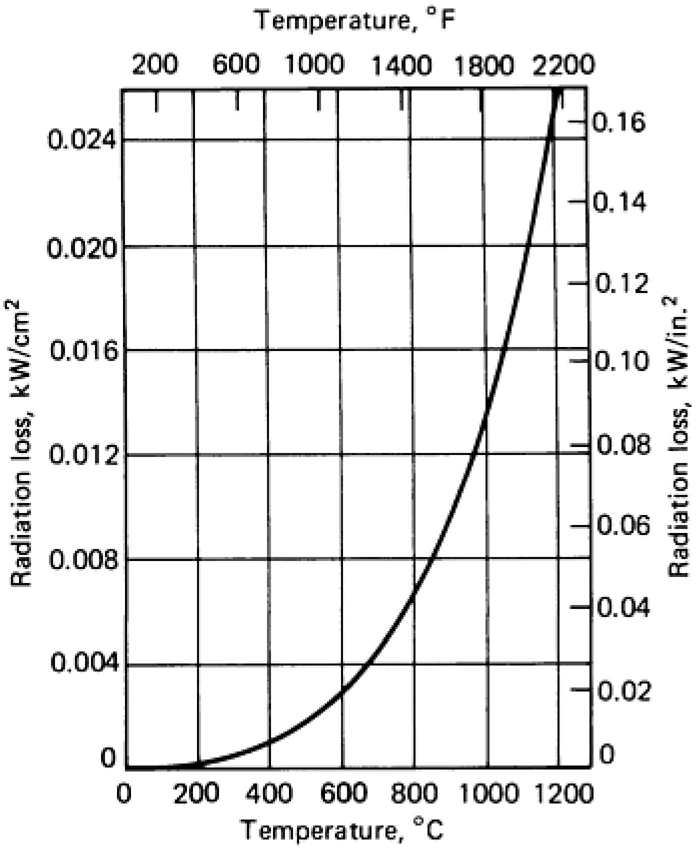


Fig. 42 Radiation heat loss as a function of surface temperature. Losses are based on blackbody radiation into surroundings at 20 °C (70 °F).

In order to avoid calculations of power requirements, tables of power densities ordinarily used for through heating of steel (for hardening as well as other uses, such as forging) are available. One such listing is shown in Table 9. These values of power densities are based on typical electrical efficiencies and proper selection of frequency (which lead to *a*/*d* ratios in the range of four to six). It may be noted that the larger-diameter bars, which can be heated efficiently with lower-cost, lower-frequency power supplies, typically employ smaller power densities than small-diameter bars (see Table 10). This is because of the greater times required for heat to be conducted to the center of the larger pieces. Also, it can be seen that lower frequencies such as 60 and 180 Hz are not ordinarily recommended for through heating of steel when temperatures above approximately 760 °C (1400 °F) are desired. This is due to the increased reference depth (and decreased skin effect) above the Curie temperature where the relative magnetic permeability drops to unity. An exception to this practice is the use of 60 Hz sources for induction heating of very large parts such as steel slabs in steel mills. Tempering treatments may also use 60 Hz sources (Table 11).

Table 9 Approximate power densities required for through-heating of steel for hardening, tempering, or forming operations

Frequency[(a)], Hz	Input[(b)]									
	150-425 °C (300-800 °F)		425-760 °C (800-1400 °F)		760-980 °C (1400-1800 °F)		980-1095 °C (1800-2000 °F)		1095-1205 °C (2000-2200 °F)	
	kW/cm²	kW/in.²	kW/cm²	kW/in.²	kW/cm²	kW/in.²	kW/cm²	kW/in.²	kW/cm²	kW/in.²
60	0.009	0.06	0.023	0.15	[(c)]	[(c)]	[(c)]	[(c)]	[(c)]	[(c)]

180	0.008	0.05	0.022	0.14	(c)	(c)	(c)	(c)	(c)	(c)
1000	0.006	0.04	0.019	0.12	0.08	0.5	0.155	1.0	0.22	1.4
3000	0.005	0.03	0.016	0.10	0.06	0.4	0.085	0.55	0.11	0.7
10,000	0.003	0.02	0.012	0.08	0.05	0.3	0.070	0.45	0.085	0.55

(a) The values in this table are based on use of proper frequency and normal overall operating efficiency of equipment.

(b) In general. these power densities are for section sizes of 13 to 50 mm ($\frac{1}{2}$ to 2 in.). Higher inputs can be used for smaller section sizes. and lower inputs may be required for larger section sizes.

(c) Not recommended for these temperatures

Table 10 Typical operating conditions for progressive through-hardening of steel parts by induction

Section size		Material	Frequency[a], Hz	Power[b], kW	Total heating time, s	Scan time		Work temperature				Production rate		Inductor input[c]	
								Entering coil		Leaving coil					
mm	in.					s/cm	s/in.	°C	°F	°C	°F	kg/h	lb/h	kW/cm^2	$kW/in.^2$
Rounds															
13	$\frac{1}{2}$	4130	180	20	38	0.39	1	75	165	510	950	92	202	0.067	0.43
			9600	21	17	0.39	1	510	950	925	1700	92	202	0.122	0.79
19	$\frac{3}{4}$	1035 mod	180	28.5	68.4	0.71	1.8	75	165	620	1150	113	250	0.062	0.40
			9600	20.6	28.8	0.71	1.8	620	1150	955	1750	113	250	0.085	0.55
25	1	1041	180	33	98.8	1.02	2.6	70	160	620	1150	141	311	0.054	0.35
			9600	19.5	44.2	1.02	2.6	620	1150	955	1750	141	311	0.057	0.37
29	$1\frac{1}{8}$	1041	180	36	114	1.18	3.0	75	165	620	1150	153	338	0.053	0.34
			9600	19.1	51	1.18	3.0	620	1150	955	1750	153	338	0.050	0.32
49	$1\frac{15}{16}$	14B35H	180	35	260	2.76	7.0	75	165	635	1175	195	429	0.029	0.19
			9600	32	119	2.76	7.0	635	1175	955	1750	195	429	0.048	0.31

Flats															
16	$\frac{5}{8}$	1038	3000	300	11.3	0.59	1.5	20	70	870	1600	1449	3194	0.361	2.33
19	$\frac{3}{4}$	1038	3000	332	15	0.79	2.0	20	70	870	1600	1576	3474	0.319	2.06
22	$\frac{7}{8}$	1043	3000	336	28.5	1.50	3.8	20	70	870	1600	1609	3548	0.206	1.33
25	1	1036	3000	304	26.3	1.38	3.5	20	70	870	1600	1595	3517	0.225	1.45
29	$1\frac{1}{8}$	1036	3000	344	36.0	1.89	4.8	20	70	870	1600	1678	3701	0.208	1.34
Irregular shapes															
17.5-33	$\frac{11}{16}$-1$\frac{5}{16}$	1037 mod	3000	580	254	0.94	2.4	20	70	885	1625	2211	4875	0.040	0.26

(a) Note use of dual frequencies for round sections.

(b) Power transmitted by the inductor at the operating frequency indicated. This power is approximately 25% less than the power input to the machine, because of losses within the machine.

(c) At the operating frequency of the inductor

Table 11 Operating and production data for progressive induction tempering

Section size		Material	Frequency, Hz	Power[a], kW	Total heating time, s	Scan time		Work temperature				Production rate		Inductor input[b]	
								Entering coil		Leaving coil					
mm	in.					s/cm	s/in.	°C	°F	°C	°F	kg/h	lb/h	kW/cm^2	$kW/in.^2$
Rounds															
13	$\frac{1}{2}$	4130	9600	11	17	0.39	1	50	120	565	1050	92	202	0.064	0.41
19	$\frac{3}{4}$	1035 mod	9600	12.7	30.6	0.71	1.8	50	120	510	950	113	250	0.050	0.32
25	1	1041	9600	18.7	44.2	1.02	2.6	50	120	565	1050	141	311	0.054	0.35
29	$1\frac{1}{8}$	1041	9600	20.6	51	1.18	3.0	50	120	565	1050	153	338	0.053	0.34
49	$1\frac{15}{16}$	14B35H	180	24	196	2.76	7.0	50	120	565	1050	195	429	0.031	0.20
Flats															
16	$\frac{5}{8}$	1038	60	88	123	0.59	1.5	40	100	290	550	1449	3194	0.014	0.089
19	$\frac{3}{4}$	1038	60	100	164	0.79	2.0	40	100	315	600	1576	3474	0.013	0.081
22	$\frac{7}{8}$	1043	60	98	312	1.50	3.8	40	100	290	550	1609	3548	0.008	0.050
25	1	1043	60	85	254	1.22	3.1	40	100	290	550	1365	3009	0.011	0.068
29	$1\frac{1}{8}$	1043	60	90	328	1.57	4.0	40	100	290	550	1483	3269	0.009	0.060
Irregular shapes															

17.5-33	$\frac{11}{16}$ - $1\frac{5}{16}$	1037 mod	9600	192	64.8	0.94	2.4	65	150	550	1020	2211	4875	0.043	0.28
17.5-29	$\frac{11}{16}$ - $1\frac{1}{8}$	1037 mod	9600	154	46	0.67	1.7	65	150	425	800	2276	5019	0.040	0.26

(a) Power transmitted by the inductor at the operating frequency indicated. For converted frequencies, this power is approximately 25% less than the power input to the machine, because of losses within the machine.

(b) At the operating frequency of the inductor

One mitigating effect which must be considered when establishing power requirements for austenitizing is the delay between the time at which the power is turned off and the time at which the quench is applied. Following heating, the temperature at the surface drops more rapidly than that at the center of the workpiece. Eventually, the center temperature becomes greater. Because of this, the heating and cooling cycles can often be adjusted to compensate for the nonuniform heating which characterizes induction processes. Thus, greater input power and higher heating rates can sometimes be realized than when quenching follows immediately after heating.

Induction Heat Treatments

Electromagnetic induction affords one way to develop the necessary heat for a number of different heat-treatment operations such as:

- Surface and through hardening
- Tempering and stress-relieving
- Normalizing and annealing
- Precipitation hardening or aging
- Grain refinement

Surface Hardening by Induction. Surface hardening of a steel part consists of raising a surface layer above the transformation temperature (denoted by Ac_3 on the Fe-C phase diagram) at which it will be transformed to austenite and rapidly cooling the part to produce a hard martensitic structure in this region. Design of surface-hardening treatments demands consideration of the work-piece material and its starting condition, the effect of rapid heating on Ac_3 or Ac_{cm} temperature, property requirements, and equipment selection.

Induction surface hardening is applied mostly to hardenable grades of steel, although some carburized and slow-cooled parts are often reheated in selected areas by induction heating. Some typical induction surface hardened steels are:

- Medium-carbon steels, such as 1030 and 1045, used for automotive drive shafts, gears, and so forth
- High-carbon steels, such as 1070, used for drill and rock bits, hand tools, and so forth
- Alloy steels used for bearings, automotive valves, and machine-tool components

As described earlier in this article, frequency and power selection influence the case depth. A shallow fully-hardened case ranging in depth from 0.25 mm to 1.5 mm (0.010 to 0.060 in.) provides a part with good wear resistance for applications involving light to moderate loading. For this kind of shallow hardening, the depth of austenitizing may be controlled by using frequencies on the order of 10 kHz to 2 MHz, power densities to the coil of 800 to 8000 W/cm^2 (5 to 50 kW/in.^{2}), and heating time of not more than a very few seconds. Pump shafts, rocker arm shafts, and sucker rods are typical parts which benefit from a shallow hardened case for wear resistance.

Where high loading stresses penetrate well below the surface, whether it be bending, torsion, or brinneling, the metal needs to be strengthened so at any depth its yield strength exceeds the maximum applied stress at that depth. Because loading stresses drop off exponentially from the surface to the center of a shaft, it is obvious a deep case with high hardness can be effective in strengthening below the surface. Consequently, parts subjected to heavy loads, particularly cyclic bending, torsion, or brinneling, may require a thicker case depth (that is, deeper hardness). The hardened depth might then be increased to 1.5 to 6.4 mm (0.60 to 0.250 in.), which would require:

- Frequencies ranging from 10 kHz down to 1 kHz
- Power densities on the order of 80 to 1550 W/cm^2 ($\frac{1}{2}$ to 10 kW/in.^{2})
- Heating times of several seconds

Heavy duty gears, drive axles, wheel spindles, and heavily loaded bearings are typical parts to which this kind of strengthening surface heat treatment is most applicable.

Required hardness patterns can be determined from stress calculations, because hardness values can be translated to yield strength. The required case depth also depends on the distribution of the residual compressive stresses (induced by the transformation hardening of the surface region) and the loading stresses within the body of the part. Where a transformation hardened case ends, either in depth or at the termination of a hardened surface pattern, a stress reversal will most likely occur. This condition should be avoided in any region of the part that carries any significant portion of the load.

For example, the hardness pattern on a load-carrying gear should not terminate in the root when bending stresses tend to concentrate. On the other hand, fly wheel ring gears and some sprockets are just hardened on the tooth flanks only to resist wear. The discontinuous pattern reduces distortion because there is no hoop stress from hardening a continuous ring. If a spline or a keyway is in the torsional load transmitting part of a shaft, it should be hardened below the root or notch.

Selective Hardening. The ability to limit the heated surface area as well as the depth makes induction heating particularly attractive for parts in which the loading stresses or the need for wear resistance is concentrated in some portion of the part. Localized hardening not only increases the metal's outer layer strength (where most of the operating load is carried), but it may also bestow favorable residual compressive stresses in those same surface layers. Selective treatment also saves time and energy, and will minimize thermally-induced distortion. One precaution to be observed concerning the hardening of selective regions is that the area of transition from compressive residual stresses to tensile residual stresses is located away from stress concentrations.

Volume Surface Hardening. Another category of surface induction hardening is achieved by austenitizing and quenching ferrous metals to an even greater depth; often below the hardenability of the metal, but nevertheless to a depth controlled by the induction process. This technique is sometimes referred to as volume surface hardening. Depths of hardness up to 25 mm (1 in.) over 600 HB have been achieved with a 1% C, 1.3 to 1.6% Cr steel that has been water quenched. Frequencies from 60 Hz to 1 kHz are used, with power densities expressed as a fraction of a kW/in.^{2} and heating times from about 20 to 140 s. Typical of parts hardened in this manner are mill rolls 180 to 915 mm (7 to 36 in.) in diameter, track rollers, and railway axle boxes.

Through hardening with induction heating is often accomplished with medium frequencies (180 Hz to 10 kHz), and at times with line-frequency equipment. In some applications it may be advantageous to use two frequencies: a lower frequency to preheat the steel to some subcritical temperature, followed by a higher frequency to achieve full austenitizing temperature. The choice of using a lower frequency to preheat might be dictated by economics (that is, less expensive equipment with a bit higher conversion efficiency); however, it may also provide application benefits such as reduced thermal shock and/or shorter heating time.

To date, the high-tonnage operations using through hardening with induction heating involve the processing of pipe and tube. These operations can also include tempering, normalizing, or stress relieving. High-strength, round and rectangular bar stock, truck frame channels, and other long members are also heated and quenched horizontally one after the other. The tempering portion of a quench-and-temper treatment may follow in line directly after quenching, often using the same frequency as preheating because both preheating and tempering only heat to a subcritical temperature. Few piece parts are through hardened with induction methods, unless a localized heat treatment or a special pattern of hardness is specified.

Tempering for the purpose of decreasing hardness and increasing toughness is a subcritical heat treatment which can be accomplished at high efficiency with induction heating. As suggested above, tempering is often applied in line in a continuous heat-treating system, directly after through hardening. Other applications of induction tempering include:

- Localized tempering of carburized or furnace hardened parts in areas which require further machining such as threading or broaching. A typical example is the splined bore of carburized gear tempered to facilitate final sizing with a broach
- Induction tempering to increase the ductility of work hardened parts. Typical examples include the tempering of deep drawn steel cylinders between drawing operations and the tempering of cold headed bolts and cold rolled splines or threads

Tempering may be preferable to normalizing or full annealing for some ductility and machinability needs because as a subcritical treatment there is no danger of forming any hard products of transformation.

However, induction tempering of hardened steel can be limited by the type of temperature gradients developed during induction heating. Tempering is a very temperature-sensitive application because the mechanical properties of a hardened and tempered iron or steel are primarily a function of the ultimate tempering temperature achieved. Therefore some degree of temperature uniformity is undertaken in this operation. This consideration limits induction tempering of property-sensitive parts and materials to fairly uniform sections, primarily those approaching a round shape. If the treated

part is anything but a smooth round, surface temperature differentials can occur at corners or in light sections during high-temperature tempering. Some metal may also reach austenitizing temperature. If so, a real danger of rehardening from mass quenching exists, particularly if the steel is an alloy grade. Slow deep heating, or a heat-soak, and reheat (two or three times) cycle has been found helpful in achieving a hardness which is machinable. A frequency as low as practical for the product size and configuration should be used to minimize overheating of thin sections and corners.

Stress relieving is not intended to significantly modify mechanical properties. Instead, the purpose is to relieve residual stresses from hardening or cold working. If the as-quenched hardness is high and/or the part geometry is such that high localized residual stresses can occur, stress relieving should take place immediately after hardening. However, if the residual stresses can improve the load-carrying ability and the fatigue life of the part, then stress-relieving temperatures should be below 260 °C (500 °F) to retain the highest practical value of the compressive residual stress.

Parts heated and quenched in one position may be stress relieved after quenching by applying low power to the hardening inductor. The resultant temperature pattern will not be uniform over the entire pattern of hardened metal so this should only be considered where the stress-relieving operation is not critical and temperature variation can be tolerated. Therefore, some prefer to perform stress relieving in an oven or furnace for reasons of time and uniformity.

Nonetheless, parts such as drive axles, power take-off shafts, and wheel spindles have been stress relieved by induction after quenching. Surface hardened parts either scanned or locally treated on indexing fixtures may be stress relieved at a second heating station using some lower level of power. The energy can be supplied at reduced level either from the hardening power supply, or from a second smaller unit, perhaps even at a lower frequency. A coil which is designed to heat the entire area uniformly can be used at the stress-relieving station.

A low-temperature stress-relieving effect may occur after induction hardening by terminating the quench at a time when the surface is at quench temperature but some residual heat remains in the layers below. This residual heat can provide a measure of stress relief by conducting back into the quench-hardened metal. When scanning or progressive hardening is vertical, stress relieving with residual heat is not practical because the surface contact time of the quenchant cannot be controlled and will vary along the part length. This technique can only be considered practical when scan hardening is horizontal. A low-power heat application on a return stroke is also a possibility for stress relieving in any scanning operation, but any of these methods need to be studied carefully.

Annealing heat treatments with induction heating include a variety of different methods and heat treatments. The methods of induction annealing can range from localized annealing to the continuous annealing of sheet and strip, and different types of anneal treatments are performed on both ferrous and nonferrous alloys. For the purposes of this discussion, the variety of induction anneals are briefly reviewed in terms of the following three categories:

- Localized annealing of welded tubular products or cold formed fasteners
- Continuous annealing of sheet or strip
- Annealing treatments for ferritic (magnetic) steels

Localized Induction Annealing. A wide variety of parts are locally annealed specifically to improve their cold-working properties or machinability, or simply to develop a microstructure with certain needed mechanical properties. Cold rolled threads and cold formed heads on studs, or the mouth and neck of steel and brass cartridge cases are examples of locally annealed parts.

Both weld metal and metal adjacent to an arc weld, a pressure butt weld, or a friction weld may be locally induction annealed to improve the weld zone ductility and remove any hard products of transformation. Continuous seam welded pipe and friction welded oil field tool joints are typical examples of manufactured products. Post annealing of arc welded alloy steel pipe in such places as refineries and electric power plants may be accomplished with induction heaters using 60 Hz or 400 Hz from either a portable transformer or motor-generator. Energy is applied through thermally insulated cable wrapped around the pipe and spaced with insulating board. Some equipment is designed specifically for this kind of application and also to preheat pipe prior to welding, although welding power supplies are sometimes used.

Continuous Induction Annealing. Transverse flux (Fig. 28) induction heating is being used to continuously anneal both ferrous and nonferrous strip. Here frequency considerations are based less upon the thickness of the strip, and more upon the separation of currents on the face and how they will affect uniformity of heating. New application techniques improve

the process flexibility so a single inductor can handle a wider range of strip widths, and computer modelling has shown how to heat more uniformly.

Induction Annealing of Magnetic Steels. Ferritic (magnetic) steels, which can be annealed either above or below the critical temperature for ferrite-austenite transformation, require careful attention to heating and cooling characteristics when induction methods are used for heating. In subcritical annealing, for example, the objective is to reduce hardness and improve ductility by heating only in the range of tempering temperatures (below 760 °C, or 1400 °F). In this subcritical process, however, undesirable transformation can occur because induction heating has the potential for producing high-temperature gradients (see the discussion in the previous section on Tempering).

Critical annealing (or normalizing), which involves heating above the transformation temperature to effect recrystallization, also requires careful attention to temperature gradients and cooling procedures. Products which lend themselves to continuous horizontal annealing (or normalizing) are steel wire, bar, tubulars, and simple shapes. The appropriate frequency will be determined by the metal cross section or thickness. In some cases, two frequencies are used during critical annealing, one for the initial subcritical (magnetic) stage followed by a higher frequency for supercritical (nonmagnetic) heating.

Annealing, in the strict sense, is not often performed by just induction heating alone, but induction heated parts are sometimes control cooled in a chamber. For example, stacked flywheel ring gears are heated in an induction coil, then transferred to a insulated thermally-controlled cooling tunnel. However, if localized heating is used, then induction annealing is generally followed by air cooling because the adjacent cold metal accelerates the cooling process. Some grades of steel may have a tendency to produce hard products of transformation with this type of treatment, similar to the undesirable transformations that can occur during induction tempering.

Localized Induction Heating for Grain Refinement. With the rapid local heating capabilities of the induction process, grain refinement can be achieved in the critical outer layers of steel bar or billet by allowing the colder core metal to recrystallize the transformed outer layer metal in a staged heating process. Induction heating is also used to effect recrystallization for the purpose of refining a coarse grain from the high temperatures of welding on continuous electrically welded pipe. For arctic service, where low-temperature impact properties are an important consideration, two to four successive recrystallization heaters have been placed in line after the welding station. As a thermal process, the grain refinement is accomplished by heating the steel above the transformation temperature to effect recrystallization, followed by rapid cooling to restore the original ferrite structure.

Precipitation Hardening or Aging. Heat produced from induced currents, if fairly uniform, can be effectively used to accelerate aging and produce precipitation hardening in metal with a supersaturated constituent. Certain cold worked steels (typically continuously scanned bars) are strengthened by a subcritical induction heat treatment, called strain aging. Because aging is time and temperature dependent, induction aging parameters can differ from furnace aging.

Quench Systems

Quenching techniques are as important a design feature of induction hardening lines as the equipment and coil used for austenitizing. The important questions to be answered when determining quenching systems include the following:

- Part size and geometry
- Type of austenitizing operations (surface or through hardening)
- Type of heating method (single-shot or scanning)
- Hardenability of steel and quenchant needed

The two most common types of systems consist of spray quench rings and immersion techniques. When quench rings are used for round bars, their shape, like the coil, is generally round (Fig. 43). The ring may be located concentric with the coil or directly underneath or alongside it (Fig. 24a) as in single-shot induction hardening setups. In those using induction scanning, parts move through the quench ring and coil, with quenching occurring immediately after heating (Fig. 24b). For nonsymmetric parts, the quenching apparatus, like the coil, is generally of the same shape as the part.

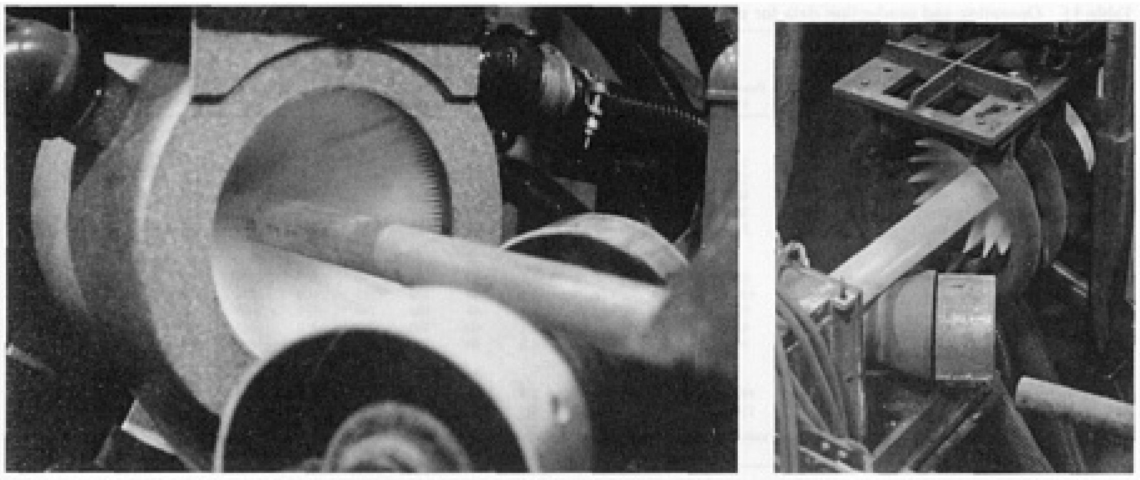


Fig. 43 Examples of quench rings for continuous hardening and quenching of tubular members. Courtesy of Ajax Magnethermic Corporation

In addition to the coil-and-quench-ring arrangements mentioned above, eleven basic arrangements for quenching induction hardened parts are shown schematically in Fig. 44. In correlation with the lettering here, these arrangements are briefly described as follows:

- (a) Heat in coil; manually lift part out of coil; submerge part in tank of agitated quench medium. Used where limited production does not warrant the cost of an automated quench
- (b) Heat and quench in one position; quench by means of integral quench chamber in inductor. Called single-shot method
- (c) Heat in coil with part stationary; quench ring moves in place. Single-shot adaptation of scanning method
- (d) Part is hydraulically lowered into quench tank after single-shot heating. Quench medium is agitated by submerged spray ring or propeller
- (e) Vertical or horizontal scanning with integral spray quench. Single-turn inductor. Used for shallow hardening
- (f) Vertical or horizontal scanning with multiturn coil and separate multirow quench ring. Used for deep-case or through hardening
- (g) Coil scans and heats workpiece; self-quench or compressed air quench. Used in special applications with high-hardenability steels
- (h) Horizontal cam-fed parts are pushed through coil, then dropped onto submerged quench conveyor
- (i) Vertical scanning with single-turn inductor in combination with integral dual quench: one quench ring for scan hardening, the second for stationary quenching when the scanning travel stops. Used for parts having a diameter or a flange section too large to travel through the inductor, wherein it is desired to harden up to the shoulder or flange
- (j) Vertical scanning with single-turn inductor with integral spray quench and submerged quench in tank
- (k) Split inductor and integral split quench ring. Used for hardening crankshaft bearing surfaces

Sufficient quenchant flow must be maintained to cool the part or section being quenched. Because induction heating systems are themselves compact, quenching systems are frequently designed smaller than they should be. To avoid this, the capacity of the pumping system should be at least three or four times the flow rate needed for proper quenching, and the quenching flow rate should be adjusted so that quenchant does not boil off once the part leaves the quench-ring location. Furthermore, if part rotation is used during heating and quenching, its rate must be kept low enough to avoid excessive quenchant from being thrown off.

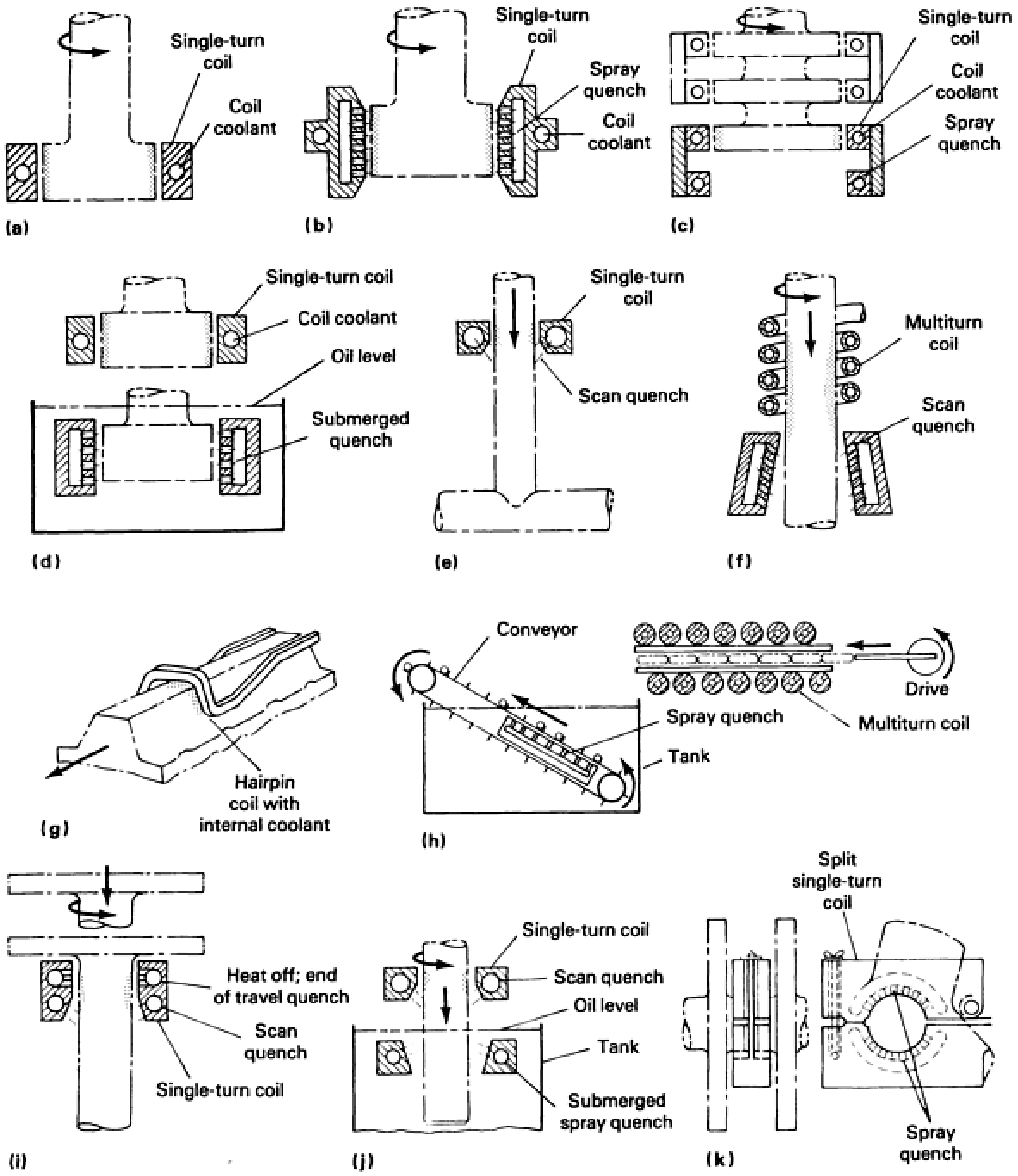


Fig. 44 Eleven basic arrangements for quenching induction hardened parts. See text for details.

As with furnace heat treatments, water and oil are frequently used as quench media in induction heat-treatment practice. Water is the more common. Oil is typically used only when heat treatment is to be performed on steels of high hardenability, or on parts in which cracking or distortion are likely to occur.

When water is used, it is best to select a supply which is reasonably clean and not extremely hard. Dirt may tend to clog the orifices of the quench tooling; similarly, hard-water deposits, which may build up slowly in quench rings, cut down on their efficiency and may necessitate replacement or extensive cleaning. Besides cleanliness requirements, the water temperature should also be controlled, preferably in the range of 15 to 40 °C (60 to 105 °F). This is most easily done when the water supply is large and when specialized recirculating systems are used.

Oils for quenching come in three generalized categories: general-purpose quenching oils (paraffin-type oils), "fast-quenching" oils, and soluble oil-water mixtures. Care must be exercised with all of these oils to provide adequate

ventilation for removal of oil vapors from the air and, thus, to prevent flash fires. This is especially important with some of the low-flash point, fast-quenching oils. The best way to control and minimize the presence of oil vapors is to supply a large amount of oil which completely covers the heated portion immediately below the inductor until the temperature of the quenched area is below the vaporization temperature of the oil.

Equally common and successful quenchants for induction hardening applications include polyvinyl alcohol solutions and compressed air. The former have become very popular in recent years and are used in hardening parts with borderline hardenability for which oil does not cool fast enough and water quenching leads to distortion or cracking. Unlike oil, polyvinyl alcohol, one of the so-called polymer quenchants, is not flammable and does not produce objectionable fumes or irritate the skin. Compressed-air quenching is typically used for high-hardenability, surface-hardened steels from which relatively little heat needs to be removed. Typical applications include gear teeth.

Quench Control. Adequate controls are necessary to ensure consistent results in induction heat treatment. Such controls for spray quenches include those for quenchant flow, temperature, timing, and so forth. The overall flow rate, *per se*, is controlled by adjustments of the pumping system itself. However, other considerations such as quench-device coupling and hole spacing in the quench device are also important. Often in single-shot operations, coupling--or the distance between the quench ring and part to be hardened--is very close, sometimes as little as 1.3 mm (0.051 in.). When several different sizes are to be treated, however, this distance may vary. Large distances are not desirable, however, because the velocity of the quenchant stream drops as the stream lengthens. This explains why the quench ring is often contoured to the part, that is, to maintain uniform coupling between the two.

The size and spacing of the orifices in the spray-quench device are a second important consideration in quench control. These can be adjusted to produce uniform quenching and avoid cracking or soft spots. Usually, this involves designs with many small holes rather than a few large ones. The lower limit on size is the minimum size that can be drilled on a production basis, as well as that which can be kept free of dirt. Also, smaller pieces heat treated by single-shot methods generally require smaller holes than large ones.

Spacing of the holes in the quench device must be such that each one has approximately the same amount of area to quench. Sometimes, staggering or overlapping of these areas is useful to be sure that the entire part is quenched. In practice, however, spacing may vary although the ratio of quench-device surface area to orifice area is typically about 10 to 1 or 20 to 1 for setups with narrow or wide coils, respectively. In either case, however, additional holes are placed at the end in order to provide quenchant flow to the ends of parts in single-shot applications.

The number of rows of holes in the quench device depends on the cooling rate necessary to harden the steel, the depth of heating (surface or through), the properties of the quench medium, the rate of travel (in scanning operations), and the configuration of the part. The desired surface finish may even affect the quench design and quench action. One of the major differences between quench rings for single-shot and scanning arrangements lies in the angular orientation of the holes. Single-shot spray-quench devices have orifices which are perpendicular (that is, radial) to the axis of the part. By contrast, the optimal angle between the axis of the holes and part axis in induction scanning setups is 30 °. This angle is selected to allow sufficient quenching action while at the same time preventing the quenchant from interfering with the heating part of the operation.

Control of the temperature of the quenching medium and its timing are also important. To this end, heat exchangers or cooling towers are often integral parts of an induction heating installation. In addition, electronic controls are often used to maintain timing of the quench cycle. This is particularly important when a tempering operation directly follows the hardening one or a so-called "autotempering" process is employed. In the former instance, the quench duration is typically adjusted so that the part temperature does not drop completely to room temperature. Leaving a small amount of residual heat in the component makes subsequent induction heating easier but does not affect the quality of the temper. In the latter case, the quench time may be controlled to bring the part temperature down precisely to tempering temperature, for instance, when a tempered pearlite or a tempered bainite microstructure is needed. Such an operation frequently involves precise temperature monitoring equipment and electronic feedback circuitry. One of the most interesting applications of this technique is the hardening and tempering of railroad rails (see the following section "Applications of Induction Heat Treatment"). Following austenitizing, the surface of the rail is air quenched to 425 °C (800 °F). Subsequently, the surface temperature climbs back to 595 °C (1100 °F) because of residual heat from the interior of the rail, leading to autotempering. Finally, a sustained cold-water quench is applied to bring the entire rail down to room temperature.

When quenching is done improperly, several problems may arise, including soft spots, quench cracks, and part distortion. Soft spots sometimes occur when water is used as the quenchant; they result from the formation of steam pockets on the part surface which prevent rapid enough cooling for the formation of martensite. As might be expected, this problem is

most severe in low-hardenability steels and can be alleviated by improved quench ring design or changes in the quenching device/part configuration. Quench cracks are typically due to one or more of four separate factors:

- Excessive quench severity (which is particularly troublesome in higher-carbon steels)
- Nonuniformity of quenching
- Changes in part contours with insufficient transitional areas
- Surface roughness (for example, tool marks)

Part distortion is commonly caused by relief of residual stresses, uneven heating, nonuniform quenching, or part geometry. In many cases, these can be controlled by modifications to the heating and quenching operations.

Applications of Induction Heat Treatment

Since its introduction in the 1930s, induction heat treatment has been applied to a large variety of mass-produced, commercial products. The initial applications involved hardening of the surfaces of axisymmetric steel parts such as shafts. Subsequently, surface-hardening techniques were developed for other parts whose geometries were not so simple. Most recently, induction hardening and tempering techniques have been developed for purposes of heat treating to large case depths and heat treating of entire cross sections. Types of parts to which induction is commonly applied include the following:

Surface-Hardening Applications

- *Transportation field:* crankshafts, camshafts, axle shafts, transmission shafts, splined shafts, universal joints, gears, valve seats, wheel spindles, and ball studs
- *Machine-tool field:* lathe beds, transmission gears, and shafts
- *Metalworking and hand-tool fields:* rolling-mill rolls, pliers, hammers, and so forth

Through-Hardening Applications

- Oil-country tubular products
- Structural members
- Spring steel
- Chain links

In this section, applications and advantages of induction methods of heat treatment for some of the parts listed above will be discussed.

Surface-Hardening Applications

Crankshafts for internal-combustion engines were probably the first parts to which induction hardening techniques were applied. Because the explosive forces of the engine must pass through the crankshaft, severe demands in terms of strength and wear resistance are placed on the steel used in manufacturing the crankshaft. These demands are ever-increasing with the rising horsepower ratings of engines used in automobiles, tractors, and other vehicles.

The most stringent demands are placed on the journal and bearing surfaces. Journals are the parts of the rotating shaft which turn within the bearings. Prior to the advent of induction heating, methods such as furnace hardening, flame hardening, and liquid nitriding were used. However, each of these processes presented problems such as inadequate or nonuniform hardening and distortion. Induction hardening overcomes many of these problems through rotation of the part during heat treating and selection of frequency and power to obtain adequate case depth and uniform hardness. In one of the most common steels used for crankshafts, 1045, case hardnesses of about 55 HRC are readily obtained. Other advantages of the induction process for crankshafts include:

- Only the portions which need to be hardened are heated, leaving the remainder of the crankshaft relatively soft for easy machining and balancing
- Induction hardening results in minimum distortion and scaling of the steel. The rapid heating associated with induction heat treating is advantageous in avoiding scaling in other applications as well
- Because induction heat-treating processes are automated, an induction tempering operation immediately following the hardening treatment is readily feasible
- The properties of induction hardened crankshafts have been found to be superior to those of crankshafts produced by other techniques. These properties include strength and torsional and bending fatigue resistance. These improvements have enabled crankshafts to be reduced in size and weight

Presently, crankshafts are being made from steel forgings as well as from cast iron. In the latter case, surface hardness levels of 50 HRC are easily obtainable after induction heating and air quenching. The resultant microstructure is a mixture of bainite and martensite, the pure martensite phase being avoided altogether. Such a dual microstructure minimizes the danger of crack formation at holes and eliminates the need for chamfering and polishing in these regions. The air quench allows residual heat left in the workpiece to minimize quench stresses and to autotemper the bainite which forms during cooling. After a prescribed period of time, the air quench is followed by a water quench during which the martensite phase is produced from the remaining austenite.

Axle shafts used in cars, trucks, and farm vehicles are, with few exceptions, surface hardened by induction. Although in some axles a portion of the hardened surface is used as a bearing, the primary purpose of induction hardening is to put the surface under a state of compressive residual stress. By this means, the bending and torsional fatigue life of an axle may be increased by as much as 200% over that for parts conventionally heat treated (Fig. 45). Induction hardened axles consist of a hard, high-strength outer case with good torsional strength and a tough, ductile core. Many axles also have a region in which the case depth is kept very shallow so that the part can be readily straightened following heat treatment. In addition to substantially improving strength, induction hardening is very cost-effective. This is because most shafts are made of inexpensive, unalloyed medium-carbon steels which are surface hardened to case depths of 2.5 to 8 mm (0.1 to 0.3 in.) depending on the cross-sectional size. As with crankshafts, typical hardness (after tempering) is around 50 HRC Such hard, deep cases improve yield strength considerably as well.

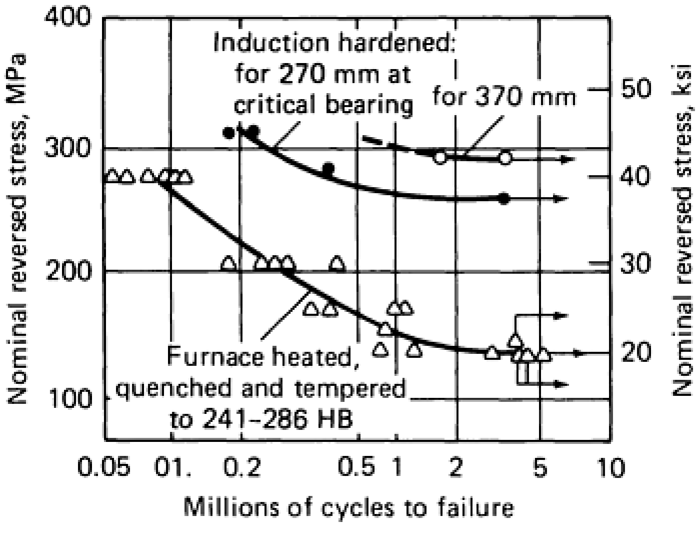
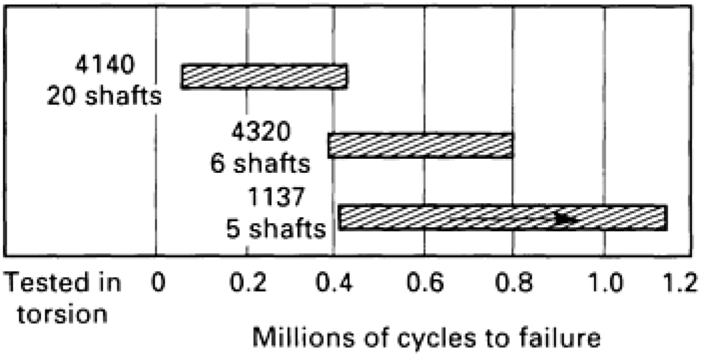


Fig. 45 Bending fatigue response of furnace hardened and induction hardened medium-carbon steel tractor axles. Shaft diameter: 70 mm (2.75 in.). Fillet radius: 1.6 mm (0.063 in.)

Modern transmission shafts --particularly those for cars with automatic transmissions--are required to have excellent bending and torsional strength besides surface hardness for wear resistance. Under well-controlled conditions, induction hardening processes are most able to satisfy these needs, as shown by the data in Fig. 46, which compares the fatigue resistance of through-hardened, case carburized, and surface induction hardened axles. The induction hardening methods employed are quite varied and include both single-shot and scanning techniques.



Steel	Surface hardness, HRC	Method of hardening
4140	36-42	Through-hardened
4320	40-46	Carburized to 1.0-1.3 mm (0.040-0.050 in.)
1137	42-48	Induction hardened 3.0 mm (0.120 in.) min effective depth and 40 HRC

Fig. 46 Comparison of fatigue life of induction surface hardened transmission shafts with that of through-hardened and carburized shafts. Arrow in lower bar (induction hardened shafts) indicates that one shaft had not failed after testing for the maximum number of cycles shown.

Induction hardening of crankshafts, axles, and transmission shafts is becoming an increasingly automated process. Often, parts are induction hardened and tempered in-line. One such line for heat treating of automotive parts is depicted schematically in Fig. 47. It includes an automatic handling system, programmable controls, and fiber-optic sensors. Mechanically, parts are handled by a quadruple-head, skewed-drive roller system (QHD) after being delivered to the heat-treatment area by a conveyor system. The roller drives, in conjunction with the chuck guides, impart rotational and linear motion to the incoming workpiece. Once a part enters the system, the fiber-optic sensor senses its position and initiates the heating cycle for austenitization. This sensor is also capable of determining if the operation is proceeding abnormally (for example, if the part is being fed improperly) and can automatically shut down the system.

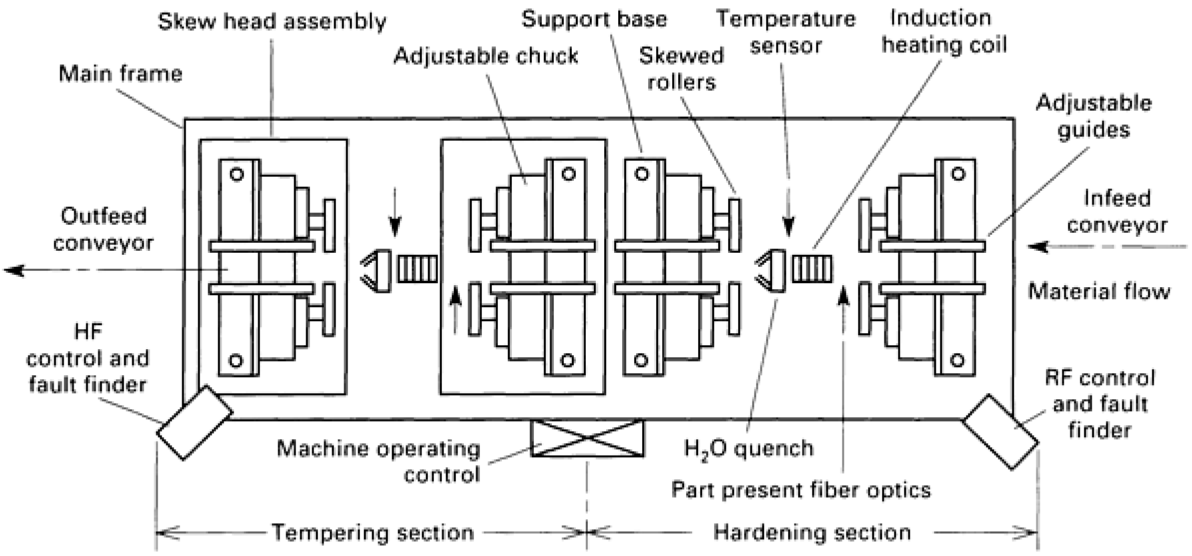


Fig. 47 Automated, quadruple-head, skewed drive roller system used for in-line induction hardening and tempering of automotive parts

In the hardening cycle of the QHD system, the induction generator frequency is generally either in the radio-frequency range (approximately 500 kHz) for shallow cases or in the range from 3 to 10 kHz for deeper cases. In either instance, a temperature controller automatically senses if the part has been heated to a temperature too high or too low, in order to prevent an improperly austenitized piece from passing through the system. Assuming that the part has been heated properly, it then passes through a quench ring, which cools it to a temperature of 95 °C (200 °F) to form a martensitic case, prior to moving into the tempering part of the heat-treatment line. Again, a fiber-optic system senses the presence of the part and begins the heating cycle, using low-frequency current generally around 3 kHz, since the desired tempering temperature is approximately 400 °C (750 °F)--a temperature at which the steel still has a large magnettic permeability. Once again, the part is automatically heated, quenched, and moved from the heat-treatment station, this time onto a conveyor which takes it to the machining area for grinding.

The control system of this line is designed to allow decision making by programmable controls. Thus, all aspects of the heat-treating process and mechanical operations are preprogrammed and may be changed easily to accommodate different part sizes and heat-treating parameters. With such a process users have been able to increase production rates more than threefold over those obtainable with conventional heat-treating lines.

Gears. Reliability and high dimensional accuracy (to ensure good fit) are among the requirements for gears such as those used in transmissions for farm equipment and related applications. Keeping distortion as low as possible during heat treatment is very important. Thus, induction is probably the best process for such parts. Among the other advantages of induction heat treatment of gears are the following:

- Gear teeth and roots can be selectively hardened
- Heating is rapid with minimum effect on adjacent areas
- Uniform hardening of all contact areas results in high wear resistance. The improvement of wear resistance often permits substitution of inexpensive steels, such as 1045 or 1335, for more highly alloyed steels

When using induction, however, extreme care is needed in positioning the gear in relation to the coil, particularly in setups in which all gear teeth are heated and hardened at once. In these instances, the coil goes entirely around the gear, and a quench ring concentric to it is used (Fig. 48a). A typical hardening pattern for this kind of arrangement is shown in Fig. 48(b). In such single-shot setups, a two-stage process is often preferable, however. In the first step, a relatively low frequency is used for heating of the root diameter of the gear and for partial heating of the flank areas between the roots and tooth tips. Then, the tooth tips themselves are heated with a much higher radio frequency. As with surface hardening of shafts, gears are usually rotated during processing to effect uniformity of heating and hardening. Part transfer between

stations in this and similar processes is carried out by specialized Systems or robots. In this way, a uniform or contoured hardness pattern which follows the outline of the gear is obtained. This hardness pattern improves not only the wear resistance of the teeth, but their bending strength as well. Modifications of single-shot techniques may be employed for preferential hardening of only certain portions of the teeth, such as tooth tips or flank regions, depending on specific applications. Unfortunately, as the gear becomes larger, the capacity of the induction generator needed for surface hardening increases dramatically, as shown in Table 12 for various gear geometries.

Table 12 Power requirements for induction hardening of gear teeth

Tooth	Diametral pitch	Approximate length of tooth profile		Surface area per tooth[(a)]		Power required per tooth[(b)], kW	Total power required[(c)], kW
		mm	in.^{2}	cm^2	in.^{2}		
A	3	50	2.0	12.9	2.0	20	800
B	4	38	1.5	9.7	1.5	15	600
C	5	33	1.3	8.4	1.3	13	520
D	6	25	1.0	6.5	1.0	10	400
E	7	23	0.9	5.8	0.9	9	360

(a) For a face width of 25 mm (1 in.).

(b) At a power density of 1.55 kW/cm^2 (10 kW/in.^{2}).

(c) For a gear having 40 teeth

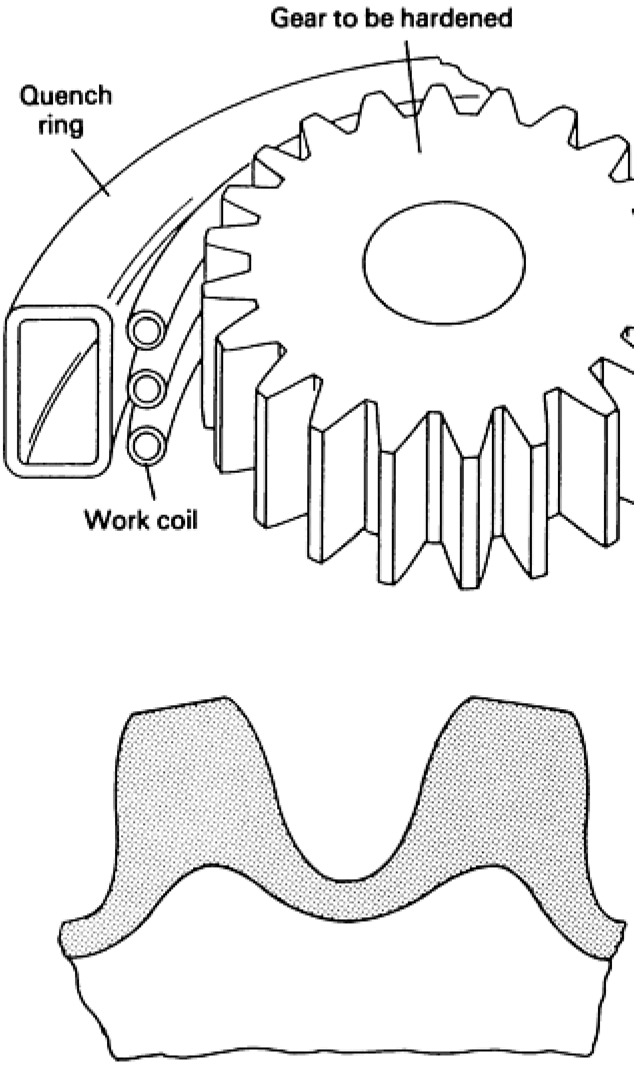


Fig. 48 Induction hardening of gear teeth by a single-shot technique. (a) Solenoid coil and concentric quench ring around gear to be hardened. (b) Schematic of case-hardness pattern obtained with such an arrangement

An alternative technique for surface hardening of gears is the so-called tooth-by-tooth technique. As the name implies, each tooth is individually heated and quenched. By this means, induction generators of modest capacity can be used for large gears which otherwise would require large coils and large amounts of power. A typical inductor for such a process consists of a copper coil that is slightly larger than the gear tooth (Fig. 49). If only flank and root hardening are desired, a coil whose outer corners are chamfered is employed (Fig. 50a). Without the chamfers, the tooth tips would be heated as well, often in a very nonuniform manner. Alternatively, auxiliary water sprays, which are used for quenching, may be adjusted to cool the tooth tips (Fig. 50b), or the coil can be shortened.

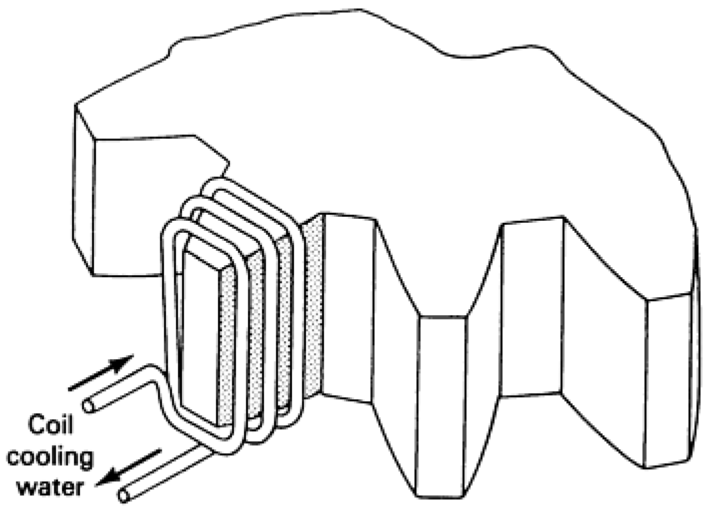


Fig. 49 Setup for tooth-by-tooth hardening of gears

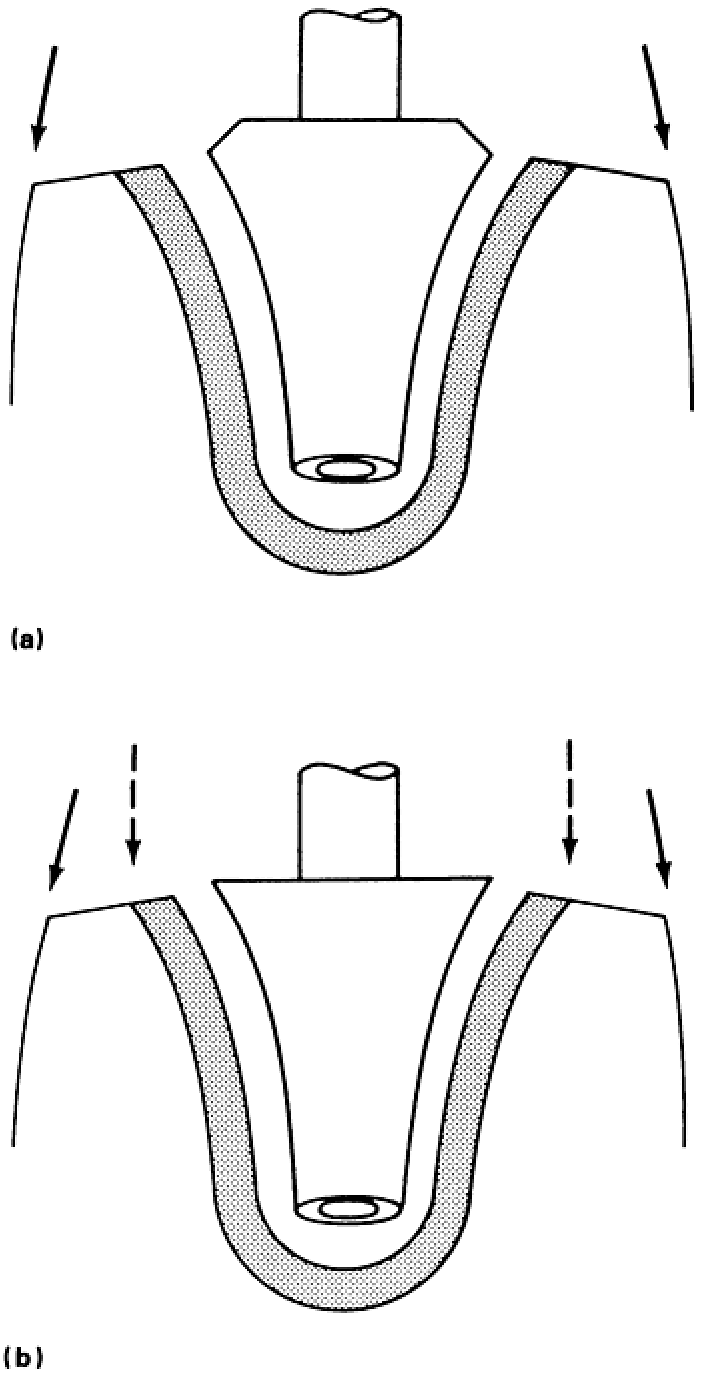


Fig. 50 Inductor designs for tooth-by-tooth hardening of gear flanks. (a) Inductor design with chamfered corners. (b) Inductor design without chamfers in which tooth-tip hardening is prevented by adjusting water sprays. In both sketches, arrows indicate direction of preferred water spray; solid arrows in (a) and dashed arrows in (b).

Valve seats in automobiles are yet another application of surface hardening by induction. Prior to the advent of catalytic converters and the need to use unleaded gasoline, wear resistance of valve seats was afforded by deposits of lead oxide. These deposits acted as a lubricant between the seat and valve. Without the lead oxide from gasoline, other means of preventing premature valve wear were required. In order to avoid the expense of hardened inserts, an induction heat-treating method by which all the seats in a single engine head can be processed at one time was developed. This is done with a specially designed machine in which the surfaces are heated rapidly and self-quenched to produce a case depth of 1.8 to 2 mm (0.06 to 0.08 in.) and a hardness of 50 to 55 HRC. Figure 51 shows the improvement over untreated parts that such processing affords. The durability of the induction hardened seats is even superior to that of conventional seats in engines which use leaded fuel.

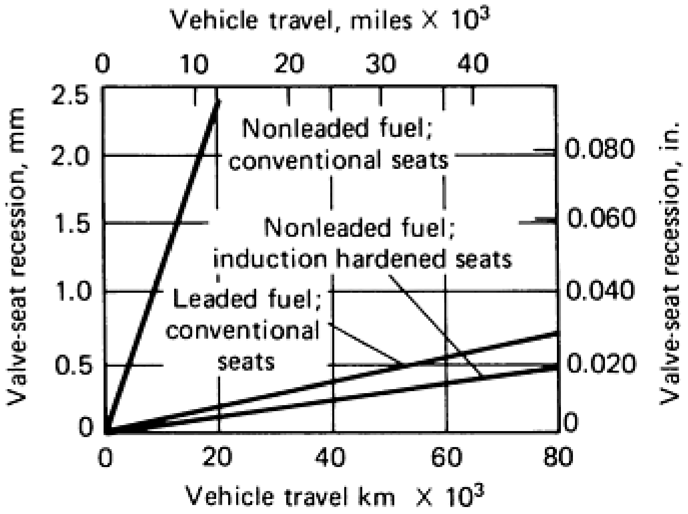


Fig. 51 Effect of induction surface hardening on wear of engine valve seats

Railroad Rails. Surface hardening of railroad rails is one of the more recent applications of heat treatment. The heads (top portions) of rails wear rapidly in curved sections where high-tonnage freight-car traffic is common. The abrasive action of the wheels combined with high stresses can result in a very short rail life, sometimes as little as one year or less. With the move toward heavier cars and increased speeds, these kinds of problems are becoming more severe.

Conventional railroad rails are manufactured from 1080 steel by hot (shape) rolling using a preheat temperature of 1290 °C (2350 °F). Following rolling, they are controlled cooled, and a finished product of only moderate hardness (250 HB $\approx$ 24.5 HRC) results. In the induction process, only the head of the rail is hardened since this is where failure takes place because of wear or deformation during service. A relatively thick case whose hardness decreases with depth (Fig. 52) is achieved by using a relatively low-frequency (approximately 1000 Hz) power source. In the actual process, rails are prebent (elastically) before heat treatment to offset distortions caused by heating and to eliminate the need for final straightening operations. The rails are then fed continuously through a U-shaped inductor and their surfaces heated to 1065 °C (1950 °F). Following heating, the surface is air quenched to 425 °C (800 °F), producing a bainitic microstructure. Residual heat left in the interior of the rail brings the surface layers back to a temperature of 595 °C (1100 °F), thereby bringing about autotempering. Finally, a controlled cold-water quench is applied to cool the rail to room temperature and to ensure straightness. Rails produced thereby have been found to last from $2\frac{1}{2}$ to 8 times as long as conventionally manufactured rails.

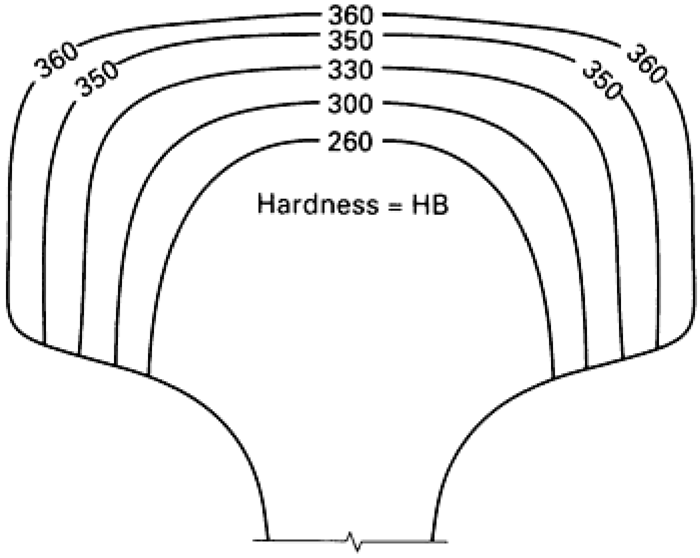


Fig. 52 Brinell hardness pattern in induction surface hardened railroad rail

Rolling-Mill Rolls. Induction hardening of rolling-mill rolls is analogous to induction hardening of rails in that relatively deep cases are produced. During service, roll life is limited by abrasive wear. As the diameter is reduced by wear, adjustments are made to bring the rolls closer together in order to maintain a given rolling reduction. These adjustments are sufficient until the rolls have worn approximately 40 mm (1.5 in.); once this amount of wear is exceeded, the rolls must be replaced. The objective of induction heat treatment is, therefore, to produce a hardened case approximately 20 to 40 mm (0.75 to 1.5 in.) deep. This is done employing a low-frequency (60 Hz) power supply.

In the scanning method of induction hardening, the roll, hanging vertically, is lowered into the induction coil, in which its surface temperature is gradually raised to 955 °C (1750 °F). By controlling the power input and feed rate, a temperature profile is developed such that the temperature ranges from 900 °C (1650 °F) at 40 mm (1.5 in.) below the surface to less than 260 °C (500 °F) at 40 mm (2 in.) below the surface. Following heating, the roll is quenched using water precooled to 5 °C (40 °F). Because roll steels usually contain 0.8 to 0.9% C and substantial amounts of nickel, chromium, molybdenum, and vanadium, they have high hardenability and develop high hardness to the entire depth to which the steel was austenitized. A typical hardness profile is shown in Fig. 53. Here, the drop in hardness beyond about 25 mm (1 in.) can be attributed to heat losses due to conduction, which could have resulted in the formation of pearlite or bainite prior to quenching, at which time the remaining austenite would have transferred to martensite.

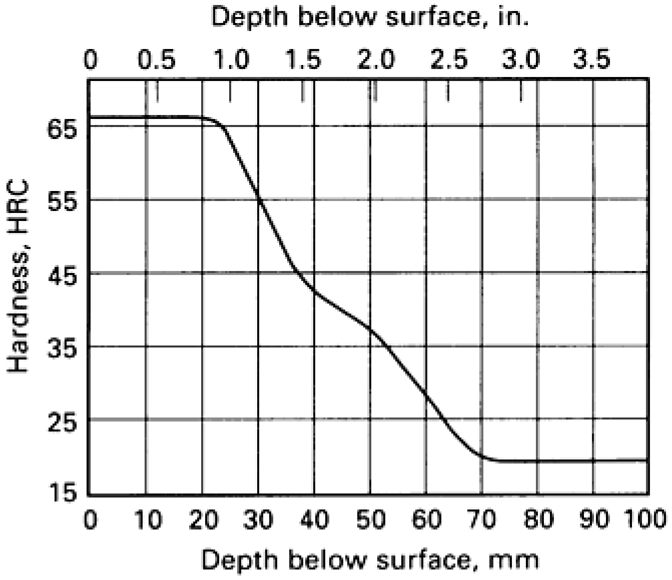


Fig. 53 Hardness pattern developed in rolling mill rolls induction hardened using a 60 Hz generator

Miscellaneous Applications. There are many other applications of induction surface hardening. These include uses in the ordnance, hand-tool, and automotive fields.

In the ordnance area, induction heating has been used for both surface hardening and through-hardening of armor-piercing projectiles. The induction process allows a very uniform bainitic microstructure to be obtained. During World War II, it was found that batch furnace heat treatment could not produce as uniform and high-quality a product at such a low cost as could the induction method.

Induction heating has also been found useful for selective through-hardening and surface hardening of heads for tools such as hammers, axes, picks, and sledges. These tools are usually made of 1078 steel. Lead baths were once used in the hardening of such parts, but use of lead baths has diminished because of health and safety regulations. Other applications include steels for automobile coil springs, leaf springs, and torsion bars and wheel spindles.

Through-Hardening Applications

Although not as common as surface hardening and tempering, through-hardening and tempering via induction methods have been found to be practical for a number of applications such as piping, structural members, saw blades, and garden tools.

Pipe-Mill Products. Probably the largest application of induction through-hardening (and tempering) involves piping or tubular goods used for oil wells and gas pipelines, for example. For these uses, relatively low-frequency induction generators are selected so that the reference depth is of the same order of magnitude as the wall thickness of the workpiece. Since the workpiece is hollow, there is no problem of loss of electrical efficiency arising from the eddy-current cancellation such as the losses which occur at the centers of solid bars. In fact, to a point, the efficiency of induction heating of tubular products increases as the wall thickness decreases, because the resistance of the material increases with decreasing wall thickness and becomes much larger than that of the coil. However, if the thickness is very small, the current developed in the workpiece goes down and relatively little I^2R heat is generated.

Pipe-mill products fall into two major categories: electric resistance welded (ERW) and seamless. The ERW pipe is made from steel strip which is formed and welded. After welding, the weld may be annealed to avoid cracking during shipment or subsequent operations, which may include reduction to obtain a smaller diameter or different wall thickness. In any case, ERW products tend to have a very uniform wall thickness, which is an important consideration in induction heating and heat treatment. Nonuniformities in wall thicknesses usually lead to temperature nonuniformities; thicker regions are heated to lower temperatures than thinner ones during induction heat treatment. In contrast to ERW pipe, seamless piping tends to have a much less uniform wall thickness. It is manufactured by piercing and extruding a heated, round-cornered square billet. To maintain quality, seamless piping for oil-country applications is typically required to have a wall thickness variation of no more than 12.5%. Because of its uniformity, ERW pipe is the preferred choice for induction heat treatment.

In a typical installation for heat treatment of piping, processing is carried out in a continuous line in which the steel is austenitized, quenched, tempered, and finally cooled to room temperature at successive stations. A typical arrangement is depicted in Fig. 54. In this system, each pipe is loaded onto an entry table and fed onto the conveyor as soon as the heat treatment of the pipe preceding it is completed. As each pipe passes through the austenitizing station (consisting of five coils), it is rotated on skewed rollers to ensure temperature uniformity. Also, because only a small portion of the pipe is heated at one time, distortion is readily controlled. Using 180-Hz current, pipes are heated uniformly through the thickness to approximately 900 °C (1650 °F). A suitable power density is chosen for this purpose as well. With a maximum generator capacity of 4500 kW, piping up to 405 mm (16 in.) in outside diameter can be handled by the austenitizing unit. For this largest diameter, the 1.5 m (5 ft) length of the heating section results in a maximum power density of roughly 0.23 kW/cm^2 (1.5 kW/in.^{2}), assuming 100% efficiency, when the total power of the generator is utilized.

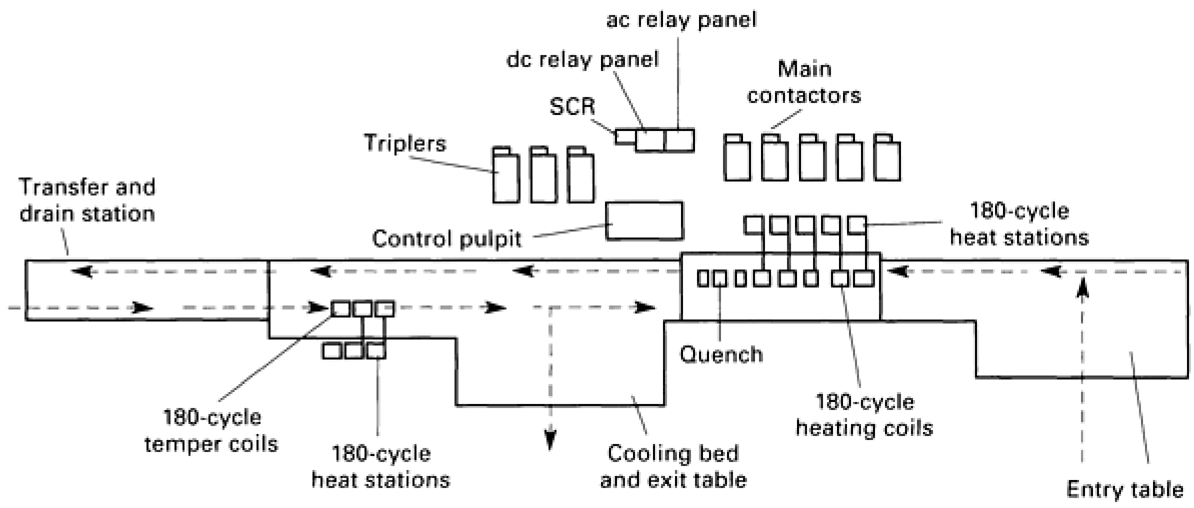


Fig. 54 Schematic diagram of equipment used for in-line induction through hardening and tempering of pipe-mill products. Pipe enters from the right, is austenitized, quenched, drained, and tempered. Following tempering, the pipe is transferred to cooling beds for air cooling.

After austenitizing, the pipe enters the quench ring several feet down the line. After the water has been drained off, the pipe moves to the tempering station which is powered by generators with a total capacity of 2700 kW and also at a frequency of 180 Hz. The power capacity for this operation is lower than that for austenitizing because the workpiece is heated to temperatures of only about 540 to 650 °C (1000 to 1200 °F). Following tempering, the pipe continues along the conveyor to cooling beds and is rotated during the entire cooling cycle to ensure straightness and lack of ovality.

Structural Members and Bar Stock. A process similar to hardening and tempering of pipe-mill products is used to heat treat structural members of uniform section thickness. In these cases, the structural member is passed through a series of induction preheating and heating stages for austenitizing and then is quenched while being restrained by a set of rolls which prevent distortion. The various coils for austenitizing are connected to generators of frequencies ranging from 180 Hz (preheating) to 10 kHz (final heating stages) in processing of steel shapes 6 to 13 mm (0.25 to 0.5 in.) in section thickness. After quenching, the structural shape is tempered in-line using induction heating frequencies of 180 to 3000 Hz and is prevented from distorting during subsequent cooling by another set of restraining rolls.

The above process is used to make high-strength structural members from 1025 steel strip in the form of U-channels, T's, and I-sections. For U-channels, a variety of coil designs are possible. These include hairpin, oval, pancake, and L-shape coils, all of which induce eddy currents whose paths lie in the plane of the structural member and which follow directions similar to those of the currents in the coil.

Miscellaneous Applications. Other induction hardening and tempering applications are often very specialized, requiring special coil designs and control of heating. Typical examples include hardening and tempering of circular-saw blade segments, garden trimmer blades, snow plow blades, and coil springs.

Process and Quality Control Considerations

Induction heat treatment precludes many of the problems associated with furnace methods. Among its advantages is the rapid heating that can be achieved. For this reason, induction heat treatment is particularly well-suited to high-volume continuous heat-treatment operations. With the advent of microprocessor technology, the controls necessary for such techniques have become readily available. The rate of heating is limited only by the power rating of the ac power supply. Because heating times are usually short, surface problems such as scaling and decarburization and the need for protective atmospheres can often be avoided. In addition, induction tends to be energy-efficient. With proper coil design and equipment selection, more than 80% of the electrical energy can be converted into heat for treatment of the workpiece. Such efficiencies are not possible with gas-fired furnaces, in which a fairly substantial proportion of the consumed energy is lost with the hot gases leaving the furnaces. Induction heating is also free of pollution.

Among the disadvantages of induction are those related to coil design and equipment selection, both of which must be tailored to the particular part to be heat treated and the temperature at which the heat treatment is to be carried out. In the

automotive and oil-drilling equipment industries, production rates are high and the induction heat-treating method finds wide application. In situations where only a few parts of a given design are to be made, induction heat treatment is usually not economically feasible.

Temperature Sensing. A kilowatt time meter can sense the amount of energy applied to the output of an induction heater, and providing all other conditions remain the same, it can be a good measure of the heat energy in the product. Besides temperature, energy usage can also be evaluated with kilowatt-time meters. However, the principal methods of temperature measurement utilize thermocouples, radiation sensing, or eddy current sensing. Each has its limitations.

Spring loaded thermocouples are used to measure and control the temperature of softer, nonferrous metals during an induction heating cycle. Thermocouples can be attached to parts, and measurement is then quite accurate, but only at the place where the thermocouple is attached. Because of the work involved in attaching and detaching, this temperature measurement technique is limited to test work or for very slow programmed heating applications such as stress relieving welds on installed piping systems.

Radiation Sensing. More typically, induction heating operations are monitored by sensing the energy radiated from the surface. Infrared systems of the two and three color variety are most widely used, but the work should be free of loose scale to obtain useful readings. Emissivity must not vary a great deal to obtain reliable readings and shiny surfaces are poor targets (see the article "Furnace Temperature Control" in this Volume for more information on temperature measurement by radiation sensing).

A basic disadvantage of temperature measurement by surface radiation is that the system only measures surface temperature; it tells nothing about the temperature profile, which is so important to surface hardening. The accuracy is also subject to vagaries in the surface condition of the metal.

Eddy Current Sensing. In the method of eddy current sensing, electrical conditions of the metal are sensed through the induction heating field, providing comparative sensing of both temperature and current depth in iron and steel, particularly when the metal is austenitized. The electrical resistivity (ρ) and the depth of current penetration (Eq 1) in a metal both increase with temperature, thus changing the eddy currents and heating pattern as the temperature rises. In addition, the magnetic permeability of ferromagnetic steel also changes with temperature, with the most dramatic change occurring at the Curie temperature where relative permeability drops to unity. Because the steep drop to a permeability of 1 occurs as the metal approaches its transformation to austenite, the sensing of this radical electrical change is most significant in hardening, and annealing or normalizing steel or cast iron.

By measuring the characteristics of the induction heating field (phase, amplitude, and frequency) in real time, the electrical and magnetic changes during heating can provide a signature that relates to the metal temperature and the temperature profile. This can then be used to critically monitor the process throughout the heating cycle. Eddy current sensing technology is thus a means for determining proper heating during the induction cycle. Improper part positioning, gross differences in microstructure, cracks, and other abnormalities may also be sensed, sometimes at the moment of power-on in which power can be removed immediately. Because the electrical load condition information during each cycle is fed into a computer, any trend to deviate from a normal signature overtime can be transmitted to a statistical computer program for analysis and correction.

Cost Factors in Induction Heat Treating. On just the basis of energy costs, induction heating seldom competes with gas or even oil. However, because of its ability to rapidly heat metal, savings may accrue from reduced processing time, increased production, reduced labor, or the ability to heat treat in a production line or automated manufacturing system. Surface and selective hardening may be energy competitive because a small portion of the metal is heated.

Hardening by induction may also enable one to use a plain carbon grade of steel instead of a more expensive alloy steel. The inherently short heating time of induction heating permits the use of higher austenitizing temperatures than with conventional heating practices. Consequently, it is generally possible to obtain satisfactory hardness with lower carbon steels using such higher temperatures.

Control of Surface Hardness. The ultimate surface hardness depends on the carbon content of steel. When the carbon content of the steel exceeds about 0.50%, additional carbon content has no effect on the hardness obtained; however, there is a pronounced effect on the ease of obtaining full hardness. During selective surface hardening, the quenching rate may be faster than a through heated material and a slightly higher hardness value may be achievable. Residual stresses from

selective heating and quench may also add a point or two to the readable hardness, which at one time was termed superhardness.

Low hardness values measured on an induction hardened part may be caused by any one of the following:

- Surface decarburization
- Lower carbon content than specified
- Inadequate austenitizing temperature
- Prior structure
- Retained austenite (mostly in high-carbon alloy steels)
- Unsatisfactory quenching

These problems are not unique to induction hardening, although the methods of correction may involve different options. In the event of inadequate austenitizing temperatures, for example, an adequate temperature can be achieved by increasing power density and/or heating time.

Distortion of Induction Hardened Steel. Steel parts that have been surface hardened by induction generally exhibit less total distortion or distortion more readily controllable than that for the same parts quenched from a furnace. The decrease in distortion is a result of the support given by the rigid, unheated core metal, and of uniform, individual handling during heating and quenching. In scanning, distortion is controlled further by heating and quenching only a narrow band of the steel at one time. Unless a part through hardened by induction is scanned, the distortion encountered will approach the distortion that is experienced in furnace hardening.

As in furnace heat treating, the distortion from induction hardening arises during austenitizing or quenching. Distortion during austenitizing usually results from relief of residual stresses introduced during forging, machining, and so forth, or from nonuniform heating. When the part is only surface austenitized and hardened, the cool metal in the core of the workpiece minimizes distortion. Small amounts of distortion in induction surface hardened parts with shallow cases are often eliminated by means of a subsequent mechanical sizing (for example, straightening) operation. Furthermore, the use of induction scanning, in which only a small portion of the workpiece is heated at any one time, is helpful in preventing problems of this type. Scanning is also helpful in keeping distortion levels low in through-hardening applications. In these instances, rotation of the part, provided that it is symmetrical, enhances the uniformity of heating and decreases the likelihood of non-uniformities in the final shape.

Distortion resulting from quenching is largely a function of the austenitizing temperature, the uniformity of the quench, and the quench medium. Higher austenitizing temperatures, which give rise to higher residual stresses, increase the amount of non-uniform contraction during cooling. Severe quenches such as water or brine, which also tend to produce high residual stresses, can lead to severe distortions as well. This problem can be especially troublesome when alloy steels are quenched in water. However, these steels usually have sufficient hardenability such that oil can often be employed instead.

In extreme cases, distortion may lead to cracking. This cracking is intimately related to part design, as well as to the residual stresses which are developed. Components with large discontinuities in cross section are particularly difficult to heat treat for this reason. In addition, there often is a limiting case depth beyond which cracking will occur; in these instances, tensile stresses near the surface of the induction hardened part, which balance the compressive residual stresses generated, can be blamed for the cracking problem.

Steel composition also plays a role in the tendency toward cracking in induction hardening applications. This tendency increases as the carbon or manganese content is increased. This is not to say, however, that critical levels of either element can be specified, because other factors such as case depth (in surface hardening applications), part design, and quench medium are also important. The effect of carbon content on the tendency toward quench cracking is greatest in through-hardened parts and arises because of its influence on the depression of the martensite-start (M_s) temperature and the hardness of the martensite.

Cold Treating and Cryogenic Treatment of Steel

Revised by Earl A. Carlson, Lindberg Heat Treating Company

Introduction

COLD TREATING of steel is widely accepted within the metallurgical profession as a supplemental treatment that can be used to enhance the transformation of austenite to martensite and to improve stress relief of castings and machined parts. Common practice identifies -84 °C (-120 °F) as the optimum temperature for cold treatment. There is evidence, however, that cryogenic treatment of steel, in which material is brought to a temperature of the order of -190 °C (-310 °F), improves certain properties beyond the improvement attained at cold-treatment temperatures. This discussion will explain the practices employed in the cold treatment of steel and will present some of the experimental results of using cryogenic treatment to enhance steel properties.

Cold Treating of Steel

Cold treatment of steel consists of exposing the ferrous material to subzero temperatures to either impart or enhance specific conditions or properties of the material. Increased strength, greater dimensional or microstructural stability, improved wear resistance, and relief of residual stress are among the benefits of the cold treatment of steel. Generally, 1 h of cold treatment for each inch of cross section is adequate to achieve the desired results.

All hardened steels are improved by a proper subzero treatment to the extent that there will be less tendency to develop grinding cracks and therefore they will grind much more easily after the elimination of the retained austenite and the untempered martensite.

Hardening and Retained Austenite

Whenever hardening is to be done during heat treating, complete transformation from austenite to martensite is generally desired prior to tempering. From a practical stand-point, however, conditions vary widely, and 100% transformation rarely, if ever, occurs. Cold treating may be useful in many instances for improving the percentage of transformation and thus for enhancing properties.

During hardening, martensite develops as a continuous process from start (M_s) to finish (M_f) through the martensite-formation range. Except in a few highly alloyed steels, martensite starts to form at well above room temperature. In many instances, transformation is essentially complete at room temperature. Retained austenite tends to be present in varying amounts, however, and when considered excessive for a particular application, must be transformed to martensite and then tempered.

Cold Treating versus Tempering. Immediate cold treating without delays at room temperature or at other temperatures during quenching offers the best opportunity for maximum transformation to martensite. In some instances, however, there is a risk that this will cause cracking of parts. Therefore, it is important to ensure that the grade of steel and the product design will tolerate immediate cold treating rather than immediate tempering. Some steels must be transferred to a tempering furnace when still warm to the touch to minimize the likelihood of cracking. Design features such as sharp corners and abrupt changes in section create stress concentrations and promote cracking.

In most instances, cold treating is not done before tempering. In several types of industrial applications, tempering is followed by deep freezing and retempering without delay. For example, such parts as gages, machineways, arbors, mandrils, cylinders, pistons, and ball and roller bearings are treated in this manner for dimensional stability. Multiple freeze-draw cycles are used for critical applications.

Cold treating is also used to improve wear resistance in such materials as tool steels, high-carbon martensitic stainless steels, and carburized-alloy steels for applications in which the presence of retained austenite may result in excessive wear. Transformation in service may cause cracking and/or dimensional changes that can promote failure. In some

instances, more than 50% retained austenite has been observed. In such cases, no delay in tempering after cold treatment is permitted, or cracking can develop readily.

Process Limitations. In some applications in which explicit amounts of retained austenite are considered beneficial, cold treating might be detrimental. Moreover, multiple tempering, rather than alternate freeze-temper cycling, is generally more practical for transforming retained austenite in high-speed and high-carbon/high-chromium steels.

Hardness Testing. Lower than expected HRC readings may indicate excessive retained austenite. Significant increases in these readings as a result of cold treatment indicate conversion of austenite to martensite. Superficial hardness readings, such as HR15N, can show even more significant changes.

Precipitation-Hardening Steels. Specifications for precipitation-hardening steels may include a mandatory deep freeze after solution treatment and prior to aging.

Shrink Fits. Cooling the inner member of a complex part to below ambient temperature can be a useful way of providing an interference fit. Care must be taken, however, to avoid the brittle cracking that may develop when the inner member is made of heat-treated steel with high amounts of retained austenite, which converts to martensite on subzero cooling.

Stress Relief

Residual stresses often contribute to part failure and frequently are the result of temperature changes that produce thermal expansion and phase changes, and consequently, volume changes.

Under normal conditions, temperature gradients produce nonuniform dimensional and volume changes. In castings, for example, compressive stresses develop in lower-volume areas, which cool first, and tensile stresses develop in areas of greater volume, which are last to cool. Shear stresses develop between the two areas. Even in large castings and machined parts of relatively uniform thickness, the surface cools first and the core last. In such cases, stresses develop as a result of the phase (volume) change between those layers that transform first and the center portion, which transforms last.

When both volume and phase changes occur in pieces of uneven cross section, normal contractions due to cooling are opposed by transformation expansion. The resulting residual stresses will remain until a means of relief is applied. This type of stress develops most frequently in steels during quenching. The surface becomes martensitic before the interior does. Although the inner austenite can be strained to match this surface change, subsequent interior expansions place the surface martensite under tension when the inner austenite transforms. Cracks in high-carbon steels arise from such stresses.

The use of cold treating has proved beneficial in stress relief of castings and machined parts of even or nonuniform cross section. The following are features of the treatment:

- Transformation of all layers is accomplished when the material reaches -84 °C (-120 °F)
- The increase in volume of the outer martensite is somewhat counteracted by the initial contraction due to chilling
- Rewarm time is more easily controlled than cooling time, allowing equipment flexibility
- The expansion of the inner core due to transformation is somewhat balanced by the expansion of the outer shell
- The chilled parts are more easily handled
- The surface is unaffected by low temperature
- Parts that contain various alloying elements and that are of different sizes and weights can be chilled simultaneously

Advantages of Cold Treating

Unlike heat treating, which requires that temperature be precisely controlled to avoid reversal, successful transformation through cold treating depends only on the attainment of the minimum low temperature and is not affected by lower temperatures. As long as the material is chilled to -84 °C (-120 °F), transformation will occur; additional chilling will not cause reversal.

Time at Temperature. After thorough chilling, additional exposure has no adverse effect. When heat is used, holding time and temperature are critical. In cold treatment, materials of different compositions and of different configurations may be chilled at the same time, even though each may have a different high-temperature transformation point. Moreover, the warm-up rate of a chilled material is not critical as long as uniformity is maintained and gross temperature-gradient variations are avoided.

The cooling rate of a heated piece, however, has a definite influence on the end product. Formation of martensite during solution heat treating assumes immediate quenching to ensure that austenitic decomposition will not result in the formation of bainite and cementite. In large pieces comprising both thick and thin sections, not all areas will cool at the same rate. As a result, surface areas and thin sections may be highly martensitic, and the slower-cooling core may contain as much as 30 to 50% retained austenite. In addition to incomplete transformation, subsequent natural aging induces stress and also results in additional growth after machining.

Aside from transformation, no other metallurgical change takes place as a result of chilling. The surface of the material needs no additional treatment. The use of heat frequently causes scale and other surface deformations that must be removed.

Equipment for Cold Treating

A simple home-type deep freezer can be used for transformation of austenite to martensite. Temperature will be approximately -18 °C (0 °F). In some instances, hardness tests can be used to determine if this type of cold treating will be helpful. Dry ice placed on top of the work in a closed, insulated container also is commonly used for cold treating. The dry ice surface temperature Is -78 °C (-109 °F), but the chamber temperature normally is about -60 °C (-75 °F).

Mechanical refrigeration units with circulating air at approximately -87 °C (-125 °F) are commercially available. A typical unit will have the following dimensions and operational features: chamber volume, up to 2.7 m^3 (95 ft^3); temperature range, 5 to -95 °C (40 to -140 °F); load capacity, 11.3 to 163 kg/h (25 to 360 lb/h); and thermal capacity, up to 8870 kJ/h (8400 Btu/h).

Although liquid nitrogen at -195 °C (-320 °F) may be employed, it is used less frequently than any of the above methods because of its cost.

Cryogenic Treatment of Steels

The value of cryogenic treatment of steel and other materials has been debated for many years; even today many metallurgical professionals have serious reservations about its value. Notwithstanding these concerns, it is the intent of this discussion to review some of the current literature and practices of those who believe that cryogenic treatment enhances steel properties.

Cryogenic Treatment Cycles

Typical cryogenic treatment consists of a slow cool-down (~2.5 °C/min, or 4.5 °F/min) from ambient temperature to liquid nitrogen temperature. When the material reaches approximately 80 K (-315 °F), it is soaked for an appropriate time (generally 24 h). At the end of the soak period, the material is removed from the liquid nitrogen and allowed to warm to room temperature in ambient air. The temperature-time plot for this cryogenic treatment is shown in Fig. 1. By conducting the cool-down cycle in gaseous nitrogen, temperature can be controlled accurately and thermal shock to the material is avoided. Single-cycle tempering is usually performed after cryogenic treatment to improve impact resistance, although double or triple tempering cycles are sometimes used.

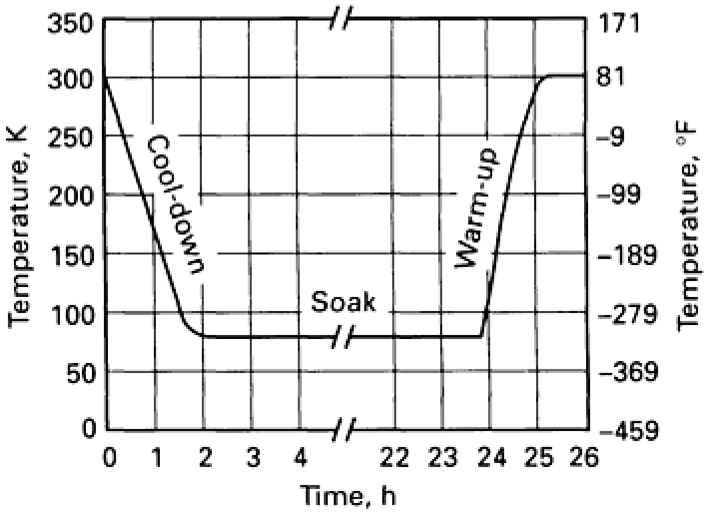


Fig. 1 Plot of temperature versus time for the cryogenic treatment process. Source: Ref 1

Kinetics of Cryogenic Treatment

There are several theories concerning reasons for the effects of cryogenic treatment. One theory involves the more nearly complete transformation of retained austenite into martensite. This theory has been verified by x-ray diffraction measurements. Another theory is based on the strengthening of the material brought about by precipitation of submicroscopic carbides as a result of the cryogenic treatment. Allied with this is the reduction in internal stresses in the martensite that happens when the submicroscopic carbide precipitation occurs. A reduction in microcracking tendencies resulting from reduced internal stresses is also suggested as a reason for improved properties.

The absence of a clear-cut understanding of the mechanism(s) by which cryogenic treatment improves performance has hampered its widespread acceptance by metallurgists. Nonetheless, it is important to review the studies done to determine the effects of cryogenic treatment on the performance of steel in a variety of applications.

Case Studies of Cryogenically Treated Steels

Resistance to abrasive wear was investigated in a parametric study. Five tool steels were tested after conventional heat treatment, after cold treatment at -84 °C (-120 °F), and after being cryogenically treated at -190 °C (-310 °F). Figure 2 and Table 1 show the results of these abrasive wear tests. Cold treatment at -84 °C (-120 °F) improved the wear resistance by 18 to 104%, but the cryogenic treatment results show 104 to 560% improvement.

Table 1 Wear resistance as a function of cryogenic soak temperature for five high-carbon steels. (Data taken in the Department of Mechanical Engineering, Louisiana Tech University, Ruston, Louisiana, April 9-30, 1973).

Alloy	Wear resistance, R_W[(a)]		
	Untreated	Soaked	
		-84 °C (-120 °F)	-190 °C (-310 °F)
52100	25.2	49.3	135
D2	224	308	878

A2	85.6	174.9	565
M2	1961	2308	3993
O1	237	382	996

Source: Ref 2

(a) $R_W = FV/WH_V$, where F is the normal force in newtons, N, pressing the surfaces together; V is the sliding velocity in mm/s; W is the wear rate in mm^3/s; and H_V is the Vickers hardness in MPa. R_W is dimensionless.

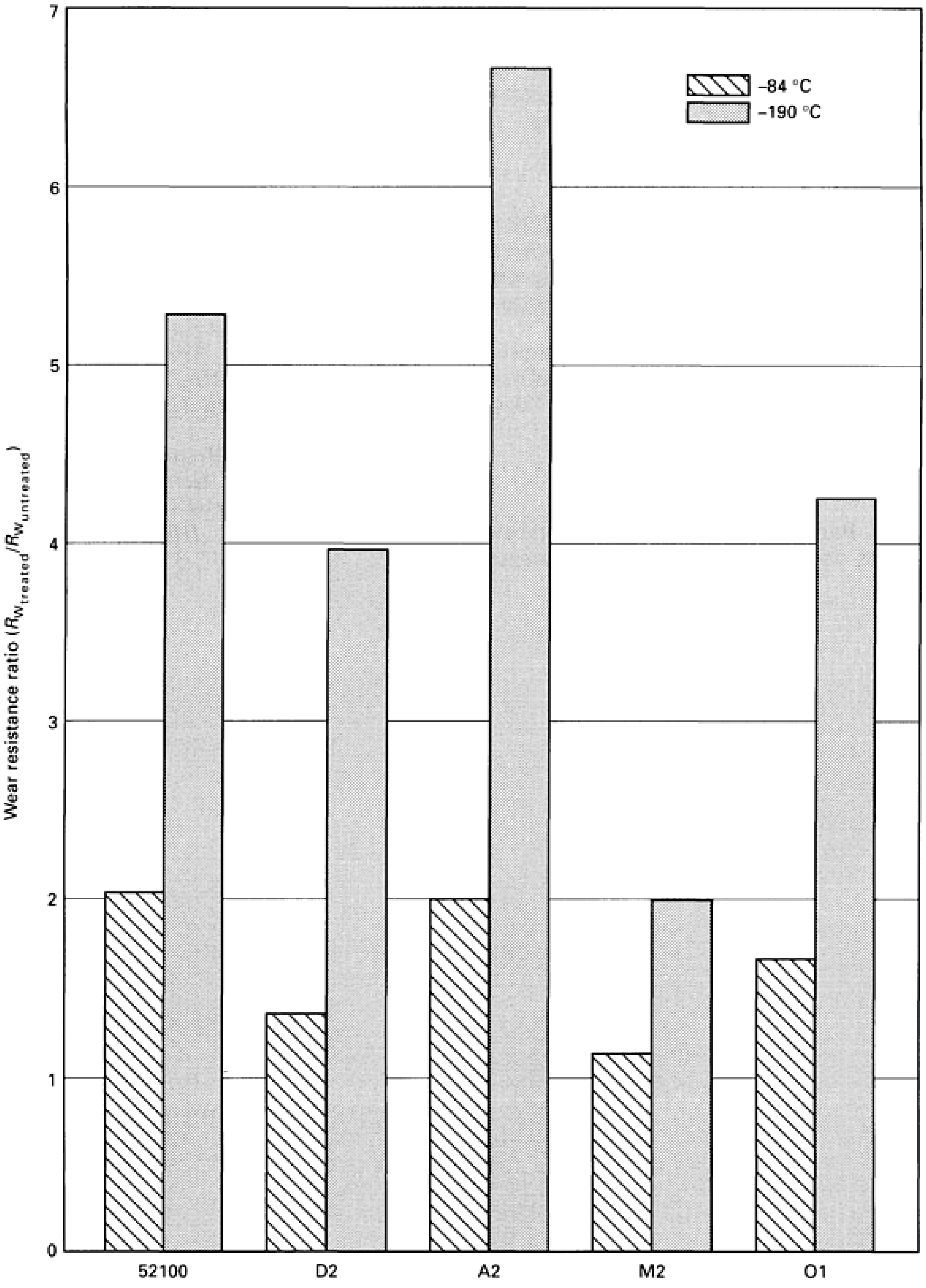


Fig. 2 Comparison of wear-resistance ratios for five high-carbon steels soaked at -84 °C (-120 °F) and at -190 °C (-310 °F). The study also showed that soaking at temperatures below -84 °C (-120 °F) does not significantly change the hardness of the material. The samples were soaked to ensure that their mass was at -84 °C (-120 °F) and -190 °C (-310 °F). Source: Ref 2

Corrosion resistance to water-saturated hydrogen sulfide gas was determined on conventionally processed and cryogenically treated stainless steel and tool steel samples. The results are shown in Table 2. The decrease in corrosion

rate ranged from a modest 1.035 to a significant 1.786. The mechanism Suggested by these data is a refinement in grain boundaries, which limits the diffusion of hydrogen sulfide into the metal. Type 316, an austenitic stainless steel, is susceptible to intergranular corrosion, and apparently refinement of the grain boundaries did not have as much of an effect on the corrosion rate.

Table 2 Corrosion rate of five high-carbon steels exposed for 30 days to a water-saturated hydrogen sulfide gas at a pressure of 2 atm. Test coupons measured 64 × 64 × 1.6 mm (2.5 × 2.5 × 0.062 in.) with a 9.5 mm ($\frac{3}{8}$ in.) hole in the center of the coupon.

Alloy	Composition, wt%										Density		Mass loss				Corrosion rate				Corrosion rate ratio
													Control		Treated		Control		Treated		
	C	Mn	Si	Cr	Ni	V	Mo	W	P	Cu	g/cm^3	lb/in.^{3}	mg	lb × 10^{-3}	mg	lb × 10^{-3}	µm/year	µin./year	µ/year	µin./year	
316	0.04	1.55	0.64	17.18	12.39	. . .	2.07	. . .	0.023	0.52	7.953	0.2873	49.40	0.1089	47.79	0.1054	8.28	331	8.00	320	1.035
410	0.11	0.44	0.38	12.28	0.37	. . .	0.05	. . .	0.024	. . .	7.754	0.2802	67.75	0.1494	63.80	0.1406	11.35	454	10.69	428	1.188
4142	0.42	0.88	0.27	0.95	. . .	. . .	0.20	. . .	0.040	. . .	7.811	0.2822	86.85	0.1915	80.10	0.1766	14.43	577	13.31	532	1.084
S2	0.50	0.50	1.00	. . .	. . .	0.20	0.50	. . .	. . .	. . .	7.315	0.2643	50.1	0.1104	28.1	0.0619	8.89	356	4.98	199	1.786
M1	0.83	0.23	0.39	4.10	. . .	1.81	4.88	6.15	0.017	. . .	8.137	0.2940	27.0	0.0595	22.0	0.0485	4.32	173	3.51	140	1.232

These two scientifically designed studies serve to highlight the effects of cryogenic treatment. Many other case studies with varying results appear in technical journals and engineering publications. The variability of results listed in these articles does not disprove the effectiveness of the cryogenic treatment; however, it does provide a cautionary note to anyone considering cryogenic treatment. The need for study of any potential application should be apparent, and a careful technical and cost-effectiveness analysis should be made before embarking on such a program.

Equipment for Cryogenic Treatment

Liquid nitrogen systems have become the customary method for achieving cryogenic temperatures. The two types of systems are described below.

The heat-exchanger system passes liquid nitrogen through a heat exchanger, and the exhaust gas from the unit is piped into the main gaseous-nitrogen header line. The chamber atmosphere is drawn over the heat-exchanger coils by a fan. In some versions of the system, the cooling is boosted by spraying liquid nitrogen directly into the chamber.

The direct spray system sprays liquid nitrogen directly into the chamber, while a fan circulates the gases over the work. In this system, the spent gas cannot be recovered for use as a furnace atmosphere. The equipment design does not permit the liquid nitrogen to come into direct contact with the work, thereby reducing the probability of thermal shock.

In both systems, temperature controllers are used to control the flow of liquid nitrogen (through a solenoid valve) and to monitor the work temperature. Temperature charts of the cycle provide a record of the processing.

References cited in this section

1. R.F. Barron and R.H. Thompson, Effect of Cryogenic Treatment on Corrosion Resistance, in *Advances in Cryogenic Engineering,* Vol 36, Plenum Press, 1990, p 1375-1379
2. R.F. Barron, "How Cryogenic Treatment Controls Wear," 21st Inter-Plant Tool and Gage Conference, Western Electric Company, Shreveport, LA, 1982

Heat Treating of Ultrahigh-Strength Steels

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Introduction

ULTRAHIGH-STRENGTH STEELS are heat treated by use of equipment and techniques similar to those employed for heat treating constructional alloy steels. With ultrahigh-strength steels, emphasis is placed on the maximum section size that a given alloy will respond to during heat treatment, and thus machining is generally done prior to heat treatment to optimize final property response. The ultrahigh-strength steels ordinarily are quenched and tempered to specific hardnesses, but for critical applications it may be necessary to pull tensile specimens to ensure that a required combination of strength and ductility has been achieved. In still other instances, it may be necessary to conduct impact or fracture-toughness tests to ensure that a required level of resistance to brittle fracture has been attained.

The majority of ultrahigh-strength steels are available in varying quality levels. The quality level is usually dictated by the method of primary or secondary melting used in the manufacture of that alloy. Recent improvements in refining techniques such as argon-oxygen decarburization (AOD) along with vacuum induction melting (VIM) as primary melting techniques are used. Remelting is typically performed with vacuum arc remelting (VAR) techniques to further enhance microstructural cleanliness. Currently some of the grades are being processed by electroslag remelting (ESR). Although heat treatment of the different quality level materials is similar, the premium quality provides increased fracture toughness, tensile ductility, and fatigue life at a given strength level. Some property improvements are given in this article.

Types of High-Strength Steels

Ultrahigh-strength steels, which are classified in Volume 1 of this *ASM Handbook* series as those commercial structural steels capable of a minimum yield strength of 1380 MPa (200 ksi), include several distinctly different families of steels. Three types of ultrahigh-strength steels are:

- Medium-carbon low-alloy steels
- Medium-alloy air-hardening steels
- High-alloy hardenable steels

Of these steels, this article covers only the heat treatment of the medium-carbon low-alloy steels, medium-alloy air-hardening steels, and high-fracture-toughness 9Ni-4Co steels listed in Table 1 . This article does not cover 18 Ni maraging steels, which are described in the article "Heat Treating of Maraging Steels" in this Volume. Ultrahigh-strength steels of the stainless type (martensitic, martensitic precipitation hardenable, semiaustenitic precipitation hardenable, and cold-rolled austenitic steels) are covered in the article "Heat Treating of Stainless Steels" in this Volume.

Table 1 Compositions of ultrahigh-strength steels described in this article

Designation or trade name	**Composition[(a)], %**							
	C	**Mn**	**Si**	**Cr**	**Ni**	**Mo**	**V**	**Co**
Medium-carbon low-alloy steels								
4130	0.28-0.33	0.40-0.60	0.20-0.35	0.80-1.10	. . .	0.15-0.25	. . .	. . .
4140	0.38-0.43	0.75-1.00	0.20-0.35	0.80-1.10	. . .	0.15-0.25	. . .	. . .
4330 Mod (AMS 6411)	0.28-0.33	0.65-1.00	0.15-0.35	0.75-1.00	1.65-2.00	0.35-0.50	0.05-0.10	. . .
4340	0.38-0.43	0.60-0.80	0.20-0.35	0.70-0.90	1.65-2.00	0.20-0.30	. . .	. . .
300M	0.40-0.46	0.65-0.90	1.45-1.80	0.70-0.95	1.65-2.00	0.30-0.45	0.05 min	. . .
D-6A	0.42-0.48	0.60-0.90	0.15-0.30	0.90-1.20	0.40-0.70	0.90-1.10	0.05-0.10	. . .
6150	0.48-0.53	0.70-0.90	0.20-0.35	0.80-1.10	. . .	. . .	0.15-0.25	. . .
8640	0.38-0.43	0.75-1.00	0.20-0.35	0.40-0.60	0.40-0.70	0.15-0.25	. . .	. . .
Medium-alloy air-hardening steels[(b)]								
H11 Mod	0.37-0.43	0.20-0.40	0.80-1.00	4.75-5.25	. . .	1.20-1.40	0.40-0.60	. . .
H13	0.32-0.45	0.20-0.50	0.80-1.20	4.75-5.50	. . .	1.10-1.75	0.80-1.20	. . .

High fracture toughness steels								
AF 1410	0.13-0.17	0.10 max	0.10 max	1.80-2.20	9.50-10.50	0.90-1.10	. . .	13.50-14.50
HP 9-4-20	0.16-0.23	0.20-0.40	0.20 max	0.65-0.85	8.50-9.50	0.90-1.10	0.06-0.12	4.25-4.75
HP 9-4-30	0.29-0.34	0.10-0.35	0.20 max	0.90-1.10	7.0-8.0	0.90-1.10	0.06-0.12	4.25-4.75

(a) Phosphorus and sulfur contents may vary with steelmaking practice. Usually, these steels contain no more than 0.035 P and 0.040 S; 9Ni-4Co steels and premium-quality VAR steels are typically specified to have 0.010 max P and 0.010 max S.

(b) ASTM A 681; composition ranges used by some producers are narrower.

In addition to the steels discussed in this article, many other proprietary and standard steels are used for essentially the same types of applications but at strength levels slightly below the arbitrary lower limit of 1380 MPa (200 ksi) established above for the ultrahigh-strength class of constructionalsteels. Medium-alloy steels such as 4330V and 4335V (vanadium-modified versions of the corresponding AISI standard steels) are among the more widely used steels for yield strengths of 1240 to 1380 MPa (180 to 200 ksi), The medium-carbon low-alloy 8630 steel is also used for yield strengths around 1240 MPa (180 ksi). Finally, certain proprietary steels such as Hy Tuf (a silicon-modified steel similar to 300M) exhibit excellent toughness at strengths to or slightly above 1380 MPa. Hy Tuf has about the same toughness as a maraging steel in this strength range. For properties and other information on steels and strength ranges not discussed here, the reader is referred to sources such as *Aerospace Structural Metals Handbook* (Ref 1) and to producer data sheets.

Decarburization Control. During the heat treatment of high-strength steels, decarburization is very critical. Total decarburization is not acceptable, whereas partial surface decarburization to a depth of 0.075 to 0.125 mm (0.003 to 0.005 in.) is often permitted. Decarburization control can be achieved by the use of:

- Copper plating
- Controlled atmospheres: endothermic (-40 °C dew point), vacuum, or inert gas
- Salt bath heating (limited to maximum of 45 min for 0.075 mm, or 0.003 in., partial decarburization)

More information on this topic is provided in the article "Control of Surface Carbon Content in Heat Treating of Steel" in this Volume. Restoration of carbon is discussed in the article "Evaluation of Carbon Control in Processed Parts" in this Volume.

Heat treatments associated with machining, forming, or welding operations include stress relieving, spheroidizing, or heat treatments to allow adequate machinability. Stress relief, which is used after machining, forming, or welding operations, can be performed either before or after hardening and tempering. Table 2 lists the typical temperatures for stress relief prior to hardening and tempering. Stress relief at about 25 °C (50 °F) below the tempering temperature can also be performed after hardening and tempering.

Table 2 Typical heat-treatment temperatures of various medium-carbon low-alloy steels with yield strengths above 1380 MPa (200 ksi)

Steel type	Normalizing[(a)]	Annealing[(b)]	Hardening[(a)]	Tempering[(c)]	Stress relief[(d)]	Maximum spheroidizing temperature[(e)]

	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F
4130	870-925	1600-1700	830-870	1525-1600	845-870 (WQ) 860-885 (OQ)	1550-1660, or 1575-1625	200-700	400-1300	650-675	1200-1250	760-775	1400-1425
4140	870-900[f]	1600-1650[f]	830-870	1525-1600	840-870 (OQ)	1550-1600[f]	175-230 385-705	350-450, or 725-1300	650-675	1200-1250	760-775	1400-1425
4330 Mod	870-925	1600-1700	830-870	1525-1600	845-870 (OQ)	1550-1600	260-595	500-1100	650-675	1200-1250	. . .	. . .
4340	870-925	1600-1700	830-860	1525-1575	800-830 (OQ)	1475-1525[f]	455-650	850-1200	650-675	1200-1250	750	1375
300M	915-940	1675-1725	See text for spheroidizing		855-885 (OQ)	1575-1625	300	575	. . .	. . .	730	1350
D-6A and D-6AC	925-955[f]	1700-1750[f]	815-860	1500-1575	845-925 (OQ)	1550-1700	315-650	600-1200	540-675	1000-1250	730	1350
6150	870-955	1600-1750	830-860[f]	1525-1575[f]	845-900 (OQ)	1550-1650	200-650	400-1200	650-675	1200-1250	730	1350
8640	870-925	1600-1700	845-870	1550-1600	815-845 (OQ)	1500-1550	200-650	400-1200	650-675	1200-1250	700-720	1300-1325

Note: See the section. "Medium-Carbon Low-Alloy Steels" for possible variations in heating and cooling procedures.

(a) Typical hold time at indicated austenitizing temperatures is about 1 h minimum or 15 to 20 min for each 25 mm (1 in.) of section thickness followed by air cooling (AC), water quenching (WQ), or oil quenching (OQ).

(b) Typical hold time at annealing temperatures is 1 h for each 25 mm (1 in.) of section thickness followed by furnace cooling to about 480 to 540 °C (900 to 1000 °F) at a rate of about 15 °C/h (30 °F/h) but no more than 25 °C/h (50 °F/h).

(c) Minimum tempering times can vary from $\frac{1}{2}$ to 3 h depending on desired properties; snap temper at 175 °C (350 °F) if tempering is not started within 1 h.

(d) These high-temperature stress reliefs are performed prior to hardening and tempering and are used for enhancing machinability or postweld treatment. For stress relief after hardening and tempering, stress relief at 25 °C (50 °F) below the tempering temperature can be used for

machining stress or cold forming.

(e) See the section "Medium-Carbon Low-Alloy Steels" for specification of any intermediate temperatures and cooling procedures.

(f) See text for less-restrictive temperature ranges.

Prior to machining, usual practice for medium-carbon low-alloy steels is to normalize at 870 to 925 °C (1600 to 1700 °F) and temper at 650 to 675 °C (1200 to 1250 °F), or, if the steel is a deep air-hardening grade, to anneal by furnace cooling from 815 to 845 °C (1500 to 1550 °F) to about 540 °C (1000 °F). These treatments impart moderately hard microstructures suitable for machining. If blanks for parts are produced by flame cutting, they are annealed before forming or machining.

Spheroidizing. A very soft spheroidized structure can be obtained by full annealing. Such a structure is not as well suited for machining as the normalized and tempered structure. However, for severe cold-forming operations such as spinning, deep drawing, and wiredrawing, the soft and ductile spheroidized structure is preferred. Spheroidizing treatments are described in the text of this article.

Weld Stress Relief. Welded parts, especially if complex, are Stress relieved immediately after welding. Typical stress-relief temperatures for medium-carbon low-alloy ultrahigh-strength steels are listed in Table 2. Welded parts are stress relieved (and often normalized) prior to hardening and tempering.

Hydrogen Bakeout after Plating. Although hydrogen bakeout is not a standard heat-treatment procedure, it is necessary when ultrahigh-strength steels are exposed to hydrogen, such as in pickling or electroplating operations. Steel parts exposed to hydrogen are susceptible to hydrogen embrittlement when the parts have been heat treated to tensile strengths greater than about 1400 MPa (200 ksi). Ductility can be restored after pickling or electroplating of ultrahigh-strength steels by baking at 185 to 195 °C (365 to 385 °F) for at least 8 h, and for 24 h if thicker than 38 mm ($1\frac{1}{2}$ in.), as soon as possible after pickling or plating.

Reference cited in this section

1. W.F. Brown, Jr., *Aerospace Structural Metals Handbook,* Code 1224, Metals and Ceramics Information Center, 1989, p 1-30

Medium-Carbon Low-Alloy Steels

The medium-carbon low-alloy steels considered in this article are types 4130, 4140, 4330 Mod, 4340, 6150, 8640, and two modifications of 4340, namely, 300M and D-6A. These steels are generally supplied by the mill in either the normalized and tempered or annealed condition and are readily hot forged. To avoid stress cracks resulting from air hardening (especially for geometries with significant variation in section size), the forged part may be slowly cooled in a furnace or in an insulating medium. As previously mentioned, decarburization control is also critical in the heat treatment of these steels.

Alloy 4130 is a water-hardening alloy steel of low to intermediate hardenability. The following standard heat treatments apply to type 4130 steel:

- *Normalizing:* Heat to 870 to 925 °C (1600 to 1700 °F) and hold for a minimum of 1 h or 15 to 20 min per 25 mm (1 in.) of maximum section thickness; air cool. Tempering at 480 °C (900 °F) or above is often done after normalizing to decrease yield strength
- *Annealing:* Heat to 830 to 870 °C (1525 to 1600 °F) and hold for a period that depends on section thickness (Table 2) or furnace load; furnace cool at a rate of about 15 °C/h (30 °F/h) to 480 °C (900 °F) and then air cool
- *Hardening:* Heat to 845 to 870 °C (1550 to 1600 °F) and hold, and then water quench, or heat to 860 to

885 °C (1575 to 1625 °F) and hold, and then oil quench. Holding time depends on section thickness and is typically 1 h minimum or 15 to20 min per 25 mm (1 in.) of maximum section thickness

- *Tempering:* Temper at least $\frac{1}{2}$to 2 h at 200 to 700 °C (400 to 1300 °F); air cool or water quench. Tempering temperature and time at temperature depend mainly on desired hardness or strength
- *Spheroidizing:* Heat to 760 to 775 °C (1400 to 1425 °F) and hold 4 to 12 h; cool slowly

Properties. Table 3 summarizes the typical properties obtained by tempering water-quenched and oil-quenched 4130 steel bars at various temperatures. Because 4130 steel has low hardenability, section thickness must be considered when heat treating to high hardness or strength. Effects of mass on typical properties of heat-treated 4130 steel are indicated in Table 4.

Table 3 Typical mechanical properties of heat-treated 4130 steel

Tempering temperature		**Tensile strength**		**Yield strength**		**Elongation in 50 mm (2 in.), %**	**Reduction in area, %**	**Hardness, HB**	**Izod impact energy**	
°C	**°F**	**MPa**	**ksi**	**MPa**	**ksi**				**J**	**ft · lb**
Water quenched and tempered[(a)]										
205	400	1765	256	1520	220	10.0	33.0	475	18	13
260	500	1670	242	1430	208	11.5	37.0	455	14	10
315	600	1570	228	1340	195	13.0	41.0	425	14	10
370	700	1475	214	1250	182	15.0	45.0	400	20	15
425	800	1380	200	1170	170	16.5	49.0	375	34	25
540	1000	1170	170	1000	145	20.0	56.0	325	81	60
650	1200	965	140	830	120	22.0	63.0	270	135	100
Oil quenched and tempered[(b)]										
205	400	1550	225	1340	195	11.0	38.0	450	. . .	. . .
260	500	1500	218	1275	185	11.5	40.0	440	. . .	. . .
315	600	1420	206	1210	175	12.5	43.0	418	. . .	. . .
370	700	1320	192	1120	162	14.5	48.0	385	. . .	. . .

425	800	1230	178	1030	150	16.5	54.0	360	. . .	. . .
540	1000	1030	150	840	122	20.0	60.0	305	. . .	. . .
650	1200	830	120	670	97	24.0	67.0	250	. . .	. . .

(a) 25 mm (1 in.) diam round bars quenched from 845 to 870 °C (1550 to 1600 °F).

(b) 25 mm (1 in.) diam round bars quenched from 860 °C (1575 °F)

Table 4 Effects of mass on typical properties of heat-treated 4130 steel

Bar size		Tensile strength		Yield strength		Elongation in 50 mm (2 in.), %	Reduction in area, %	Surface hardness, HB
mm	in.	MPa	ksi	MPa	ksi			
25	1	1040	151	880	128	18.0	55.0	307
50	2	740	107	570	83	20.0	58.0	223
75	3	710	103	540	78	22.0	60.0	217

Note: Round bars oil quenched from 845 °C (1550 °F) and tempered at 540 °C (1000 °F); 12.83 mm (0.505 in.) diam tensile

Steel alloy 4140 is similar in composition to 4130 except for a higher carbon content, which imparts greater hardenability and strength. The following standard heat treatments apply to 4140 steel:

- *Normalizing:* Heat to 845 to 925 °C (1550 to 1700 °F) and hold for 1 h minimum or 15 to 20 min per 25 mm (1 in.) of maximum section thickness; air cool. More restrictive normalizing temperatures are listed in Table 2
- *Annealing:* Heat to 830 to 870 °C (1525 to 1600 °F) and hold for a period that depends on section thickness (Table 2) or furnace load; furnace cool at a rate of about 15 °C/h (30 °F/h) to 480 °C (900 °F) and then air cool
- *Hardening:* Heat to 830 to 870 °C (1525 to 1600 °F) and hold; oil quench. (For water quenching, which is rarely used because of the likelihood of cracking, hardening temperatures are 815 to 845 °C, or 1500 to 1550 °F.) Holding time is typically 1 h minimum or 15 to 20 min per 25 mm (1 in.) of maximum section thickness. Polymer quenchants, which preferably should have cooling capabilities similar to that of oil, are less likely than oil to catch fire
- *Tempering:* Temper at least $\frac{1}{2}$ to 2 h at 175 to 230 °C (350 to 450 °F) for "ultra-high" strength, or 385 to 705 °C (725 to 1300 °F) for yield strength below 1380 MPa (200 ksi); air cool or water quench. Tempering temperature and time at temperature depend mainly on desired hardness. To avoid blue brittleness, 4140 usually is not tempered between 230 and 370 °C (450 to 700 °F)
- *Spheroidizing:* Heat to 760 to 775 °C (1400 to 1425 °F) and hold 4 to 12 h; cool slowly

Properties. Table 5 summarizes the mechanical properties obtained by tempering oil-quenched 4140 steel at various temperatures. Because 4140 is not a deep-hardening steel, section size should be considered, especially when specifying heat treatment for high strength levels. The effects of mass on hardness and tensile properties of 4140 steel are shown in Table 6.

Table 5 Typical mechanical properties of heat-treated 4140 steel

Tempering temperature		**Tensile strength**		**Yield strength**		**Elongation in 50 mm (2 in.), %**	**Reduction in area, %**	**Hardness, HB**	**Izod impact energy**	
°C	**°F**	**MPa**	**ksi**	**MPa**	**ksi**				**J**	**ft · lb**
205	400	1965	285	1740	252	11.0	42	578	15	11
260	500	1860	270	1650	240	11.0	44	534	11	8
315	600	1720	250	1570	228	11.5	46	495	9	7
370	700	1590	231	1460	212	12.5	48	461	15	11
425	800	1450	210	1340	195	15.0	50	429	28	21
480	900	1300	188	1210	175	16.0	52	388	46	34
540	1000	1150	167	1050	152	17.5	55	341	65	48
595	1100	1020	148	910	132	19.0	58	311	93	69
650	1200	900	130	790	114	21.0	61	277	112	83
705	1300	810	117	690	100	23.0	65	235	136	100

Table 6 Effects of mass on typical properties of heat-treated 4140 steel

Diameter of bar		**Tensile strength**		**Yield strength**		**Elongation in 50 mm (2 in.), %**	**Reduction in area, %**	**Surface hardness, HB**
mm	**in.**	**MPa**	**ksi**	**MPa**	**ksi**			
25	1	1140	165	985	143	15	50	335
50	2	920	133	750	109	18	55	202

75	3	860	125	655	95	19	55	293

Note: Round bars oil quenched from 845 °C (1550 °F) and tempered at 540 °C (1000 °F); 12.83 mm (0.505 in.) diam tensile specimens cut from center of 25 mm diam bars and from midradius of 50 and 75 mm diam bars

4330 Mod Steel. Type 4330 Mod is a deep-hardening, vanadium-modified steel with improved toughness. Vanadium forms a stable, high-melting-point carbide that acts to pin grain-boundaries, prohibiting grain growth during hot-working operations. The following standard heat treatments apply to 4330 Mod steel:

- *Normalizing:* Heat to 870 to 925 °C (1600 to 1700 °F) for a minimum of 1 h or 15 to 20 min per 25 mm (1 in.) of maximum thickness, and then air cool
- *Annealing:* Heat to 830 to 870 °C (1525 to 1600 °F) for 1 h per 25 mm (1 in.) of maximum thickness, furnace cool (approximately 15 °C/h, or 30 °F/h) to 480 °C (900 °F), and then air cool
- *Hardening:* Heat to 845 to 870 °C (1550 to 1660 °F) for 1 h minimum or about 15 min per 25 mm (1 in.) of maximum thickness, quench in warm oil at 25 to 60 °C (75 to 140 °F), and air cool
- *Tempering:* Temper at least 2 h at 260 to 595 °C (500 to 1100 °F) depending upon desired tensile strength. For ultimate tensile strength of 1515 to 1655 MPa (220 to 240 ksi), temper between 260 and 370 °C (500 to 700 °F)
- *Stress relieving:* After being straightened, formed, or machined, parts may be stress relieved at 650 to 675 °C (1200 to 1250 °F) prior to hardening. Stress relief of hardened material should not exceed tempering temperatures

Properties. Table 7 summarizes the tensile and impact properties obtained by tempering oil-quenched 4330 Mod steel at various temperatures. Through hardening of 4330 Mod steel up to 50 mm (2 in.) in diameter can be achieved by the above practice.

Table 7 Typical properties of heat-treated 4330 Mod steel

Tempering temperature		**Tensile strength**		**Yield strength**		**Elongation in 50 mm (2 in.), %**	**Reduction in area, %**
°C	**°F**	**MPa**	**ksi**	**MPa**	**ksi**		
290	550	1620	235	1345	195	11	51
315	600	1550	225	1297	188	13	55
370	700	1440	209	1248	181	15	59
480	900	1330	193	1185	172	17	60
595	1100	1228	178	1145	166	18	62

4340 Steel. Type 4340, the most popular steel in this class, is a deep-hardening steel. In thin sections, the steel is air hardening, although in practice it is usually oil quenched. The following standard heat treatments apply to 4340 steel:

- *Normalizing:* Heat to 870 to 925 °C (1600 to 1700 °F) and hold for 1 h minimum or 15 to 20 min per 25 mm (1 in.) of maximum section thickness, and then air cool
- *Annealing:* Heat to 830 to 860 °C (1525 to 1575 °F) and hold for a period that depends on section thickness (Table 2) or furnace load; furnace cool at a rate of about 15 °C/h (30 °F/h) to 480 °C (900 °F) and then air cool
- *Hardening:* Heat to 800 to 845 °C (1475 to 1550 °F) and hold 15 min for each 25 mm (1 in.) of thickness (minimum, 15 min); quench in warm oil at 25 to 60 °C (75 to 140 °F). Polymer quenchants (such as Glycol), which preferably have the same cooling capability as oil, are less likely to catch fire than oil quenchants
- *Tempering:* Temper at least 2 h at 455 to 650 °C (850 to 1200 °F); air cool. Double tempering is recommended to optimize yield strength and impact properties. Temperature and time at temperature depend mainly on desired strength or hardness. Tempering below 455 °C (850 °F) is not recommended because of susceptibility to temper embrittlement
- *Spheroidizing:* Preheat to 690 °C (1275 °F) and hold 2 h, increase temperature to 750 °C (1375 °F) and hold 2 h, cool to 650 °C (1200 °F) and hold 6 h, furnace cool to about 600 °C (1100 °F), and finally air cool to room temperature. An alternative schedule is to heat to 730 to 750 °C (1350 to 1375 °F) and hold several hours, and then furnace cool to room temperature
- *Stress relieving:* After straightening, forming, or machining, parts may be stress relieved at 650 to 675 °C (1200 to 1250 °F) prior to hardening. Stress relief of hardened material should not exceed tempering temperatures

Properties. Through hardening of 4340 steel can be achieved by oil quenching round sections up to 75 mm (3 in.) in diameter, and by water quenching larger sections (to the limit of hardenability). The influence of section size on tensile properties of oil-quenched and water-quenched 4340 is indicated by the data in Table 8. However, at this carbon level the possibility of cracking increases significantly for water quenching.

Table 8 Effects of mass on mechanical properties of 4340 steel

Section diameter		Tensile strength		Yield strength		Elongation in 50 mm (2 in.), %	Reduction in area, %	Hardness, HB
mm	in.	MPa	ksi	MPa	ksi			
Oil quenched and tempered[a]								
13	$\frac{1}{2}$	1460	212	1380	200	13	51	. . .
38	$1\frac{1}{2}$	1450	210	1365	198	11	45	. . .
75	3	1420	206	1325	192	10	38	. . .
Water quenched and tempered[b]								
75	3	1055	153	930	135	18	52	340
100	4	1035	150	895	130	17	50	330

150	6	1000	145	850	123	16	44	322

Sources: *Alloy Dig.* and Ref 2

(a) Austenitized at 845 °C (1550 °F); tempered at 425 °C (800 °F).

(b) 75 mm (3 in.) diam bar austenitized at 800 °C (1475 °F); 100 and 150 mm (4 and 6 in.) diam bars austenitized at 815 °C (1500 °F). All sizes tempered at 650 °C (1200 °F). Test specimens taken at midradius.

Hardness of type 4340 as a function of tempering temperature is plotted in Fig. 1. Typical mechanical properties of oil-quenched 4340 are given in Table 9. Additional data on mechanical properties (notch toughness and fracture toughness) of this steel tempered to different hardnesses are given in Table 10.

Table 9 Typical mechanical properties of 4340 steel

Tempering temperature		**Tensile strength**		**Yield strength**		**Elongation in 50 mm (2 in.), %**	**Reduction in area, %**	**Hardness**		**Izod impact energy**	
°C	**°F**	**MPa**	**ksi**	**MPa**	**ksi**			**HB**	**HRC**	**J**	**ft · lb**
205	400	1980	287	1860	270	11	39	520	53	20	15
315	600	1760	255	1620	235	12	44	490	49.5	14	10
425	800	1500	217	1365	198	14	48	440	46	16	12
540	1000	1240	180	1160	168	17	53	360	39	47	35
650	1200	1020	148	860	125	20	60	290	31	100	74
705	1300	860	125	740	108	23	63	250	24	102	75

Table 10 Notch toughness and fracture toughness of 4340 steel tempered to different hardnesses

Hardness, HB	**Equivalent tensile strength[(a)]**		**Charpy V-notch impact energy**		**Plane-strain fracture toughness**	
	MPa	**ksi**	**J**	**ft · lb**	**MPa** $\sqrt{m}$	**ksi** $\sqrt{in}$
550	2040	296	19	14	53	48
430	1520	220	30	22	75	68

380	1290	187	42	31	110	100

(a) Estimated from hardness

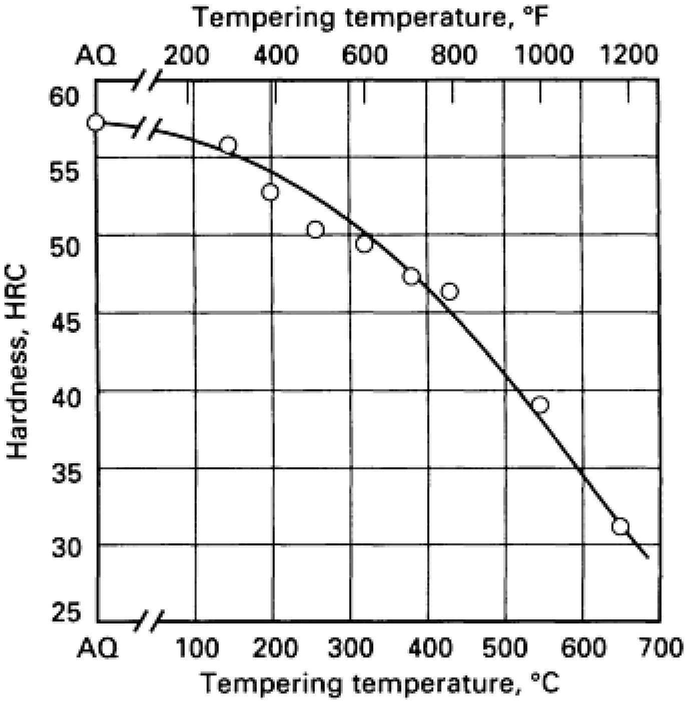

Fig. 1 Variation for hardness with tempering temperature of 4340 steel. All specimens oil quenched from 845 °C (1550 °F) and tempered 2 h at temperature. AQ, as-quenched

Alloy 300M is a silicon-modified (1.6% Si) 4340 steel that is slightly higher in carbon and molybdenum and also contains vanadium. Silicon is added to allow higher tempering temperatures, thereby improving toughness. The steel exhibits deep hardenability. Because of its high silicon and molybdenum contents, 300M is more prone to decarburization than the steels so far described; and during heat treating, care should be exercised to avoid decarburization. The following standard heat treatments apply to 300M steel:

- *Normalizing:* Heat to 915 to 940 °C (1675 to 1725 °F) and hold for 15 to 20 min per 25 mm (1 in.) of section thickness; air cool. If normalizing is done to enhance machinability, it should be tempered at 650 to 675 °C (1200 to 1250 °F)
- *Hardening:* Austenitize at 855 to 885 °C (1575 to 1625 °F). Oil quench to below 70 °C (160 °F); or quench in salt at 200 to 210 °C (390 to 410 °F), hold 10 min, and then air cool to 70 °C (160 °F) or below. For optimum dimensional stability, aus-bay quench into a furnace or salt bath at 525 °C (975 °F), equalize at temperature, quench in oil at 60 °C (140 °F) or salt at 205 °C (400 °F), and air cool
- *Tempering:* Temper 2 to 4 h at 300 ± 15 °C (575 ± 25 °F) double tempering is recommended. This procedure produces the best combination of high yield strength and high impact properties. Tempering above or below 300 °C (575 °F) results in severe deterioration of properties
- *Spheroidizing:* Heat to temperatures no higher than 730 °C (1350 °F) and hold for a period that depends on section thickness or furnace load. Temperatures above 730 °C (1350 °F) result in possible decarburization and transformation. Cool to 650 °C (1200 °F) at a rate no faster than 5.5 °C/h (10 °F/h), cool to 480 °C (900 °F) no faster than 10 °C/h (20 °F/h), and finally air cool to room temperature
- *Annealing:* Same schedule as for spheroidizing

Properties. Variations in hardness and mechanical properties of 300M with tempering temperature are presented in Table 11. This steel has deep hardenability; therefore, heat-treated bars 75 mm (3 in.) in diameter have essentially the same tensile properties as bars 25 mm (1 in.) in diameter. Reductions in tensile strength, ductility, and impact strength, however, are observed in heat-treated bars 145 mm ($5\frac{3}{4}$ in.) in diameter. Variations in properties of 300M with section size are presented in Table 12.

Table 11 Typical mechanical properties of 300M steel

Tempering temperature		Tensile strength		Yield strength		Elongation in 50 mm (2 in.), %	Reduction in area, %	Charpy V-notch impact energy		Hardness, HRC
°C	°F	MPa	ksi	MPa	ksi			J	ft · lb	
90	200	2340	340	1240	180	6.0	10.0	17.6	13.0	56.0
205	400	2140	310	1650	240	7.0	27.0	21.7	16.0	54.5
260	500	2050	297	1670	242	8.0	32.0	24.4	18.0	54.0
315	600	1990	289	1690	245	9.5	34.0	29.8	22.0	53.0
370	700	1930	280	1620	235	9.0	32.0	23.7	17.5	51.0
425	800	1790	260	1480	215	8.5	23.0	13.6	10.0	45.5

Table 12 Effects of mass on tensile and impact properties of 300M steel

Bar diameter		Tensile strength		Yield strength		Elongation in 50 mm (2 in.), %	Reduction in area, %	Charpy V-notch impact energy when tested at					
								21 °C (70 °F)		-46 °C (-50 °F)		-73 °C (-100 °F)	
mm	in.	MPa	ksi	MPa	ksi			J	ft · lb	J	ft · lb	J	ft · lb
25	1	1990	289	1690	245	9.5	34.1	30	22	26	19	24	18
75	3	1940	281	1630	236	9.5	35.0	26	19	19	14	12	9

(a) Note: Round bars, normalized at 900 °C (1650 °F), oil quenched from 860 °C (1575 °F), and tempered at 315 °C (600 °F)

D-6A and D-6AC. D-6A was designed by Ladish Company for use at room temperature at tensile strengths of 1800 to 2000 MPa (260 to 290 ksi). It is deeper hardening than 4340. The alloy is called D-6A when produced by air melting in an electric furnace and D-6AC when produced by air melting followed by VAR. Except for improvements in steel cleanliness and mechanical properties of D-6AC caused by melting practice (see Table 13), the characteristics of the two steels are similar.

Table 13 Typical fracture toughness of D-6AC with either EAF-VAR or EAF-AOD-VAR steel-making methods

	Tensile strength		**Yield strength**		**Elongation in 50 mm (2 in.), %**	**Reduction in area, %**	**Fracture toughness**	
	MPa	**ksi**	**MPa**	**ksi**			**MPa $\sqrt{m}$**	**(ksi $\sqrt{in}$)**
EAF/VAR								
5-Heat average	1434	208	1324	192	14	50	110	100
5-Heat range	1373-1469	199-213	1270-1352	184-196	14-15	48-52	107-114	98-104
EAF/AOD/VAR								
5-Heat average	1448	210	1345	195	14	52	122	111
5-Heat range	1435-1462	208-212	1330-1365	193-198	14-15	51-53	114-127	104-116

Note: All samples longitudinal direction after normalized at 900 °C (1650 °F), austenitized at 865 °C (1615 °F) 1 h, salt quenched at 163 °C (325 °F), and double tempered at 570 °C (1085 °F). Each heat tested at 3 locations

The following standard heat treatments apply to D-6A and D-6AC steels:

- *Normalizing:* Heat to 870 to 955 °C (1600 to 1750 °F) and hold for 15 to 20 min per 25 mm (1 in.) of section thickness; air cool. More restrictive normalizing temperatures are listed in Table 2
- *Annealing:* Heat to 815 to 860 °C (1500 to 1575 °F) and hold for a period that depends on section thickness (Table 2) or furnace load; furnace cool to 540 °C (1000 °F) at a rate no faster than 28 °C/h (50 °F/h), and then air cool to room temperature. Alternatively, normalizing followed by a 690 to 705 °C (1275 to 1300 °F) temper (with 1 h hold for each inch of section thickness) will result in hardness/machinability comparable to annealing at lower overall furnace time
- *Hardening:* Austenitize at 845 to 940 °C (1550 to 1725 °F) for $\frac{1}{2}$ to 2 h. Sections no larger than 25 mm (1 in.) in thickness or diameter can be air cooled. Larger sections can be oil quenched to 65 °C (150 °F) or salt quenched to 205 °C (400 °F) and then air cooled. For optimum dimensional stability, aus-bay quench into a furnace or salt bath at 525 °C (975 °F), equalize the temperature, and then quench in an oil bath held at 60 °C (140 °F), or quench in 205 °C (400 °F) salt (marquenching) and air cool (see Fig. 2). The cooling rate during quenching significantly affects fracture toughness. For high fracture toughness (with some associated reduction in ultimate tensile strength), especially in heavy sections, austenitize at 925 °C (1700 °F), aus-bay quench to 525 °C (975 °F), equalize temperature, and oil quench to 60 °C (140 °F)
- *Tempering:* Immediately after hardening, temper 2 to 4 h in the range 315 to 650 °C (600 to 1200 °F), depending on desired strength or hardness. Double tempering is recommended to optimize yield strength and impact toughness

- *Spheroidizing:* Heat to no more than 730 °C (1350 °F) because of excessive decarburization and possible transformation. Hold at temperature for 5 to 6 h; furnace cool to 690 °C (1275 °F) and hold 10 h; furnace cool to 650 °C (1200 °F) and hold 8 h; air cool to room temperature
- *Stress relieving:* Heat to a temperature from 540 to 675 °C (1000 to 1250 °F) and hold for 1 to 2 h; air cool. For hardened material, stress relieve at about 25 °C (50 °F) below the tempering temperature

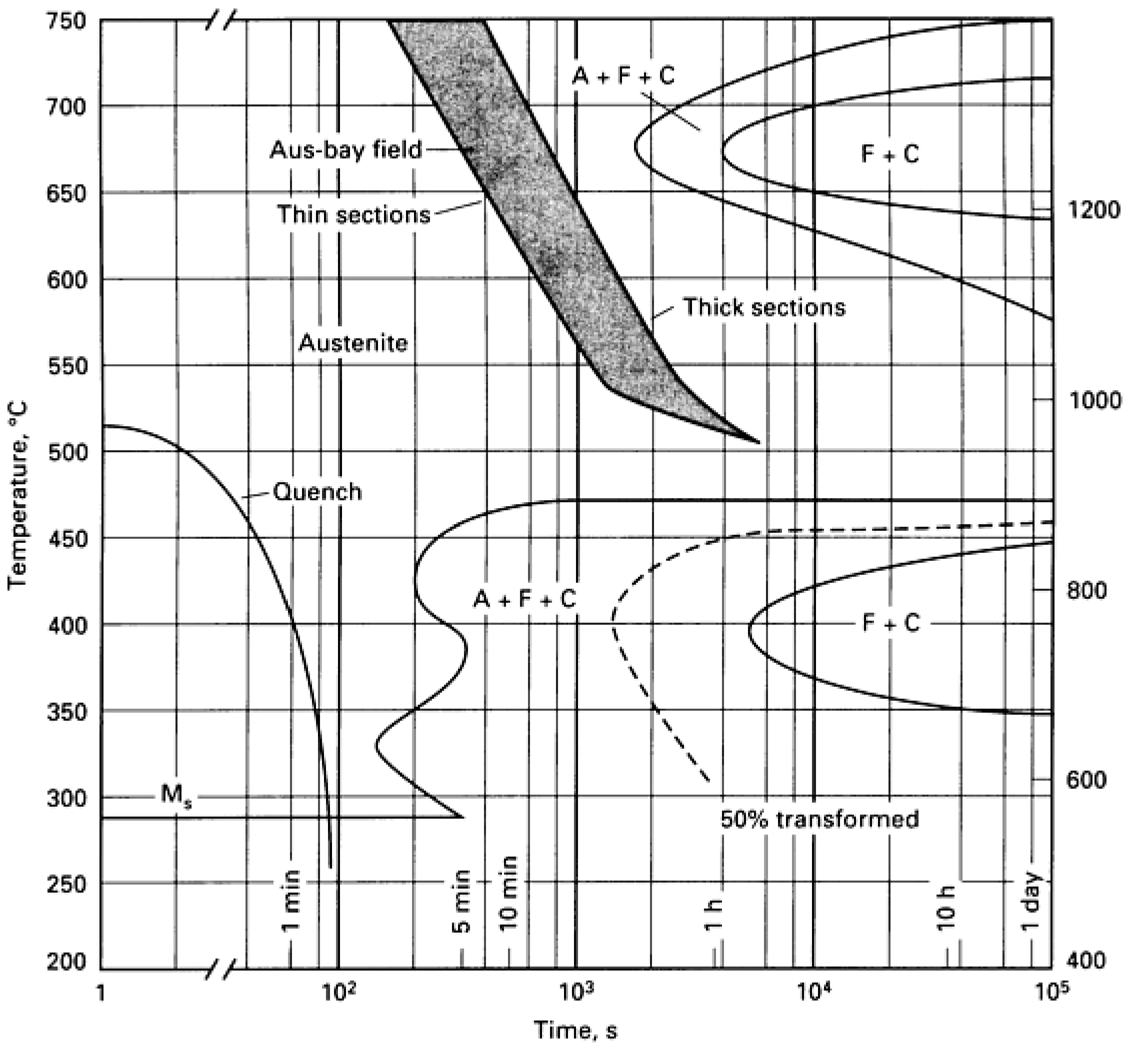

Fig. 2 Aus-bay quenching for improved dimensional stability. D-6AC has an isothermal transformation diagram characterized by a deep, wide austenitic bay region. Because of this bay, heat treaters can cool parts of varying cross sections to below 540 °C (1000 °F) at the indicated rates, hold them in the bay until all sections are at the intermediate temperature, and then quench them in hot oil or a salt bath. Cooling curves around the aus-bay region indicate the procedure.

Properties. Typical room-temperature hardness of D-6A steel bar as a function of tempering temperature is plotted in Fig. 3; other typical mechanical properties of D-6AC bar are given in Table 14. Tensile properties of heat-treated D-6AC billet material are given in Table 15. Fracture toughness levels for products with varying quench rates are given in Table 16.

Table 14 Typical mechanical properties of D-6A steel bar

Tempering temperature		Tensile strength		Yield strength		Elongation in 50 mm (2 in.), %	Reduction in area, %	Charpy V-notch impact energy	
°C	°F	MPa	ksi	MPa	ksi			J	ft · lb

150	300	2060	299	1450	211	8.5	19.0	14	10
205	400	2000	290	1620	235	8.9	25.7	15	11
315	600	1840	267	1700	247	8.1	30.0	16	12
425	800	1630	236	1570	228	9.6	36.8	16	12
540	1000	1450	210	1410	204	13.0	45.5	26	19
650	1200	1030	150	970	141	18.4	60.8	41	30

Note: Normalized at 900 °C (1650 °F), oil quenched from 845 °C (1550 °F), and tempered at various temperatures

Table 15 Typical tensile properties of double-tempered D-6AC billet

Second tempering temperature		**Tensile strength**		**Yield strength**		**Elongation in 50 mm (2 in.), %**	**Reduction in area, %**
°C	**°F**	**MPa**	**ksi**	**MPa**	**ksi**		
480	900	1686.5	244.6	1540.3	223.4	11.1	40.0
510	950	1652.7	239.7	1519.7	220.4	13.2	44.1
540	1000	1613.4	234.0	1483.8	215.2	13.7	47.2

Note: Austenitized 1 h at 900 °C (1650 °F), quenched in fused salt at 205 °C (400 °F) and held 5 min, and then air cooled to room

Table 16 Plane-strain fracture toughness of D-6AC in the long transverse direction

Condition for plate and forging	**Product form**	**K_{IC} range**		**K_{IC} average**	
		MPa $\sqrt{m}$	**ksi $\sqrt{in}$**	**MPa $\sqrt{m}$**	**ksi $\sqrt{in}$**
Quench in 60 °C oil					
Austenitize at 925 °C (1700 °F), aus-bay quench to 525 °C (975 °F) in furnace, quench in 60 °C (140 °F) oil, temper 2 + 2 h at 540 °C (1000 °F), and AC	2 mm (0.8 in.) plate 2 mm (0.8 in.) and 40-45 mm (1.5-1.8 in.) forging (CVM)	91-112	83-102	104[a]	95[a]
		93-120	85-109	104[b]	95[b]

Slack quench					
Austenitize at 900 °C (1650 °F), aus-bay quench to 525 °C (975 °F) in furnace, quench in 205 °C (400 °F) salt, temper 2 + 2 h at 540 to 550 °C (1000 to 1025 °F), and AC	2 mm (0.8 in.) plate 2 mm (0.8 in.) and 40-45 mm (1.5-1.8 in.) forging (CVM)	48-100	44-91	70(c)	64(c)
		52-105	47-96	71(d)	65(d)

Note: AC, air cool; CVM, consumable-electrode vacuum remelted.

(a) Average of 21 tests.

(b) Average of 34 tests.

(c) Average of 82 tests.

(d) Average of 60 tests

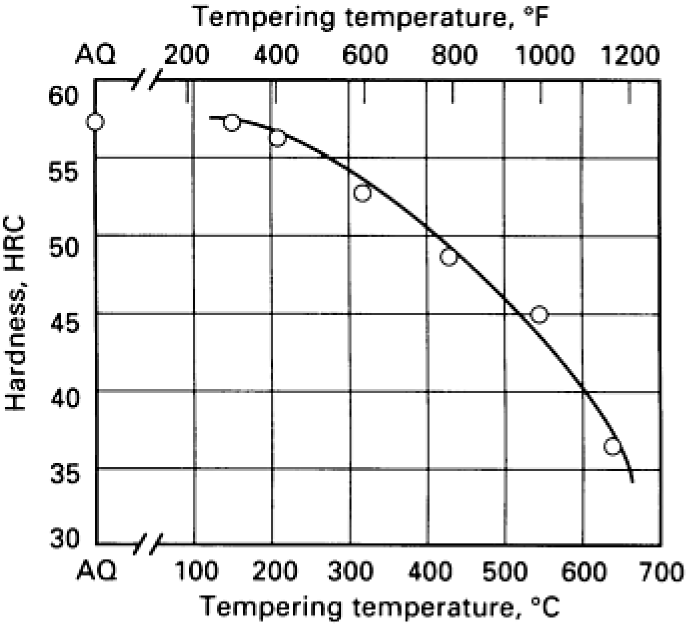

Fig. 3 Variation for hardness with tempering temperature for D-6A steel. All specimens oil quenched from 845 °C (1550 °F) and tempered 2 h at temperature. AQ, as-quenched

6150 Steel. Type 6150 can be considered an ultrahigh-strength steel, although as a constructional steel it is not as popular as the other steels in this class. It is a shallow-hardening steel. Parts made of 6150 can be readily welded; after welding, parts should be normalized, and then hardened and tempered to the desired hardness.

The following heat treatments apply to 6150 steel:

- *Normalizing:* Heat to 870 to 955 °C (1600 to 1750 °F) and hold for about 15 to 20 min per 25 mm (1

in.) of section thickness; air cool

- *Annealing:* Heat to 845 to 900 °C (1550 to 1650 °F) and hold for a period that depends on section thickness (Table 2) or furnace load; furnace cool at a rate of about 15 °C/h (30 °F/h) to 480 to 540 °C (900 to 1000 °F) and then air cool. More restrictive temperatures are listed in Table 2
- *Hardening:* Austenitize at 845 to 900 °C (1550 to 1650 °F); oil quench
- *Tempering:* Temper at least $\frac{1}{2}$ to 2 h at 200 to 650 °C (400 to 1200 °F); oil quench. The spring temper is at 385 to 480 °C (725 to 900 °F)
- *Austempering:* Austenitize in a salt bath at 845 to 900 °C (1550 to 1650 °F); quench in a salt bath at 230 to 315 °C (450 to 500 °F), hold 20 to 30 min, and then oil quench or air cool to room temperature
- *Martempering:* Austenitize in a salt bath at 845 to 870 °C (1550 to 1600 °F); quench in a salt bath at 230 to 260 °C (450 to 500 °F), equalize, and then air cool or quench to room temperature. Temper to desired hardness
- *Spheroidizing:* Heat to no more than 730 °C (1350 °F) because of danger of decarburization; hold until heated through, furnace cool to 650 °C (1200 °F) and hold several hours, followed by furnace cooling to about 425 °C (800 °F) before air cooling to room temperature

Properties. Typical mechanical properties of small-diameter round sections of 6150 tempered at various temperatures are given in Table 17. Hardness and Izod impact energy as functions of tempering temperature are plotted in Fig. 4. The effects of section size on tensile properties and hardness are given in Table 18.

Table 17 Typical room-temperature tensile properties of heat-treated 6150 steel

Tempering temperature		Tensile strength		Yield strength		Elongation in 50 mm (2 in.), %	Reduction in area, %	Hardness, HB	Izod impact energy	
°C	°F	MPa	ksi	MPa	ksi				J	ft · lb
Round bars, 14 mm (0.55 in.) in diameter[(a)]										
205	400	2050	298	1810	263	1	5	610	. . .	. . .
260	500	2070	300	1810	263	4	12	570	. . .	. . .
315	600	1950	283	1720	250	7	27	540	. . .	. . .
370	700	1770	257	1620	235	10	37	505	9	7
425	800	1585	230	1490	216	11	42	470	14	10
480	900	1410	204	1340	195	12	44	420	16	12
540	1000	1250	182	1210	175	13	46	380	20	15
595	1100	1150	167	1080	157	16	47	350	28	21

Round bars, 25 mm (1 in.) in diameter[b]										
425	800	1570	228	1450	210	10	37	461	. . .	. . .
480	900	1360	197	1210	175	11	41	401	. . .	. . .
540	1000	1180	171	1030	150	12	45	341	. . .	. . .
595	1100	1030	150	875	127	15	50	302	. . .	. . .
650	1200	920	133	760	110	19	55	262	. . .	. . .
705	1300	810	118	660	96	23	61	235	. . .	. . .

(a) Normalized at 870 °C (1600 °F), oil quenched from 860 °C (1575 °F), and tempered at various temperatures.

(b) Oil quenched from 860 °C and tempered at various temperatures

Table 18 Effects of mass on typical properties of heat-treated 6150 steel

Bar size		Tensile strength		Yield strength		Elongation in 50 mm (2 in.), %	Reduction in area, %	Hardness, HB
mm	in.	MPa	ksi	MPa	ksi			
25	1	1185	172	1040	151	14	45	341
50	2	1170	170	1030	149	13	48	341
75	3	1090	158	950	138	13	47	331

Note: Round bars, oil quenched from 830 °C (1525 °F) and tempered at 540 °C (1000 °F), 12.83 mm (0.505 in.) diam tensile

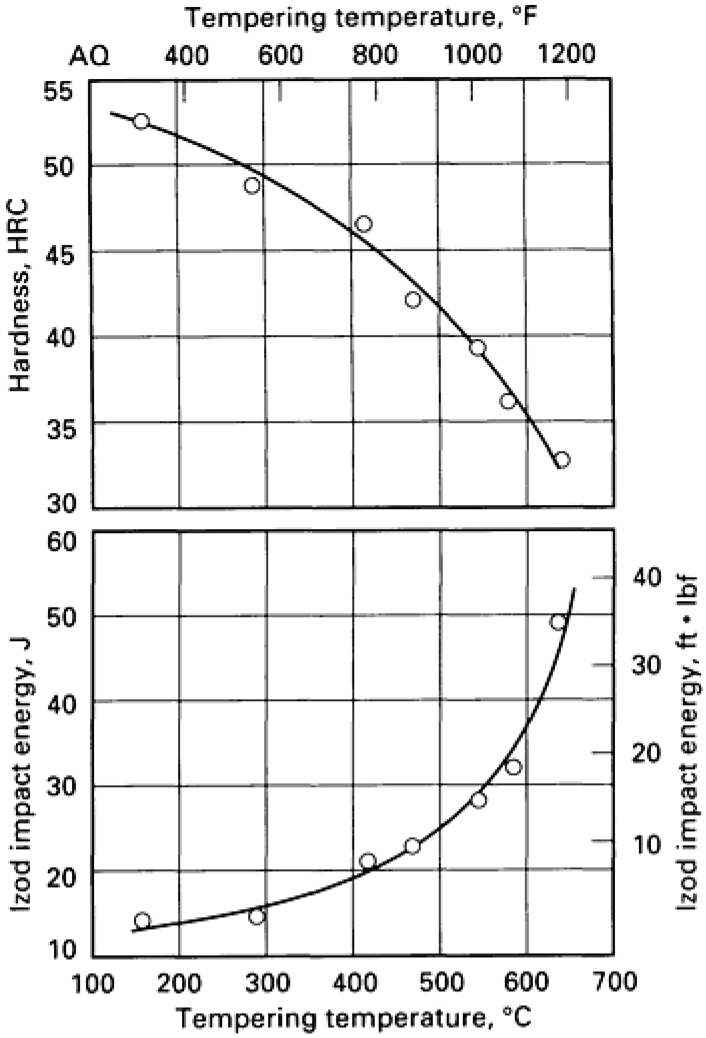

Fig. 4 Variation for hardness and impact energy with tempering temperature for 6150 steel. Specimens oil quenched from 885 °C (1625 °F) and tempered 2 h at temperature

Type 8640 steel was designed especially for maximum hardenability and the best combination of properties with minimum alloying additions. It is an oil-hardening steel but may be water hardened if precautions are taken to prevent cracking.

The following standard treatments apply to 8640 steel:

- *Normalizing:* Heat to 870 to 925 °C (1600 to 1700 °F) and hold for about 15 to 20 min per 25 mm (1 in.) of section thickness; air cool
- *Annealing:* Heat to 845 to 870 °C (1550 to 1600 °F) and hold for a period that depends on section thickness (Table 2) or furnace load; furnace cool at a rate of about 15 °C/h (30 °F/h) to 480 to 540 °C (900 to 1000 °F) and then air cool
- *Hardening:* Austenitize at 815 to 845 °C (1500 to 1550 °F); quench in oil or warm water at 45 to 60 °C (110 to 140 °F)
- *Tempering:* Temper at least $\frac{1}{2}$ to 2 h at 200 to 650 °C (400 to 1200 °F). Temperature and time at temperature depend on desired hardness
- *Spheroidizing:* Heat to 700 to 720 °C (1300 to 1325 °F) and hold several hours; furnace cool

Properties. Variations in typical properties of heat-treated round sections of 8640 with tempering temperature are given in Table 19. Variations in properties with section size (mass effect) are given in Table 20.

Table 19 Typical room-temperature mechanical properties of 8640 steel

Tempering temperature		**Tensile strength**		**Yield strength**		**Elongation in 50 mm (2 in.), %**	**Reduction in area, %**	**Impact energy**		**Hardness**	
°C	**°F**	**MPa**	**ksi**	**MPa**	**ksi**			**J**	**ft · lb**	**HB**	**HRC**
Round bars, 13.5 mm (0.53 in.) in diameter[(a)]											
205	400	1810	263	1670	242	8.0	25.8	11.5[(b)]	8.5[(b)]	555	55
315	600	1585	230	1430	208	9.0	37.3	15.6[(b)]	11.5[(b)]	461	48
425	800	1380	200	1230	179	10.5	46.3	27.8[(b)]	20.5[(b)]	415	44
540	1000	1170	170	1050	152	14.0	53.3	56.3[(b)]	41.5[(b)]	341	37
650	1200	870	126	760	110	20.5	61.0	96.9[(b)]	71.5[(b)]	269	28
Round bars, 25 mm (1 in.) in diameter[(a)]											
425	800	1382	200.5	1230	179	10	46	27[(c)]	20[(c)]	415	44
480	900	1250	181	1120	162	13	51	41[(c)]	30[(c)]	388	42
540	1000	1070	155	940	137	17	56	54[(c)]	40[(c)]	331	36
595	1100	1020	148	910	132	16	57	73[(c)]	54[(c)]	302	32

(a) Oil quenched from 830 °C (1525 °F) and tempered at indicated temperature.

(b) Izod.

(c) Charpy V-notch

Table 20 Effects of mass on typical properties of heat-treated 8640 steel

Bar size	**Tensile strength**	**Yield strength**	**Elongation in 50 mm**	**Reduction in area, %**	**Surface hardness,**

mm	in.	MPa	ksi	MPa	ksi	(2 in.), %	in area, %	HB
25	1	1070	155	940	137	17	56	331
50	2	910	132	770	112	18	57	293
75	3	860	125	710	103	19	58	277

Note: Oil quenched from 830 °C (1525 °F) and tempered at 540 °C (1000 °F)

Reference cited in this section

2. A.M. Hall, Sr., *Introduction to Today's Ultrahigh-Strength Structural Steels,* STP 498, American Society for Testing and Materials, 1971

Medium-Alloy Air-Hardening Steels

Heat treatments for ultrahigh-strength steels H11 Mod and H13, which are also known as 5% Cr hot-work die steels, are discussed in this section. These steels are similar in composition, heat treatment, and many properties. They have deep hardenability and can be hardened through in large sections by air cooling. Air hardening results in minimal residual stresses after hardening. Both H11 Mod and H13 are secondary hardening steels, and thus develop optimum properties when tempered at temperatures above the secondary hardening peaks at about 510 °C (950 °F). These high tempering temperatures provide substantial stress relief and stabilization of properties so that steels can be used to advantage at elevated temperatures. This also enables heat-treated parts to be warm worked or preheated for welding at temperatures as high as 55 °C (100 °F) below the prior tempering temperature.

Because H11 Mod and H13 are air-hardening steels, forged parts must be cooled slowly after forging to prevent stress cracking. After forging, parts should be charged into a furnace at about 790 °C (1450 °F), soaked until the temperature is uniform, and then slowly cooled, either in the furnace or in an insulating medium such as ashes, lime, mica, or silocel. When the forgings have cooled, they should be spheroidize annealed. Weldments, especially heavy-section weldments, should be cooled slowly in a furnace heated to the preheating temperature or in an insulating medium immediately after welding. After being cooled, weldments should be given a full spheroidizing anneal.

H11 Mod. This steel is a modification of the martensitic hot-work die steel H11, the significant difference being the slightly higher carbon content of H11 Mod. The following standard heat treatments apply to H11 Mod steel:

- *Normalizing:* This method is generally not recommended. For effective homogenization, heat to about 1065 °C (1950 °F), soak 1 h for each 25 mm (1 in.) of thickness, and air cool. Anneal immediately after the steel reaches room temperature. There is a possibility that H11 Mod may crack during this treatment, especially if the surface is significantly decarburized
- *Annealing:* Heat to 845 to 900 °C (1550 to 1650 °F) in a furnace, preferably one with controlled atmosphere, and hold to equalize temperature; cool very slowly in the furnace to about 480 °C (900 °F) and then more rapidly to room temperature. This treatment should produce a fully spheroidized microstructure free of grain-boundary carbide networks
- *Hardening:* Preheat to 760 to 815 °C (1400 to 1500 °F) and then raise the temperature to 995 to 1025 °C (1825 to 1875 °F) and hold 20 min plus 5 min for each 25 mm (1 in.) of thickness (minimum, 25 min); air cool in still air. This can be done conveniently in a neutral salt bath or a controlled-atmosphere furnace. For a few applications, oil quenching from the low end of the hardening temperature range may be done. Air cooling, which produces less distortion than oil quenching, is more commonly employed
- *Tempering:* Temper at the secondary hardening peak temperature of about 540 °C (1000 °F) for maximum hardness and strength, or preferably above the secondary peak to temper back to a lower hardness or strength with improved ductility and toughness. A minimum of 2 h at temperature should be

allowed, but it is preferable to double temper parts (2 h at temperature, cool to room temperature, and then 2 h more at ~15 °C, or 25 °F, above the previous temperature). Triple tempering is even more desirable, especially for critical parts. For high-temperature applications, parts should be tempered at a temperature above the maximum service temperature to guard against unwanted changes in properties during service

- *Stress relieving:* Heat to 650 to 675 °C (1200 to 1250 °F); cool slowly to room temperature. This treatment is often used to achieve greater dimensional accuracy in heat-treated parts by stress relieving rough-machined parts, finish machining them, and finally heat treating to the desired hardness
- *Nitriding:* For increased wear resistance, finish-machined and heat-treated parts may be nitrided. The nitriding operation can be considered as the second temper of a double-tempering operation. The parts should be gas or liquid nitrided at about 525 °C (980 °F). The nitrided case depth depends on time at temperature. For example, gas nitriding in 20 to 30% dissociated ammonia for 8 to 48 h normally produces a case depth of about 0.2 to 0.35 mm (0.008 to 0.014 in.)

Properties. Variation of hardness with tempering temperature for H11 Mod is plotted in Fig. 5. Variations in typical room-temperature longitudinal mechanical properties with tempering temperature are given in Table 21. As an indication of the deep air hardenability of this steel (to depths greater than 300 mm, or 12 in.), the transverse tensile strength and ductility obtained in large billets of air-melted and VAR H11 Mod are given in Table 22, which also shows improvement in ductility resulting from VAR. Each value is the average of four tests: two from the top and two from the bottom of the ingot.

Table 21 Typical longitudinal mechanical properties of H11 Mod steel

Tempering temperature		Tensile strength		Yield strength		Elongation in 50 mm (2 in.), %	Reduction in area, %	Charpy V-notch impact energy		Hardness, HRC
°C	°F	MPa	ksi	MPa	ksi			J	ft · lb	
510	950	2120	308	1710	248	5.9	29.5	13.6	10.0	56.5
540	1000	2010	291	1675	243	9.6	30.6	21.0	15.5	56.0
565	1050	1850	269	1565	227	11.0	34.5	26.4	19.5	52.0
595	1100	1540	223	1320	192	13.1	39.3	31.2	23.0	45.0
650	1200	1060	154	850	124	14.1	41.2	40.0	29.5	33.0
705	1300	940	136	700	101	16.4	42.2	90.6	66.8	29.0

Table 22 Effect of billet size and melting method on typical transverse strength and ductility of H11 Mod steel

Billet size		Melting method	Tensile strength		Reduction in area, %
mm	in.		MPa	ksi	

150 by 150	6 by 6	Air	1965	285	16.1
		VAR	1985	288	25.7
300 by 300	12 by 12	Air	1972	286	7.2
		VAR	2013	292	19.7

Note: Air cooled from 1010 °C (1850 °F); triple tempered, 2 + 2 + 2 h at 540 °C (1000 °F)

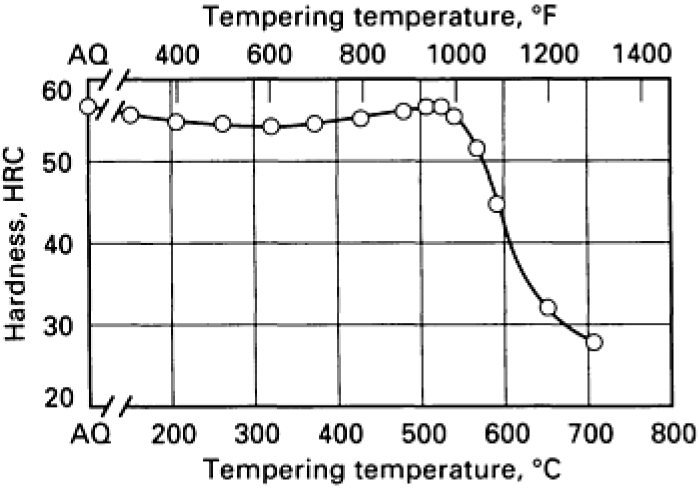

Fig. 5 Variation for hardness with tempering temperature for H11 Mod steel. All specimens air cooled from 1010 °C (1850 °F) and double tempered, 2 + 2 h at temperature. AQ, as-quenched

H13 Steel. The main difference in composition between H11 Mod and H13 is the higher vanadium content of the latter (see Table 1). This leads to a greater dispersion of hard vanadium carbides, which results in higher wear resistance. Parts made of H13 can be nitrided for additional wear resistance. H13 also has a slightly wider range of carbon content than H11 Mod. The carbon content of H13 may be nearer the high or low side of the accepted range, depending on the producer, and for a given heat treatment the properties will vary correspondingly.

The following standard heat treatments apply to H13 steel:

- *Normalizing:* This is not recommended for H13. Some improvement in homogeneity can be obtained by preheating to about 790 °C (1450 °F), heating slowly and uniformly to 1040 to 1065 °C (1900 to 1950 °F) and holding 1 h for each 25 mm (1 in.) of thickness, and then air cooling. Just before or just as the steel reaches room temperature, it should be recharged into a furnace and given a full spheroidizing anneal. There is a risk of cracking during this treatment, especially if it is done in a furnace where the atmosphere is not controlled to prevent surface decarburization
- *Annealing:* Heat uniformly to 845 to 900 °C (1550 to 1650 °F) in a controlled-atmosphere furnace, or with the part in a neutral compound, to prevent decarburization, and hold to equalize temperature; cool very slowly in the furnace to about 480 °C (900 °F) and then cool more rapidly to room temperature. This treatment should result in a fully spheroidized microstructure free from grain-boundary carbide networks
- *Hardening:* Preheat to 790 to 815 °C (1450 to 1500 °F) and then raise the temperature uniformly to 995 to 1025 °C (1825 to 1875 °F) and soak 20 min plus 5 min for each 25 mm (1 in.) of thickness (minimum, 25 min); air cool in still air. For a few applications oil quenching from the low side of the

hardening temperature can be done, but this is at risk of distortion or cracking. Air cooling is preferred and is usually done from the high side of the hardening temperature range

- *Tempering.* Temper at the secondary hardening peak of about 510 °C (950 °F) for maximum hardness and strength, but it is preferable to temper at a higher temperature to a lower level of hardness or strength with improved toughness and ductility. Double tempering--2 h at temperature, air cool, and then 2 h more at temperature--is recommended; for critical parts, triple tempering is more desirable
- *Stress relieving:* Heat to 650 to 675 °C (1200 to 1250 °F) and soak 1 h or more; cool slowly to room temperature. This treatment is often used to achieve greater dimensional accuracy in heat-treated parts by stress relieving rough-machined parts, then finish machining, and finally heat treating to the desired hardness
- *Nitriding:* Finish-machined and heat-treated parts can be nitrided. Because it is carried out at about the normal tempering temperature, nitriding can serve as the second temper in a double-tempering treatment. The nitrided case depth depends on time at temperature. For example, gas nitriding at 510 °C (950 °F) for 10 to 12 h produces a case depth of 0.10 to 0.13 mm (0.004 to 0.005 in.). For selective nitriding, copper plating is preferred for stopping off areas that are not to be nitrided; stopoffs containing lead should be avoided because lead has been found to embrittle H13 steel

Properties. The properties presented in this section are for H13 with a carbon content in the middle of the composition range (see Table 1). Somewhat different properties should be expected when the carbon content is near the high end or the low end of the range.

Variation of hardness with tempering temperature for H13 is plotted in Fig. 6. Typical room-temperature longitudinal mechanical properties of bars tempered to different hardness levels are given in Table 23. H13 has deep hardenability, although it is slightly less than that of H11 Mod. For example, an H13 bar 330 mm (13 in.) in diameter and 2745 mm (108 in.) long, when fast air cooled from 1010 °C (1850 °F), has an as-quenched hardness of 45 HRC.

Table 23 Typical room-temperature longitudinal mechanical properties of H13 steel

Tempering temperature		**Tensile strength**		**Yield strength**		**Elongation in 4 *D*, %**	**Reduction in area, %**	**Charpy V-notch impact energy**		**Hardness, HRC**
°C	**°F**	**MPa**	**ksi**	**MPa**	**ksi**			**J**	**ft · lbf**	
527	980	1960	284	1570	228	13.0	46.2	16	12	52
555	1030	1835	266	1530	222	13.1	50.1	24	18	50
575	1065	1730	251	1470	213	13.5	52.4	27	20	48
593	1100	1580	229	1365	198	14.4	53.7	28.5	21	46
605	1120	1495	217	1290	187	15.4	54.0	30	22	44

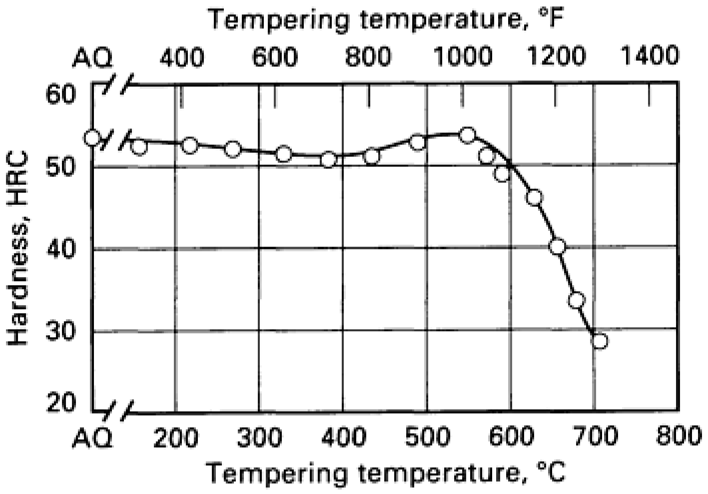

Fig. 6 Variation for hardness with tempering temperature for H13 steel. All specimens air cooled from 1025 °C (1875 °F) and tempered 2 h at temperature. AQ, as-quenched

9Ni-4Co Steels

During the 1960s, Republic Steel Corporation introduced a family of four HP 9-4 (9Ni-4Co) steels having high fracture toughness when heat treated to very high strength levels. Of these, HP 9-4-20 and HP 9-4-30 are commercially available. They nominally contain 0.20 and 0.30% C, respectively (see Table 1 for chemical compositions). The attainable strength increases with increases in carbon content, but decreases in toughness and weldability correspond. The high nickel content of 9% provides deep hardenability and toughness, and the 4% Co prevents retention of excessive austenite in heat-treated parts. Double tempering is recommended to ensure complete austenite transformation. The carbide-forming elements chromium and molybdenum also impart hardenability, but the amounts of these carbide formers are adjusted to provide a fairly flat response to tempering without pronounced secondary hardening and its attendant reduction in toughness.

HP 9-4-20, although it has good weldability and fracture toughness, cannot develop a yield strength of 1380 MPa (200 ksi), which was selected as the criterion for ultrahigh-strength steels discussed in this article. Therefore, only HP 9-4-30 is discussed further.

HP 9-4-30 steel has deep hardenability and can be fully hardened to martensite in sections up to 150 mm (6 in.) thick. Heat-treated parts can be readily welded without preheat or postheat treatment. After welding, parts may be stress relieved at about 540 °C (1000 °F) for 24 h.

The following heat treatments apply to HP 9-4-30 steel:

- *Normalizing:* Heat to 885 to 915 °C (1625 to 1675 °F) and hold 1 h for each 25 mm (1 in.) of thickness (minimum, 1 h); air cool
- *Annealing:* Heat to 620 °C (1150 °F) and hold 24 h; air cool. An alternative procedure consists of annealing at 705 °C (1300 °F) for 2 h, air cooling to room temperature, and annealing a second time at 650 °C (1200 °F) for 4 h, followed by air cooling to room temperature
- *Hardening:* Austenitize at 800 to 860 °C (1475 to 1575 °F) and hold 1 h for each 25 mm (1 in.) of thickness (minimum, 1 h); water or oil quench.Complete the martensitic transformation by refrigerating at least 1 h at -87 to -60 °C (-125 to -75 °F); let warm to room temperature
- *Tempering:* Temper at 200 to 600 °C (400 to 1100 °F), depending on desired strength; double tempering preferred. The most widely used tempering temperature is double tempering (2 h or more at temperature) from 540 to 575 °C (1000 to 1075 °F)
- *Stress relieving:* This is usually required only after welding of restrained sections. Heat to 540 to 575 °C (1000 to 1075 °F) and hold 24 h; air cool to room temperature

Properties. Room-temperature mechanical properties of HP 9-4-30 double tempered at three different temperatures are presented in Table 24. The data for material double tempered at 540 °C (1000 °F) represent the minimum mechanical properties for this condition; properties listed for the other conditions can be considered typical.

Table 24 Room-temperature mechanical properties of HP 9-4-30 steel

Property	**Typical value for hardness of**		**Minimum value[(c)]**
	49-53 HRC[(a)]	**44-48 HRC[(b)]**	
Tensile strength	1650-1790 MPa	1520-1650 MPa	1520 MPa
	(240-260 ksi)	(220-240 ksi)	(220 ksi)
Yield strength	1380-1450 MPa	1310-1380 MPa	1310 MPa
	(200-210 ksi)	(190-200 ksi)	(190 ksi)
Elongation in 4 *D*	8-12%	12-16%	10%
Reduction in urea	25-35%	35-50%	35%
Charpy V-notch impact energy	20-27 J	24-34 J	24 J
	(15-20 ft · lb)	(18-25 ft · lb)	(18 ft · lb)
Fracture toughness (K_{1c})	66-99 MPa $\sqrt{m}$	99-115 MPa $\sqrt{m}$	. . .

(a) Oil quenched from 845 °C (1550 °F), refrigerated to -73 °C (-100 °F), and double tempered at 205 °C (400 °F).

(b) Same heat treatment as (a) except double tempered at 550 °C (1025 °F).

(c) For sections forged to 75 mm (3 in.) or less in thickness (or to less than 0.016 m^2 or 25 $in.^2$, in total cross-sectional area), quenched to martensite and double tempered at 540 °C (1000 °F)

AF 1410

In the late 1970s the U.S. Air Force sponsored development work for improved submarine hull steels. From this work, AF 1410 evolved as an ultrahigh-strength steel with particularly high fracture toughness. AF 1410 is typically manufactured via VIM followed by VAR to achieve the required low levels of impurities. For improved or finer grain size, producers often recommend forging reductions of 40% below 900 °C (1650 °F). This grade is typically supplied in normalized and overaged condition for best machinability. The steel is then renormalized and austenitized or double austenitized, air cooled/quenched, cooled to -75 °C (-100 °F), and aged to attain maximum properties.

The microstructure of AF 1410 consists of iron-nickel lath martensite with carbides from age precipitation for strengthening. Quenching from the austenitizing temperature produces a highly dislocated lath martensite that has a high toughness, as measured by the Charpy V-notch impact test. Aging produces a complex series of changes in carbide structure. At approximately 425 °C (800 °F), Fe_3C is precipitated. At 455 °C (850 °F), iron-chromium-molybdenum M_2C carbide is obtained, which at 480 °C (900 °F) will begin to produce a pure molybdenum-chromium M_2C carbide. By raising the temperature to 510 °C (950 °F), the M_2C will begin to coarsen; at 540 °C (1000 °F) M_2C will begin to be replaced by M_6C, which has little strengthening effect.

The secondary hardening, which is due to the aging, produces a maximum tensile strength when aged at 480 °C (900 °F) using a 5-h aging time and a minimum impact energy when aged at 425 °C (800 °F), as shown in Fig. 7. When aged in the temperature range between 425 and 540 °C (800 and 1000 °F), the impact energy exhibits a maximum at about 508 °C (947 °F), as shown in Fig. 8. At aging temperatures above 540 °C (1000 °F), both the tensile strength and the impact energy decrease rather rapidly.

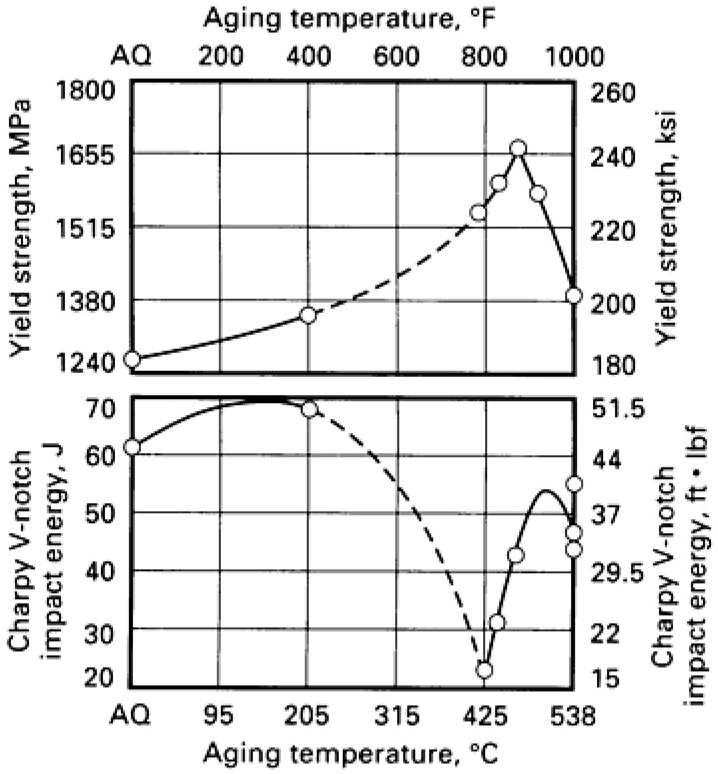

Fig. 7 Effect of aging temperature on impact energy (bottom) and yield strength (top) of AF 1410 steel (VIM/VAR plate 15 mm, or $\frac{5}{8}$ in., thick). Heat treatments: Heat at 900 °C (1650 °F) for $\frac{1}{2}$ h and water quench; heat at 815 °C (1500 °F) for $\frac{1}{2}$ h and water quench; age for 5 h at indicated temperatures and air cool. AQ, as-quenched. Source: Ref 1

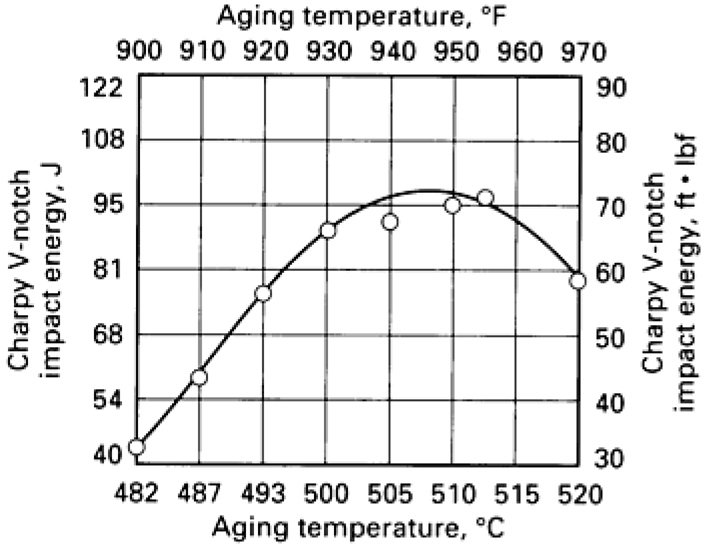

Fig. 8 Effect of aging temperature on impact energy of AF 1410 steel (VIM/VAR plate 15 mm, or $\frac{5}{8}$ in., thick). Heat treatments: See Fig. 7

The steel is subject to austenite reversion during aging. At normal aging temperatures, the retained austenite is generally less than 1% by volume. However, 540 °C (1000 °F) or higher will produce large amounts of austenite, and these will weaken the matrix of the steel. The best combination of strength and ductility results from a 480 to 510 °C (900 to 950 °F) age.

Heat Treatments. The heat treatments that apply to AF 1410 steel are:

- *Normalizing and overaging:* The material is normally normalized and overaged for best machinability. Heat between 880 and 910 °C (1620 and 1675 °F) and hold 1 h for each 25 mm (1 in.) of thickness; air cool and overage at 675 °C (1250 °F) for 5 h minimum
- *Annealing:* Usually, normalizing and overaging are used to soften and stress relieve the product. A stress relief of 675 °C (1250 °F) can be applied to relieve mechanical stresses
- *Hardening:* Renormalize and austenitize at 800 to 860 °C (1475 to 1575 °F) and hold 1 h for each 25 mm (1 in.) of thickness; oil, water, or air cool depending on section size. An alternative method, originally believed to improve toughness, involves double austenitizing, first at 870 to 900 °C (1600 to 1650 °F) with holding times of 1 h for each 25 mm (1 in.) of section thickness. Then cool with oil, water, or air, and reaustenitize as with the single austenitizing treatment
- *Quenching:* Air cooling from the austenitizing temperature will produce tensile strength, toughness, and fatigue strength essentially equal to oil or water quenching in section sizes up to 75 mm (3 in.). Refrigeration treatment of -73 °C (-100 °F) might be optional, although large forgings often fail to attain properties if not subjected to the subzero treatment. The aim is to reduce the amount of retained austenite
- *Aging:* Age at 480 to 510 °C (900 to 950 °F) 5 to 8 h. Air cooling is normally employed

Properties. Tensile strength and impact energy properties for VIM/VAR bar product austenitized and aged from various cycles are shown in Table 25. Figures 9, 10, and 11 augment Table 25 in allowing an estimate of the effect of a given aging treatment on properties by using Larson-Miller parameters. Tensile strength properties and impact energy for VIM/VAR plate quenched in air, water, or vermiculite and cooled following austenitizing are shown in Table 26. The heat treatments showed some effect on the tensile and impact properties for both 15 mm ($\frac{5}{8}$ in.) and 75 mm (3 in.) VIM/VAR plate.

Table 25 Effect of reaustenitizing and aging temperatures on mechanical properties of AF 1410 steel

Aging			Ultimate tensile strength		Yield strength		Elongation, %	Reduction in area, %	Charpy V-notch	
Temperature		Time, h								
°C	°F		MPa	ksi	MPa	ksi			J	ft · lbf
Reaustenitize 815 °C (1500 °F) for 1 h										
495	925	5	1806	262	1613	234	16	67	77	57
510	950	5	1730	251	1537	223	18	71	87	64
510	950	8	1606	233	1489	216	18	70	92	68
525	975	5	1579	229	1447	210	19	71	89	66
Reaustenitize 830 °C (1525 °F) for 1 h										
495	925	5	1847	268	1592	231	17	67	65	48
510	950	5	1716	249	1551	225	18	72	88	65
510	950	8	1620	235	1482	215	18	70	95	70
525	975	5	1599	232	1420	206	19	72	99	73
Reaustenitize 860 °C (1575 °F) for 1 h										
495	925	5	1813	263	1585	230	18	68	80	59
510	950	5	1709	248	1551	225	19	72	94	69
510	950	8	1620	235	1509	219	18	71	84	62
525	975	5	1572	223	1447	210	19	72	99	73

Note: All samples normalized at 900 °C (1650 °F) and overaged at 675 °C (1250 °F), followed by initial austenitizing at 900 °C (1650 °F) for 1 h: fast air cool and second austenitize as outlined above. All numbers are averages of at least two samples from 115 mm ($4\frac{1}{2}$

Table 26 Effect of various heat treatments on mechanical properties of a cobalt-nickel steel (VIM/VAR plate of AF 1410 steel)

Heat treatment[(a)(b)]	Ultimate strength		Yield strength		Elongation, %	Reduction in area, %	Charpy V-notch	
	MPa	ksi	MPa	ksi			J	ft · lbf
Plate of 15 mm ($\frac{3}{8}$ in.) thickness								
X + water quench per [(c)] + Z	1580	229	1515	220	16	60	91	67
X + refrigeration treatment per [(d)] + Z	1650	239	1550	225	17	69	83	61
X + vermiculite cool and refrigeration per [(e)] + Z	1620	235	1490	216	17	70	84	62
X + reaustenitization and refrigeration per [(f)] + Z	1660	241	1525	221	17	73	113	83
Average for several heats								
Heat treatment per [(g)]	1675	243	1590	231	. . .	. . .	92	68
Plate of 75 mm (3 in.) thickness								
Y + water quench per [(c)] + Z	1585	230	1540	223	16	66	65	48
Y + refrigeration treatment per [(d)] + Z	1680	244	1540	223	17	70	81	60
Y + vermiculite cool and refrigeration per [(e)] + Z	1480	215	1380	200	18	68	58	43
Y + reaustenitization, air cool, and refrigeration per [(f)] + Z	1670	242	1540	223	17	69	95	70

(a) Time at 900 °C (1650 °F) or 815 °C (1500 °F) is as follows: 1 h for the 15 mm ($\frac{3}{8}$ in.) plate or 3 h for the 75 mm (3 in.) plate.

(b) Initial and final heat treatments: X = 900 °C (1650 °F) for 1 h with air cooling and 675 °C (1250 °F) for 8 h with air cooling; Y = 900 °C (1650 °F) for 3 h with air cooling and 675 °C (1250 °F) for 8 h with air cooling; Z = 510 °C (950 °F) for 5 h with air cooling.

(c) 815 °C (1500 °F) for the time per (a) and water quenching.

(d) 815 °C (1500 °F) for the time per (a) with air cooling and a refrigeration treatment of -73 °C (-100 °F).

(e) (e) 815 °C (1500 °F) for the time per (a) with vermiculite cool and a refrigeration treatment of -73 °C (-100 °F).

(f) 900 °C (1650 °F) for time per (a) with air cooling, 815 °C (1500 °F) for time per (a) with air cooling, and refrigeration at -73 °C (-100 °F).

(g) 900 °C (1650 °F) for time per (a) with water quench, 815 °C (1500 °F) for time per (a) with water quench, 815 °C (1500 °F) for time per (a) with water quench, and 510 °C (950 °F) for 5 h with air cooling.

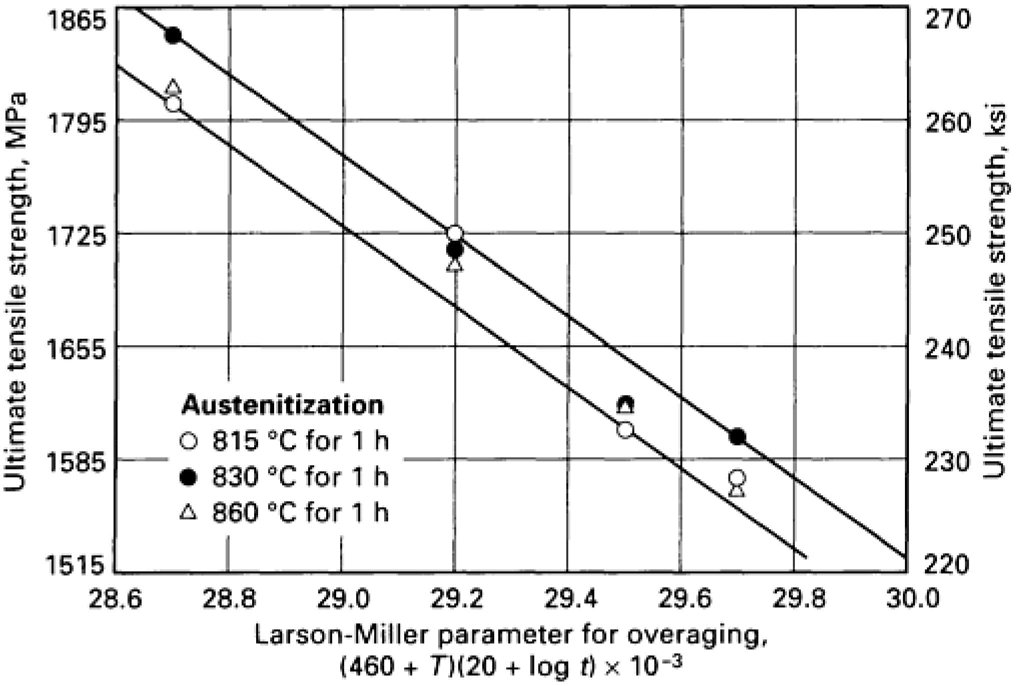

Fig. 9 Effect of heat treatment on the ultimate tensile strength of AF 1410. Larson-Miller parameter is provided with temperature (*T*) in °F and time (*t*) in hours. Source: Ref 3

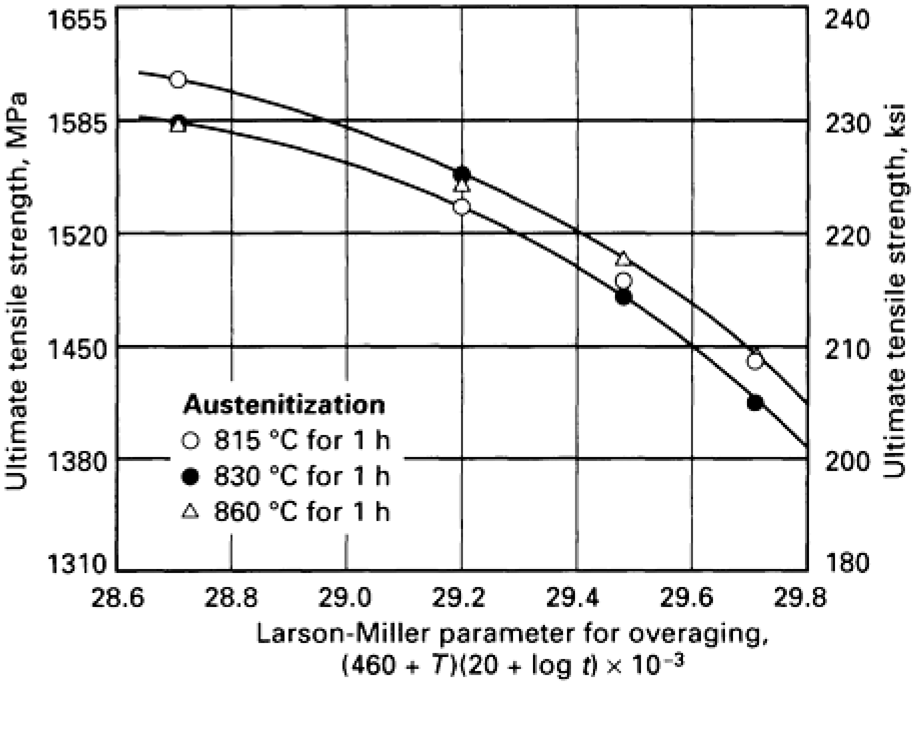

Fig. 10 Yield strength of AF 1410 determined by the overaging heat treatment. Larson-Miller parameter is provided with temperature (*T*) in °F and time (*t*) in hours. Source: Ref 3

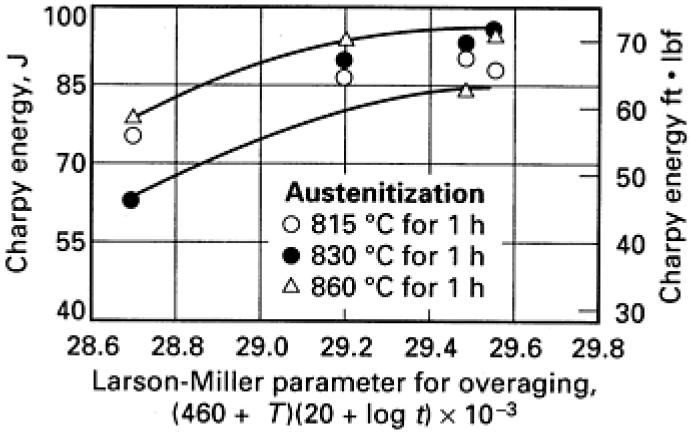

Fig. 11 Relationship between impact energy of AF 1410 and heat treatment. Larson-Miller parameter is given with temperature (*T*) in °F and time (*t*) in hours. Source: Ref 3

Fracture toughness, tensile properties, and impact energy of VIM/VAR 50 mm (2 in.) plate quenched and aged at 510 °C (950 °F) (a premachining heat treatment had been applied) are shown after quenching in different media (Table 27).

Table 27 Mechanical properties of a cobalt-nickel steel (AF 1410) in various quenching media

Quench medium	Ultimate strength		Yield strength		Elongation, %	Reduction in area, %	Charpy V-notch		Plane-strain fracture toughness (K_{1c})	
	MPa	ksi	MPa	ksi			J	ft · lbf	MPa $\sqrt{m}$	ksi $\sqrt{in}$
Air	1680	244	1475	214	16	69	69	51	174	158
Oil	1750	254	1545	224	16	69	65	48	154	140
Water	1710	248	1570	228	16	70	65	48	160	146

Note: Test specimens were 50 mm (2 in.) plate from VIM/VAR melt with the heat treatment: 675 °C (1250 °F) for 8 h with air cooling, 900 °C (1650 °F) for 1 h, quenching, 830 °C (1525 °F) for 1 h, quenching, refrigeration at -73 °C (-100 °F) for 1 h, 510 °C (950 °F) for 5 h, and air cooling.

Source: Ref 1

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Introduction

MARAGING STEELS are highly alloyed low-carbon iron-nickel martensites that possess an excellent combination of strength and toughness superior to that of most carbon-hardened steels (Fig. 1). As such, they constitute an alternative to hardened carbon steels in critical applications where high strength and good toughness and ductility are required. Hardened carbon steels derive their strength from transformation-hardening mechanisms (such as martensite and bainite formation) and the subsequent precipitation of carbides during tempering. In contrast, maraging steels derive their strength from the formation of a very low-carbon, tough, and ductile iron-nickel martensite, which can be further strengthened by subsequent precipitation of intermetallic compounds during age hardening. The term marage was coined based on the age hardening of the martensitic structure.

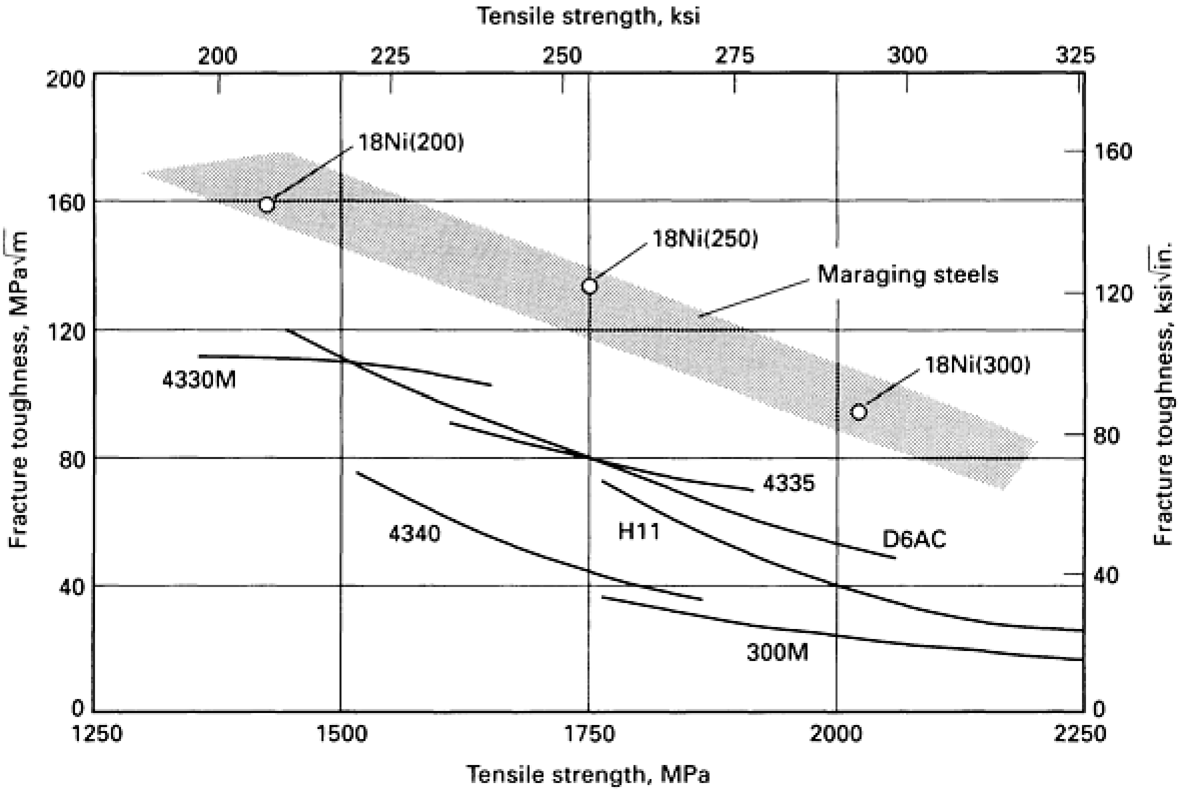

Fig. 1 Strength/toughness combination of 18 Ni maraging steels compared to conventional high-strength carbon steels. Source: Ref 1

Reference

1. J.C. Hamaker and A.M. Bayer, *Cobalt,* No. 38, 1968, p 3

Historical Development

Age hardening of martensite, or maraging, depends on the occurrence of a thermal hysteresis of phase transformations, whereby the reversion of martensite to austenite during reheating occurs at a higher temperature range than the temperature range for martensite formation during cooling. Although knowledge of this thermal hysteresis in Fe-Ni alloys was observed as early as 1927 (Ref 2), the first extensive research toward development of commercial iron-nickel maraging steels was conducted in the late 1950s by the International Nickel Company (currently Inco Ltd.). This research culminated in the development of the 20 and 25% Ni maraging steels. In addition to nickel, these two alloys contained 0.3% Al, 1.4% Ti, and 0.4% Nb, which resulted in precipitation hardening of the low-carbon martensitic structure when aged at 425 to 510 °C (800 to 950 °F). Both alloys were reported to exhibit good combinations of strength and ductility at

hardness levels of 53 to 56 HRC (Ref 3, 4); however, as reported by Hall (Ref 5), these alloys were abandoned because of their brittleness at extremely high strength levels.

Subsequent work on the iron-nickel system by Decker, Eash, and Goldman (Ref 6) revealed that the martensite formed in this binary system could be hardened to appreciable levels through the addition of cobalt and molybdenum. A nickel level of 18% was chosen for this alloy system because nickel levels significantly greater than 18% resulted in the retention of austenite in the as-quenched condition. By the early 1960s, three new maraging steels based on the Fe-18Ni-Co-Mo quaternary alloy system were introduced. These were the 18 Ni Marage 200, 250, and 300 alloys, which are capable of achieving yield strengths of approximately 1380, 1725, and 2000 MPa (200, 250, and 290 ksi), respectively, in combination with excellent ductility and toughness. The nominal compositions of these grades are shown in Table 1. In general, the strength levels attained by these alloys are determined by the cobalt, molybdenum, and titanium contents of each alloy. These three alloys replaced the phased-out 20 and 25% Ni maraging steels.

Table 1 Nominal compositions of standard commercial maraging steels

Grade	**Composition[(a)], wt%**				
	Ni	**Mo**	**Co**	**Ti**	**Al**
18 Ni Marage 200	18	3.3	8.5	0.2	0.1
18 Ni Marage 250	18	5.0	7.75	0.4	0.1
18 Ni Marage 300	18	5.0	9.0	0.65	0.1
18 Ni Marage 350	18	4.2[(b)]	12.5	1.6[(b)]	0.1

(a) The carbon content for all grades is restricted to 0.03% max.

(b) Some producers use a combination of 4.8% Mo and 1.4% Ti, nominal.

Based on the success and excellent properties of the 18 Ni Marage 200, 250, and 300 alloys, a modified version of the 18 Ni Marage 250 alloy was developed for use in casting applications in 1963 (Ref 7). In the mid- to late-1960s research was initiated at Inco Ltd. to develop maraging steels with strength levels in excess of 2100 MPa (300 ksi); as a result of this work, the 18 Ni Marage 350 steel was developed. Because of the high strength of this alloy, it is designated as an ultrahigh-strength maraging steel. As can be seen by its composition (Table 1), the 18 Ni Marage 350 alloy is essentially a modified version of the 300 grade that contains higher cobalt and titanium levels and a slightly reduced molybdenum content (Ref 8).

A number of cobalt-free maraging steels and a low-cobalt-bearing maraging steel have recently been developed (Table 2). The driving force for the development of these particular alloys was the cobalt shortage and resultant price escalation of cobalt during the late 1970s and early 1980s.

Table 2 Nominal compositions of cobalt-free and low-cobalt-bearing commercial maraging steels

Grade	**Composition[(a)], wt%**

	Ni	Mo	Co	Ti	Al	Nb
Cobalt-free 18 Ni Marage 200	18.5	3.0	. . .	0.7	0.1	. . .
Cobalt-free 18 Ni Marage 250	18.5	3.0	. . .	1.4	0.1	. . .
Low-cobalt 18 Ni Marage 250	18.5	2.6	2.0	1.2	0.1	0.1
Cobalt-free 18 Ni Marage 300	18.5	4.0	. . .	1.85	0.1	. . .

(a) The carbon content for all grades is restricted to 0.03% max.

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Physical Metallurgy

As previously mentioned, the good strength and toughness of maraging steels (Fig. 1) are achieved by the age hardening of an extremely ductile, low-carbon martensitic structure with relatively good strength (Table 3). During the aging of the martensitic structure, the basic objective is to form a uniform distribution of fine intermetallic precipitates, which serve to strengthen the martensitic matrix. Another basic objective during the aging of maraging steels is to minimize or eliminate the reversion of metastable martensite into austenite and ferrite.

Table 3 Typical range of mechanical properties developed in unaged 18 Ni maraging steels after solution annealing [815 °C (1500 °F), 1 h, air cooled]

Alloy	Yield strength		Tensile strength		Elongation, %	Reduction in area, %	HRC
	MPa	ksi	MPa	ksi			
18 Ni Marage 200	760-807	110-117	965-1000	140-145	17-18	72-79	28-30
18 Ni Marage 250	725-895	105-130	1000-1140	145-165	8-16	55-70	28-35
18 Ni Marage 300	760-895	110-130	1000-1170	145-170	6-15	45-60	30-37

Fortunately, the kinetics of the precipitation reactions that cause hardening of iron-nickel maraging steels are such that considerable age hardening--that is, approximately 20 HRC points (1035 MPa, or 150 ksi)--occurs before the onset of the reversion reactions that produce austenite and ferrite. The iron-nickel maraging steels also exhibit a thermal hysteresis in phase transformations that prevents or minimizes martensite-to-austenite reversion during aging heat treatment. This thermal hysteresis and phase behavior are illustrated in the two phase diagrams of Fig. 2, which depict the iron-rich end of the iron-nickel binary system. Figure 2(a) is the metastable diagram plotting the austenite-to-martensite transformation upon cooling and the martensite-to-austenite reversion upon heating. Figure 1(b) is the equilibrium diagram showing that at higher nickel contents the equilibrium phases at low temperatures are austenite and ferrite.

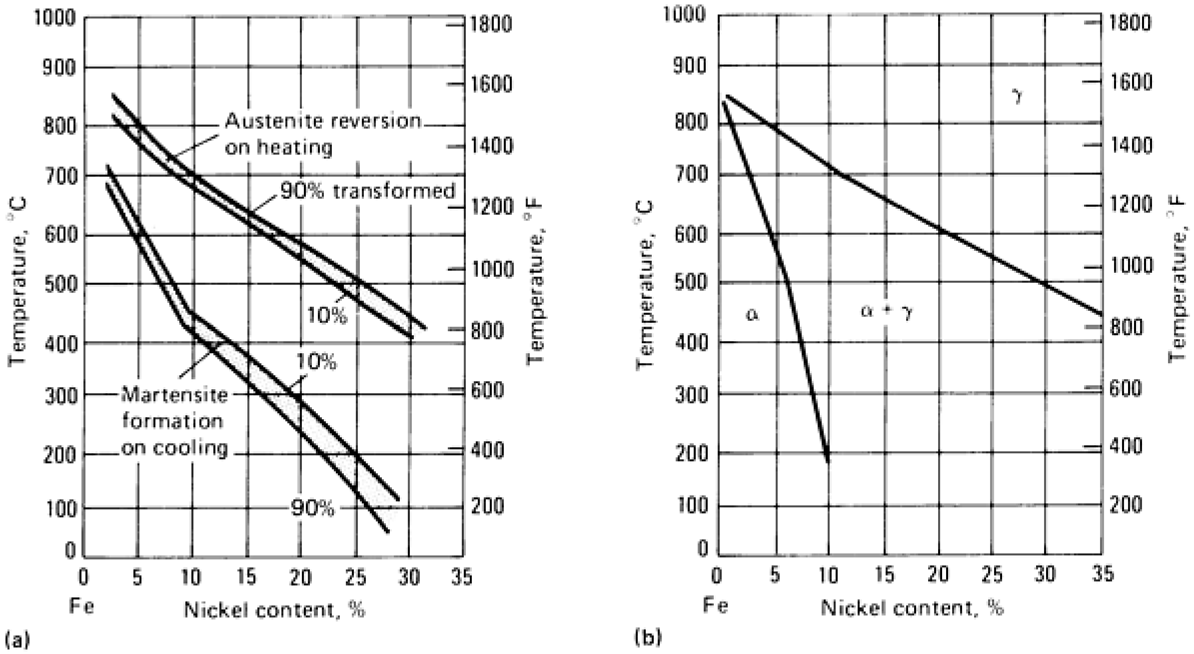

Fig. 2 Phase relationships in the iron-nickel system. (a) Metastable. (b) Equilibrium. Source: Ref 12

Martensite Formation

The martensite of maraging steels is normally a low-carbon body-centered cubic (bcc) lath martensite containing a high dislocation density but no twinning. The metastable phase diagram of Fig. 2(a) indicates the typical behavior of maraging steels during cooling from the solution-annealing (austenitizing) temperature. During cooling after solution annealing, the elevated-temperature face-centered cubic (fcc) austenite transforms to a bcc martensitic structure by a diffusionless shear reaction without decomposing into the equilibrium structures. This transformation of austenite to metastable martensite does not occur until the martensite start (M_s) temperature is reached, and the M_s temperature must be high enough so that a complete transformation to martensite occurs before the steel cools to room temperature. Most grades of maraging steels have M_s temperatures of about 200 to 300 °C (390 to 570 °F) and are fully martensitic at room temperature. The resultant martensitic structure is relatively strong and extremely ductile (Table 3).

Alloying elements alter the M_s temperature significantly, but do not alter the characteristic that transformation is largely independent of cooling rate. In maraging steels, fully martensitic structures are formed even during very slow cooling of heavy sections from the solution-annealing temperature. Consequently, there is no apparent lack of hardenability in maraging steels. This behavior is illustrated by the continuous cooling transformation (cct) diagrams for 18 Ni Marage 200, 250, 300, and 350 that appear in Fig. 3. As these cct diagrams indicate, the classical diffusion-controlled bainitic and pearlitic transformations that occur in carbon-base martensitic steels are not present in the 18 Ni maraging steels.

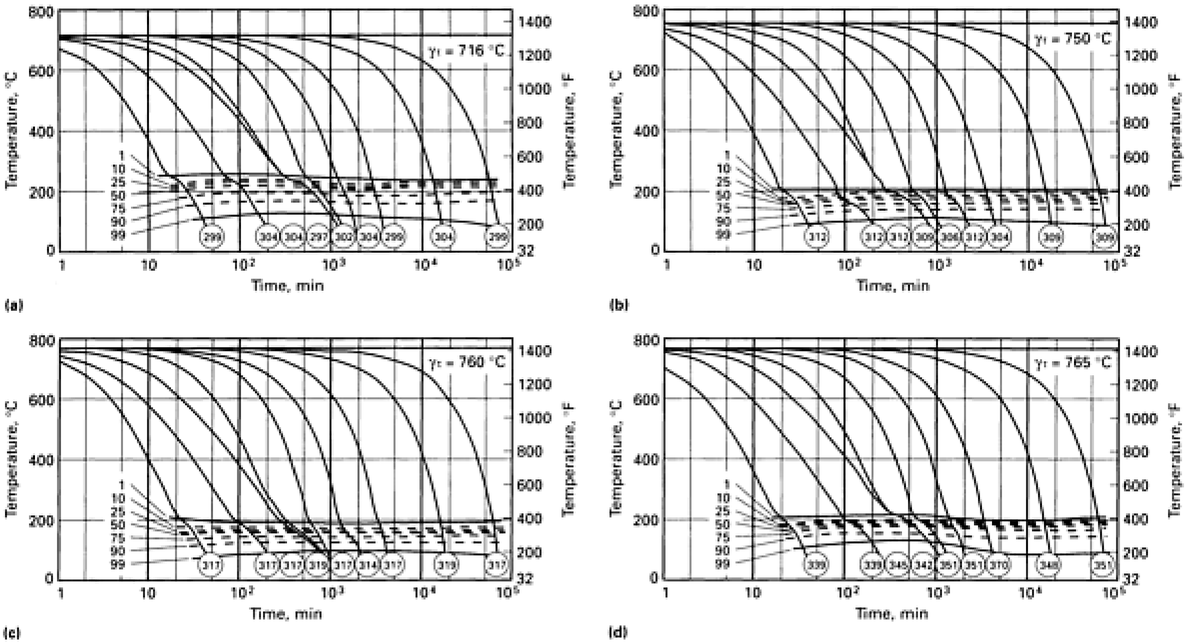

Fig. 3 Continuous cooling transformation diagrams for the 18 Ni Marage alloys solution treated at 845 °C (1550 °F) for 20 min. (a) 18 Ni Marage 200. (b) 18 Ni Marage 250. (c) 18 Ni Marage 300. (d) 18 Ni Marage 350. The Vickers hardness appears in the circles at the end of each cooling curve. The horizontal lines at the bottom of each graph represent the percentage of material transformed to martensite at a given time and temperature. Source: Ref 13

Martensite Morphology. One of two possible types of martensite might form in the iron-nickel alloy system depending on the nickel content of the material in question. At sufficiently high cooling rates, martensite will form in iron containing 5 to 10% Ni (Ref 14), and the addition of nickel in excess of 10% lowers the cooling rate necessary to form martensite in iron and ensures the formation of a completely martensitic structure. This particular type of martensite is referred to as lath martensite, and it will form in iron containing up to 25% Ni. If the nickel content is increased above 25%, the lath martensitic structure is replaced by a twinned martensite. Maraging steels typically transform from austenite to bcc lath martensite following cooling/quenching from the solution-annealing temperature, which is typically around 815 °C (1500 °F). Work on a series of Fe-7Co-5Mo-0.4Ti maraging alloys (18 Ni Marage 250) containing various nickel levels revealed that a lath martensitic structure was obtained for nickel levels as high as 23%. However, nickel contents in excess of 23% resulted in the formation of a twinned martensite (Ref 15). Generally, a lath martensitic structure is preferred in maraging steels because, following aging, this structure is tougher than a twinned martensitic structure.

Lath martensite consists of three subgrain structures, two of which are visible using standard optical metallographic techniques and one that requires transmission electron microscopy (TEM) for proper resolution. The lath martensitic structure of maraging steels consists of several martensitic packets within each prior austenitic grain and numerous blocks within each packet. Generally, the packets and blocks are planar, lie along one direction, and are parallel to each other. Packets are the predominant structure of lath martensite followed by the block structures that appear as discrete areas within each packet. These microstructural features can be resolved using standard optical metallographic techniques. The typical packet/block structure of 18 Ni Marage 250 is shown in Fig. 4(a). The substructure of each individual block of lath martensite consists of a series of fine parallel laths as shown by TEM (Fig. 4b). These martensitic laths are characterized by a high density of tangled dislocations. The orientation relationship between the lath martensite in 18 Ni maraging steels and the parent austenite from which it forms has been identified as the Kurdjumov-Sachs type: $(111)_{\gamma}//(011)_M$, $[110]_{\gamma}//[111]_M$ (Ref 16, 17).

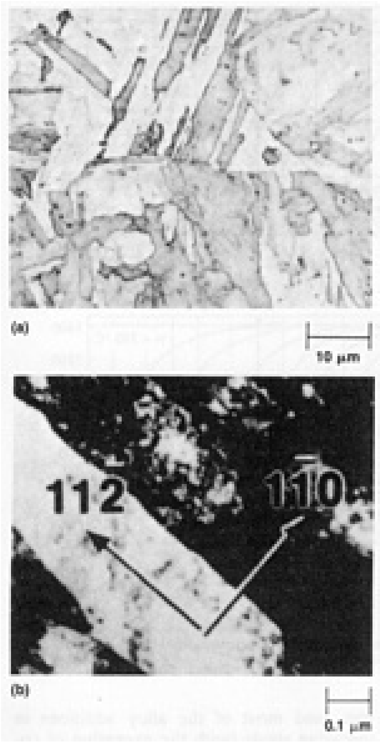

Fig. 4 Photomicrographs detailing the packet, block, and lath substructures of lath martensite in 18 Ni Marage 250. (a) Optical photomicrograph of the packet-block structure of lath martensite. (b) TEM photomicrograph of lath substructure of a block

The high density and uniform distribution of dislocations within the lath substructure promote an improved age-hardening response in maraging steels by providing a large number of preferred nucleation sites for the intermetallic precipitates that are formed in these alloys during aging. Additionally, these same dislocations also increase the diffusion rates of solute atoms by providing preferred diffusion paths. Both of these factors promote a uniform distribution of fine precipitates.

Effect of Alloying Elements on M_s and Martensite Morphology. Alloying elements have significant effects on the M_s temperature, and most of the alloy additions in maraging steels (with the exception of cobalt) suppress the M_s temperature. Most grades of maraging steel have M_s temperatures of the order of 200 to 300 °C (390 to 570 °F) and are fully martensitic at room temperature. In terms of martensite morphology, a high M_s temperature favors the formation of the desirable lath martensite morphology.

Maraging steels require careful use of M_s-suppressing alloy additions (such as nickel, molybdenum, and titanium) because these elements lower the M_s temperature and thereby promote the formation of a twinned martensite if used in excess. However, because nickel, molybdenum, and titanium are also responsible for the age-hardening mechanisms, cobalt is an important ingredient of maraging steels. One of the roles of cobalt in maraging steels is to raise the M_s temperature (Ref 18) so that greater amounts of other alloying elements (that is, titanium and molybdenum, which lower the M_s temperature) can be added while still allowing complete transformation to martensite before the steel cools to room temperature. Moderate levels of cobalt (6 to 8 wt% Co) are very useful in the design of maraging steels with strength levels in excess of 2100 MPa (300 ksi), since it helps to maintain a high enough M_s temperature in the presence of a high alloy content. Cobalt is also extremely important in maraging steels due to the influences it exerts on these alloys during the age-hardening reaction.

In the absence of cobalt, other elements such as nickel, molybdenum, and titanium must be maintained or reduced to levels to ensure an adequately high M_s temperature. Nickel lowers the M_s temperature of iron (Fig. 2a), and this effect becomes more pronounced at nickel levels in excess of 17.5% (Ref 8, 15). This is the reason nickel levels in excess of approximately 18% are no longer used in maraging steels. Molybdenum strongly depresses the M_s temperature (Ref 8, 18, 19), and chromium also exerts a negative influence on the M_s temperature of maraging steels; however, its effect is not as strong as that of nickel and molybdenum. The presence of titanium in an Fe-18Ni-8Co-5Mo maraging alloy promotes a reduction in the M_s temperature at all levels (Ref 8). The addition of up to 0.2% Al gives rise to a slight increase in the

M_s, which is then unaffected by subsequent additions (Ref 15). This effect, coupled with the deoxidizing capabilities of aluminum, is responsible for the use of approximately 0.1% Al in most maraging steels.

Retained austenite is generally not a problem in most commercially available grades of maraging steel, and, as a result, refrigeration treatments are not needed prior to aging. However, retained austenite can occur within localized regions that contain a high concentration of M_s-depressing elements such as nickel, molybdenum, chromium, and titanium. This microconstituent is generally associated with segregation, and as such, is found in heavily banded microstructures. The presence of retained austenite is generally considered to be unacceptable because this phase can result in significant variations in tensile strength, ductility, and toughness (particularly in the transverse orientation).

Martensite Aging

When the martensitic structure of maraging steels is reheated, two things can happen, depending on the temperature. If the alloy is reheated above the austenite start temperature, A_s, the previously formed martensite will transform back to austenite of the same composition by a diffusionless shear reaction. However, if the alloy is reheated to a temperature below the A_s, the martensite will initially age harden, followed by decomposition (reversion) into the equilibrium ferrite and austenite compositions. The rate at which this reversion reaction occurs is dependent upon the temperature to which the alloy is reheated. The rate of this reversion reaction at temperatures in the range of 455 to 510 °C (850 to 950 °F) is slow enough to allow considerable precipitation hardening to occur before the reversion reaction begins to dominate. This phenomenon of sluggish austenite reversion coupled with rapid age hardening forms the basis for the aging heat treatments of maraging steels.

The hardening of maraging steels during aging has been attributed to two different mechanisms. The first mechanism involves short-range ordering in the cobalt-bearing solid solution, and the second mechanism involves the precipitation of nickel-rich intermetallic compounds in the lath martensitic structure. While these two mechanisms occur separately, they are closely interrelated. According to the literature, the short-range ordering reaction occurs first, and it exerts a very significant influence on the subsequent precipitation reaction.

Ordering Reactions. The ordering reaction in maraging steels has been studied quite extensively by several investigators (Ref 20, 21, 22, 23). Neutron diffraction experiments performed on an Fe-22.7Ni-19.3Co maraging steel have revealed the presence of B2-type long-range ordering in this material upon aging (Ref 20). Similar experiments (Ref 21, 22) performed on maraging alloys with reduced nickel and cobalt levels (that is, Fe-18Ni-8 to 12% Co) have failed to reveal the presence of this long-range ordered structure. However, a neutron diffraction study performed on 18 Ni Marage 350 (Fe-18Ni-12Co-4.2Mo-0.1Al-1.5Ti) (Ref 22) revealed that a high degree of short-range ordering exists in this alloy after aging at 510 °C (950 °F) for 3 h. Based on this study, it was postulated that this short-range ordering phenomenon resulted in the formation of iron- and cobalt-rich regions and nickel-rich regions.

Rack and Kalish (Ref 23) believe that this short-range ordering reaction influences the subsequent precipitation-hardening reaction. Because the useful precipitates formed in maraging steels during aging are nickel-rich intermetallic compounds, the precipitation of the nickel-molybdenum and nickel-titanium compounds occurs primarily in the nickel-rich regions that were formed in the short-range ordered structure. Additionally, the formation of iron- and cobalt-rich regions would tend to stabilize these same precipitates because the strong interatomic attraction between iron and cobalt inhibits the diffusion of iron to the nickel-rich regions. This in turn delays the replacement of the metastable nickel-rich precipitates by equilibrium iron-rich precipitates.

Rack and Kalish's theory is quite logical based on the aging reactions that occur in maraging steels. Increased aging temperatures and/or times are necessary for the equilibrium iron-rich phases to displace the metastable nickel-rich phases, and an increase in either or both of these parameters would provide the necessary driving force for the diffusion of iron to the nickel-rich regions, which contain the metastable nickel-molybdenum and the nickel-titanium precipitates.

Precipitation Reactions. The precipitation reactions that occur in maraging steels are rather complex, and a significant amount of research has been devoted to the study of this phenomenon. The alloy elements that are involved in the precipitation reactions in maraging steels can be grouped into three broad categories (Ref 16):

- Beryllium and titanium are classified as strong hardeners
- Aluminum, niobium, manganese, molybdenum, silicon, tantalum, tungsten, and vanadium are classified as moderate hardeners

- Cobalt, copper, and zirconium are classified as weak hardeners

However, of these 13 elements, only 3 are utilized in the commercially available maraging grades. Two of these elements are titanium and molybdenum, both of which form precipitates, and the third is cobalt. Although cobalt does not form a precipitate, it participates indirectly in the age-hardening reaction through a phenomenon referred to as the cobalt/molybdenum interaction (see the section "Cobalt/Molybdenum Interaction" in this article).

The titanium- and molybdenum-bearing phases that are precipitated in this alloy system during aging are usually nucleated at dislocations or at lath boundaries. Nucleation on these two structural inhomogeneities tends to result in a uniform distribution of these phases. In general, these precipitates are coherent with the matrix; in addition, precipitate-free zones and coarsegrain-boundary precipitates are generally not found in these alloys.

The molybdenum-bearing precipitate commonly associated with the 18 Ni Marage 200, 250, 300, and 350 alloys is the metastable orthorhombic Ni_3Mo phase. These precipitates are rod shaped, they typically measure 25 Å wide × 500 Å long in the peak aged condition, and their long axis has been observed to lie parallel to the <111> directions of the bcc lath martensitic matrix (Ref 24). The strengthening that is imparted to the matrix is derived from the distorted matrix lattice that surrounds each Ni_3Mo precipitate. This effect is illustrated in Fig. 5.

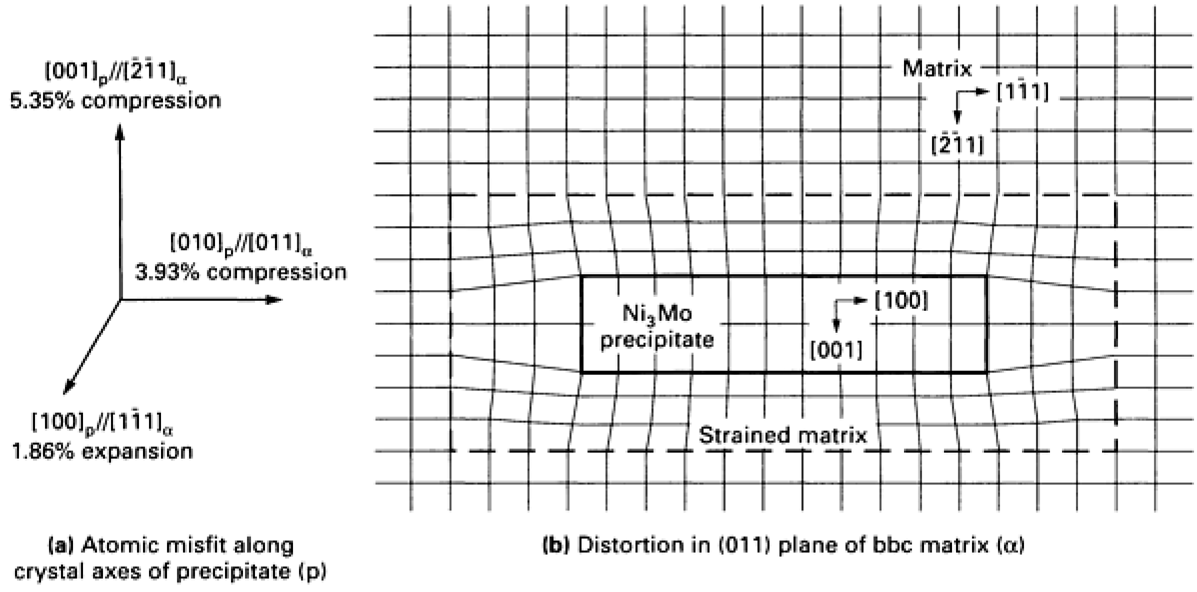

Fig. 5 Diagrams showing (a) the atomic misfit along the crystal axes of Ni_3Mo precipitate (p), and (b) the distortion that Ni_3Mo causes in the bcc matrix (α) of 18 Ni maraging steels. Source: Ref 24

Molybdenum also plays the necessary supplemental role of minimizing localized grain-boundary precipitation by lowering the diffusion coefficients of a number of elements in solid solution. Precipitation of these grain-boundary phases severely impairs the toughness of most molybdenum-free ferrous alloys. Work by Schmidt (Ref 25) has shown that discrete particles of austenite are also present on the grain and subgrain boundaries in molybdenum-free 18 Ni Marage 300. It has been theorized that the precipitation of these discrete particles of austenite at the grain and subgrain boundaries results in a nickel-depleted zone, which adversely affects the toughness and ductility of the molybdenum-free 18 Ni Marage 300 alloy on a localized scale.

Titanium-bearing precipitates are commonly associated with the 18 Ni Marage 200, 250, and 300 alloys. Titanium is used as a supplemental hardener because levels in excess of approximately 1.2% generally result in reduced ductility, both before and after aging (Ref 17). Titanium-rich precipitates identified as Ni_3Ti have been reported in 18 Ni Marage 250 and cobalt-free 18 Ni Marage 250 by Vasudevan, Kim, and Wayman (Ref 26) and in 18 Ni Marage 300 and cobalt-free 18 Ni Marage 300 by Vanderwalker (Ref 27). The η-Ni_3 Ti has a DO_{24} ordered hexagonal structure (Ref 28), and unlike Ni_3Mo,

Ni_3Ti is a stable phase. This titanium-bearing precipitate distorts the bcc martensitic matrix in a manner similar to that achieved with the molybdenum-bearing, Ni_3Mo precipitate.

Nucleation Rates. It has generally been observed that no incubation period accompanies the precipitation reaction in maraging steels. This behavior is evident in Fig. 6, which shows that significant hardening occurs after very short aging times (less than one minute). The lack of an incubation period implies the lack of a free-energy barrier to nucleation in these alloys. Peters and Cupp (Ref 29) attributed this lack of a free-energy barrier to two factors: the high degree of solute supersaturation and heterogeneous nucleation on dislocations. Cahn (Ref 30) has shown that both of these factors can effectively reduce the free-energy barrier to nucleation. Floreen (Ref 16) has also theorized that the good structural fit between A_3B precipitates and the bcc martensitic matrix is also responsible for the lack of a free-energy barrier and the low activation energies associated with 18% Ni maraging steels.

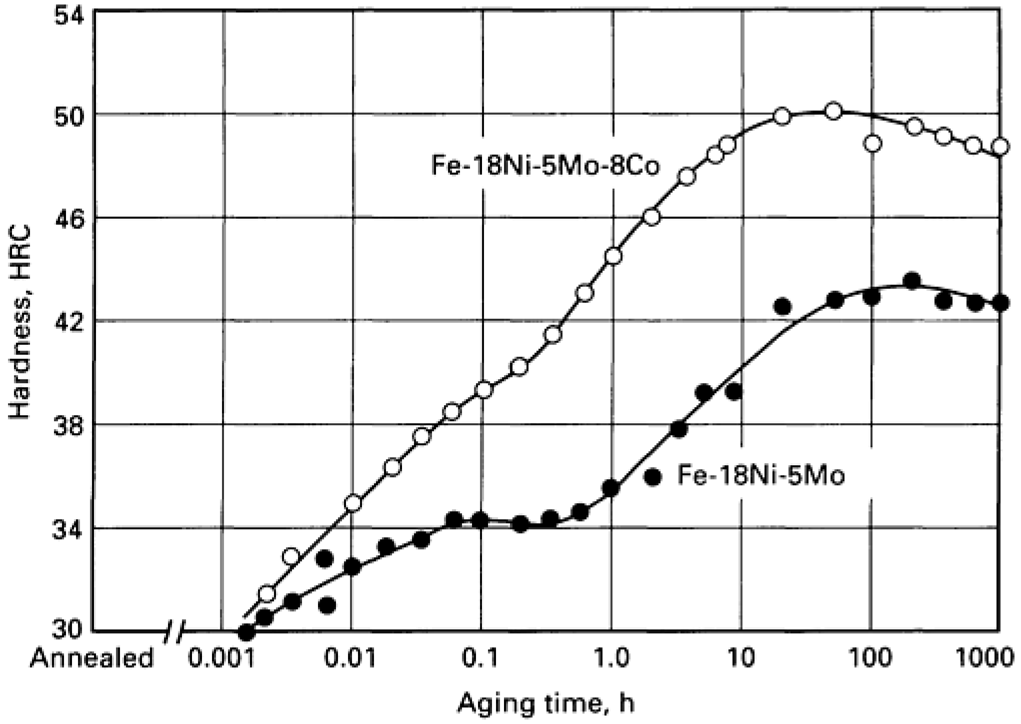

Fig. 6 Plots of aged hardness versus aging time at 455 °C (850 °F) for Fe-18Ni-5Mo and Fe-18Ni-5Mo-8Co maraging steels. Source: Ref 29

Figures 6 and 7 both indicate that the aging response of maraging steels is influenced by aging time. For example, Fig. 7 shows that the electrical resistivity of maraging alloys decreases as the aging time increases up to approximately 100 h. Because electrical resistivity is directly related to the amount of an alloy in solid solution, the electrical resistivity is influenced by the precipitation of compounds during aging. At aging times in excess of 100 h, the electrical resistivity increases. A similar effect on hardness (Fig. 6) can be observed. Aging times up to approximately 100 h promote an increase in aged hardness in Fe-18Ni-5Mo-8Co and Fe-18Ni-5Mo maraging alloys, after which a decrease is observed. This phenomenon is known as austenite reversion, which accompanies the formation of equilibrium precipitates in overaged maraging steels. (See the section "Austenite Reversion" in this article.)

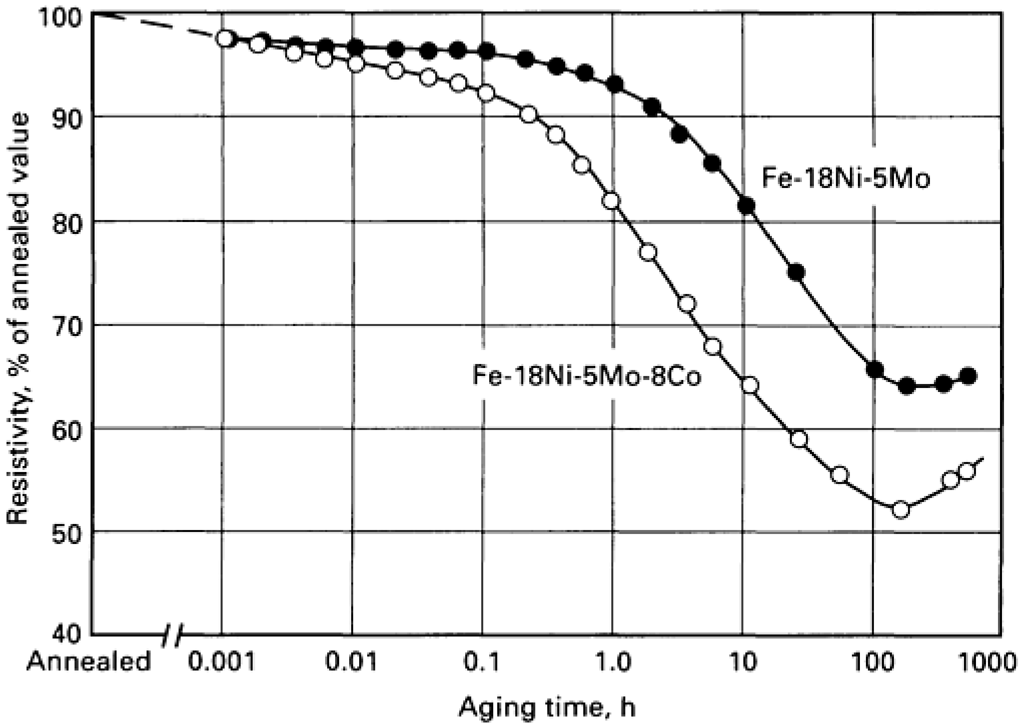

Fig. 7 Plots of electrical resistivity (percent of annealed value) versus aging time at 455 °C (850 °F) for Fe-18Ni-5Mo and Fe-18Ni-5Mo-8Co maraging steels showing cobalt/molybdenum interaction. Source: Ref 29

Cobalt/Molybdenum Interaction. Cobalt does not directly enter into the aging reaction because it does not form a precipitate. However, this element does contribute to the aging reaction indirectly through a phenomenon referred to as the cobalt/molybdenum interaction. Numerous authors have reported that a synergistic effect exists between cobalt and molybdenum (Ref 6, 21, 31, 32). In these studies, the increases in strength from cobalt and molybdenum additions were greater than the sum of the strength increases produced by individual additions of these two elements. For example, in a study performed by Floreen and Speich (Ref 31), the addition of 8% Co to ternary Fe-8Ni-*X* (where *X* = aluminum, beryllium, manganese, niobium, silicon, or titanium) alloys resulted in a 140 to 310 MPa (20 to 45 ksi) increase in the 0.2% offset yield strength of the quaternary alloy over that of the ternary, which is equivalent to the solid-solution-strengthening effect of cobalt. However, when 8% Co was added to a ternary Fe-18Ni-5Mo maraging alloy, the yield strength of the quaternary alloy was 515 MPa (75 ksi) greater than that of the ternary alloy.

This synergistic effect of cobalt on the strength of molybdenum-bearing maraging steels occurs because cobalt reduces the solubility of molybdenum in the bcc matrix and thus enhances the precipitation of Ni_3Mo. Consequently, a finer, more uniform distribution of Ni_3Mo precipitates is formed when cobalt additions are present. This theory, proposed by Peters and Cupp (Ref 29), is supported by electrical resistivity measurements and TEM work. Figure 7 indicates that the amount of molybdenum in solid solution during the age-hardening reaction is less for the alloy system containing 8% Co. Transmission electron microscopy work performed by Miller and Mitchell (Ref 33) and Floreen and Speich (Ref 31) has also shown that additions of cobalt promote a finer dispersion of Ni_3Mo precipitates. A finer distribution of precipitates will reduce the interparticle spacing, which, in turn, will increase the yield strength of the alloy system.

Austenite reversion in maraging steels is caused by nickel enrichment of the bcc matrix. As was mentioned, Ni_3Mo, which has an orthorhombic Cu_3Ti-type structure (Ref 28), is one of the primary precipitates responsible for the age-hardening reaction in maraging steels; however, this phase is metastable. Formation of Ni_3Mo depletes the matrix of nickel, and, based on the stoichiometry of this phase, this depletion occurs at a ratio of three nickel atoms for every molybdenum atom. Because of its better fit with the bcc martensitic matrix, the formation of Ni_3Mo is initially favored over that of Fe_2Mo. As the orthorhombic Ni_3Mo precipitates grow, the coherency strains between the precipitate and the matrix also increase. Eventually, the coherency strains increase to the point where the stability of the Ni_3Mo is upset. At this point the Ni_3Mo phase dissolves and is replaced by Fe_2Mo. TEM and microprobe analysis of extraction replicas by Miller and Mitchell (Ref 34) and by Fleetwood, Higginson, and Miller (Ref 35) has confirmed the presence of Fe_2Mo in overaged maraging steels. Thus, as the metastable Ni_3Mo precipitates dissolve, the matrix becomes enriched in nickel because of

the resolution of nickel, and this enrichment in nickel is further enhanced due to a depletion in iron as the Fe_2Mo phase nucleates and grows.

Austenite reversion in maraging steels cannot be eliminated entirely when these alloys are reheated to temperatures below the A_s for prolonged periods, because the martensite that is formed during solution annealing is metastable and the system wants to decompose to the equilibrium austenite and ferrite structures via diffusion-controlled reactions. However, the rate at which this reversion reaction occurs can be modified to a certain extent by the alloy content of the steel.

Peters (Ref 36) performed an extensive study on the effect of various molybdenum, cobalt, and titanium contents on the volume percent of austenite formed during aging of ternary Fe-18Ni-*X* (*X* = molybdenum, cobalt, or titanium) alloys. Additions of molybdenum in excess of approximately 1% accelerated the formation of reverted austenite. This behavior is attributed to an increase in Ni_3Mo, which in turn promotes increased Fe_2Mo formation and subsequent nickel enrichment of the matrix. In contrast to this behavior, cobalt additions up to approximately 8% retard the reversion reaction; however, further additions of cobalt tend to accelerate the formation of reverted austenite. This phenomenon has been attributed to:

- The effect of moderate cobalt levels (6 to 8%) on raising the M_s temperature
- The subsequent lowering of M_s accompanied by cobalt additions in excess of 8%

Titanium, like moderate additions of cobalt, tends to delay the onset of austenite reversion in maraging steels, although the mechanism responsible for this effect is quite different from that associated with cobalt. Titanium forms a very stable precipitate that contains significant quantities of nickel (that is, Ni_3Ti), and the formation of these stable precipitates results in a nickel-depleted matrix.

Based on the arguments presented in the preceding paragraph, care must be taken to avoid segregation in the more highly alloyed maraging grades. For example, Schmidt (Ref 25) observed bands of austenite in an Fe-18.5Ni-9.1Co-6.75Mo-0.65Ti-0.11Al maraging alloy. Microprobe analysis of these bands revealed that they were enriched in cobalt and molybdenum, and the austenite contained in this segregated region was determined to be a mixture of retained and reverted austenite. This particular specimen was aged at only 480 °C (900 °F) for 8 h. The underlying point is that segregation, particularly of the elements cobalt and molybdenum, should be minimized in these grades to minimize both retained and reverted austenite formation because these two microconstituents can severely damage both mechanical and physical properties.

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Heat Treatment of Maraging Steels

Solution Annealing. The martensitic matrix of maraging steels is prepared for later age hardening through a heat-treating procedure commonly referred to as a solution anneal. Solution annealing entails heating the alloy significantly above the austenite finish (A_f) temperature, holding a sufficient time to place the alloying elements in solid solution, and then cooling to room temperature. The most common solution-annealing cycle for the 18 Ni Marage 200, 250, and 300 alloys involves heating to 815 °C (1500 °F) for 1 h followed by air cooling.

Maraging steels are generally purchased in the solution-annealed condition for machining applications and reannealing is usually unnecessary. Product for forging applications is generally purchased in the unannealed condition because heating would negate the prior thermal-annealing cycle. It is suggested that machining follow solution annealing. If solution annealing must be performed after final machining, the use of vacuum, atmosphere-control air circulating, neutral salt bath, or fluidized bed furnaces may be necessary to minimize surface damage.

Generally, endothermic atmospheres are used in conjunction with atmosphere-control air-circulating furnaces. If vacuum furnaces are used to solution anneal maraging steels, a slight positive pressure of an inert gas, such as nitrogen or argon, should be used to minimize the possible loss of alloying elements at low vacuum levels. In addition, a neutral fluidizing gas should be usedin conjunction with a fluidized bed furnace to minimize surface damage. It may be necessary to solution treat sheet and strip products in dry hydrogen or dissociated ammonia to maintain surface integrity.

When maraging steels are required in long lengths, with a high degree of straightness, double solution-annealing treatments are sometimes applied with an intermediate straightening operation. These treatments are often performed with the product in a vertical orientation to prevent sagging. The initial solution-annealing temperature tends to be in the 815 to 980 °C (1500 to 1800 °F) range where residual stresses are more fully relieved. The product is then cooled to room temperature and straightened. This is followed by a lower-temperature vertical solution anneal in the 790 to 815 °C (1450 to 1500 °F) range to remove straightening stresses while minimizing distortion. If the product were straightened after annealing, it could return to the prior out-of-straightness condition upon aging because of a shape memory effect of the low-carbon iron-nickel lath martensite.

Castings generally receive pretreatments of 1150 °C (2100 °F) for 1 h followed by air cooling and reheating to 595 °C (1100 °F) for 1 h with another air cool. This pretreatment is a homogenizing cycle before solution annealing. The 595 °C (1100 °F) step forms reverted austenite that provides nucleation sites for recrystallization when the solution anneal is then

applied. The solution-annealing treatment that follows the homogenization and overaging cycles is similar to that for wrought product.

Effect of Annealing Time and Temperature on Aged Properties. Solution-annealing temperature has only a small effect on the strength of the aged material. This behavior is graphically depicted in Fig. 8 for Marage 250 and 300, with additional values for Marage 300 contained in Table 4. The data show that peak strength occurs with an 800 to 815 °C (1475 to 1500 °F) solution anneal, and strength is reduced up to 135 MPa (20 ksi) with higher and lower temperatures in the 760 °C (1400 °F) to 980 °C (1800 °F) range. Tensile ductility increases slightly with annealing temperatures from 760 to 815 °C (1400 to 1500 °F) and remains relatively unchanged with temperatures up to 980 °C (1800 °F). Table 4 also suggests that higher strength can be obtained with shorter annealing times.

Table 4 Effect of solution-annealing treatment on the aged properties of 18 Ni Marage 300 alloy

Solution heat treatment[(a)]	**Aged[(a)] strength**						**Aged[(a)] tensile ductility**	
	0.2% yield		**Tensile strength**		**Shear strength[(b)]**		**Elongation in 25 mm (1 in.), %**	**Reduction in area, %**
	MPa	**ksi**	**MPa**	**ksi**	**MPa**	**ksi**		
815 °C (1500 °F) for 15 min	2080	302	2095	304	1160	168	9.1	56
871 °C (1600 °F) for 15 min	2000	290	2027	294	1117	162	9.2	55
927 °C (1700 °F) for 15 min	1965	285	2005	291	1103	160	8.8	54
815 °C (1500 °F) for 1 h	2000	290	2040	296	1117	162	9.4	56

(a) All solution heat treatments followed by an aging heat treatment of 480 °C (900 °F) for 3 h.

(b) Double-shear-type test

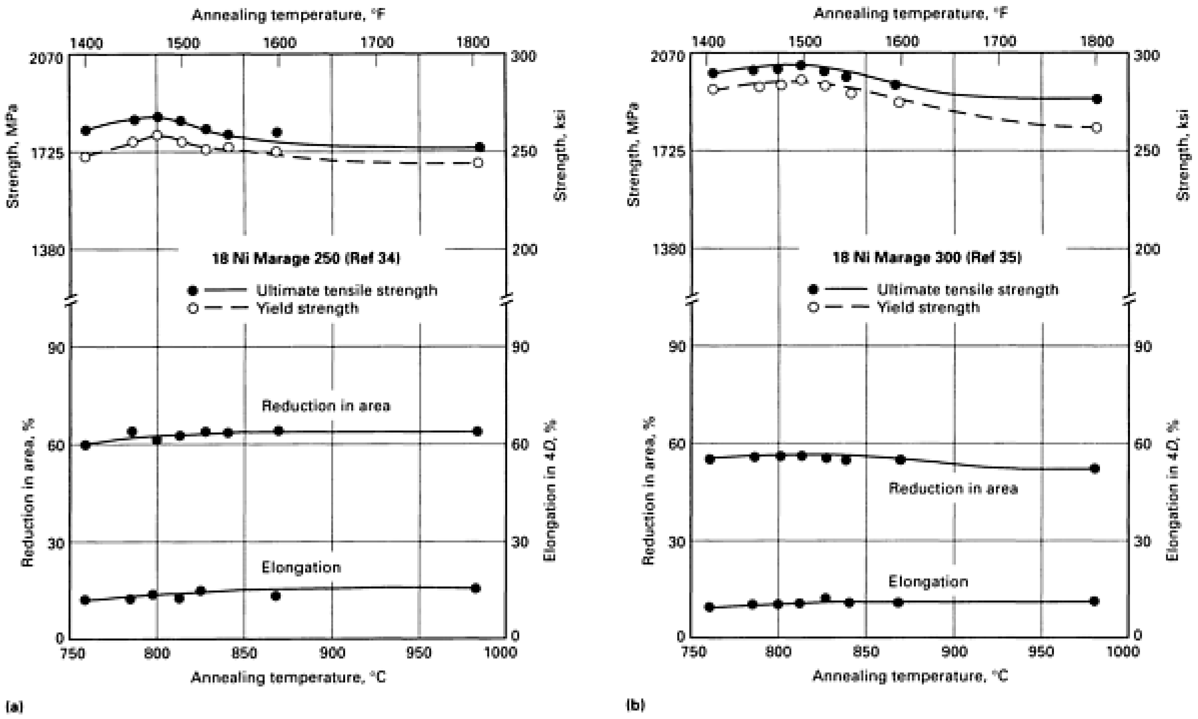

Fig. 8 Influence of solution-annealing temperature on the aged tensile properties of consumable vacuum-melted 18 Ni Marage 250 and 300. Heat treatment: Solution annealed for $\frac{1}{2}$ h at indicated temperatures, air cooled, and then aged at 480 °C (900 °F) for 3 h. Sources: Ref 10, 11

Lower strength and ductility with solution-annealing temperatures from 760 to 800 °C (1400 to 1475 °F) are attributed to incomplete solution of hardening elements. The reduction in strength associated with solution-annealing temperatures above 815 °C (1500 °F) is attributed to coarsening of the grain/packet structure. This grain growth and the subsequent reduction in strength are minimized by boron contents between 0.001 and 0.003%.

Maraging steels are usually solution annealed at a given temperature for 1 h. Table 4 indicates a benefit to strength from shorter solution-annealing times; however, care must be taken to ensure complete solution of hardening elements. Therefore, 1-h solution-annealing times are generally favored, and excessively long times are discouraged. Even boron-containing maraging steels will exhibit grain growth if exposed for more than 6 h at 955 °C (1750 °F).

The cooling rate following solution annealing is of little consequence because it has little to no effect on either the microstructure or mechanical properties (Table 5) of maraging steels. However, it is essential that parts be cooled to room temperature prior to age hardening. If parts are not completely cooled to room temperature prior to age hardening, untransformed or retained austenite may be present in the structure that could result in slightly lower than expected hardness and strength. Maraging steels are not susceptible to cracking during quenching to room temperature following solution annealing because of the extremely ductile nature of the bcc lath martensite.

Table 5 Data showing the relative insensitivity of tensile properties (a) of 18 Ni Marage 250 to variations in cooling medium following solution annealing

Cooling medium	Tensile properties[(a)]					
	0.2% yield		Tensile strength		Elongation (4*D*), %	Reduction in area, %
	MPa	ksi	MPa	ksi		

Brine	1855	269	1895	275	10.7	50.2
Air	1835	266	1875	272	10.6	50.8
Vermiculite	1835	266	1882	273	10.7	49.1

Source: Carpenter Technology Corporation

(a) Data represent transverse, midradius specimens removed from a 181 mm (7.125 in.) double-octagon billet. Heat treatment: 955 °C (1750 °F), 1 h, quench to room temperature plus; 790 °C (1450 °F), 1 h, quench to room temperature plus; 455 °C (850 °F), 9 h, air cool to room temperature.

Thermal embrittlement of maraging steels is due to the precipitation of TiC and possibly of Ti(C, N) films at austenite grain boundaries. This phenomenon is easily avoided with proper thermal handling and is, hence, quite rare. Thermal embrittlement occurs by heating maraging steels to temperatures in excess of 1175 °C (2150 °F), wherein carbon is taken into solution, followed by cooling slowly through or holding within the temperature range of 750 to 1090 °C (1380 to 2000 °F), where the carbon is then reprecipitated as a grain-boundary film.

It is permissible to heat maraging steels to temperatures in excess of 1175 °C (2150 °F) and rapidly cool or hot work through the 750 to 1090 °C (1380 to 2000 °F) range. The former time/temperature cycle will not permit time for grain-boundary carbide precipitation, whereas the latter will continually change grain-boundary location as a result of dynamic recrystallization. After a material has been heated above 1175 °C (2150 °F) and successfully cooled to room temperature, it may be heated into the 750 to 1090 °C (1380 to 2000 °F) range without problems because any carbides and possibly carbonitrides will have precipitated as discrete, stable particles during previous cooling to below 750 °C (1380 °F), and thus cannot reprecipitate as a film on reheating. In general, there is no reason to heat maraging steels over 1175 °C (2150 °F) except for initial raw material production, and therefore, no reason for an end user to cause thermal embrittlement.

Grain Refinement Using Thermal Cycling. Thermal cycling of maraging steels between the martensite finish (M_f) temperature and a temperature considerably in excess of the solution-annealing temperature can be used to refine the grain structure of coarse-grained maraging steels For example, Saul, Roberson, and Adair (Ref 37) were able to refine an ASTM grain size of 00/1 to an ASTM grain size of 6/7 in 18 Ni Marage 300 following three thermal cycles between room temperature and 1025 °C (1880 °F) The strains produced by the diffusionless shear transformations of martensite to austenite and of austenite to martensite provide the driving force for recrystallization during these thermal cycles. Grain sizes finer than ASTM 6 or 7 cannot be achieved by this process, and the process becomes less effective as the starting grain size becomes finer.

Age Hardening. A typical age-hardening treatment after solution annealing usually consists of reheating the alloy into the temperature range of 455 to 510 °C (850 to 950 °F), holding at this temperature for 3 to 12 h, and air cooling to room temperature. In typical treatments at 480 °C (900 °F), the 18 Ni Marage 200, 250, and 300 grades are held 3 to 8 h, whereas the 18 Ni Marage 350 grade is usually held 6 to 12 h at 480 °C (900 °F). The 18 Ni Marage 350 grade can also be aged for 3 to 6 h at 495 to 510 °C (925 to 950 °F). The use of marage steels in applications such as die casting tooling requires the use of an aging temperature of approximately 530 °C (985 °F) to provide an overaged structure that is more thermally stable.

Table 6 contains typical mechanical properties of the standard 18 Ni maraging steels following aging, and Table 7 contains a comparison of the typical mechanical properties associated with the 18 Ni Marage 250, low cobalt-bearing 18 Ni Marage 250 and cobalt-free 18 Ni Marage 250 grades. The standard aging treatments listed in Table 6 produce contraction in length of 0.04% in 18 Ni Marage 200, 0.06% in 18 Ni Marage 250, and 0.08% in both 18 Ni Marage 300 and 350. These very small dimensional changes during aging allow many maraging steel components to be finish machined in the annealed condition and then age hardened. When precise dimensions must be held, an allowance for contraction can be made and finish machining should be performed after aging.

Table 6 Typical mechanical properties of standard 18 Ni maraging steels in the age-hardened condition

Grade	Heat treatment[(a)]	Yield strength		Tensile strength		Elongation in 50 mm (2 in.), %	Reduction in area, %	Fracture toughness	
		MPa	ksi	MPa	ksi			MPA $\sqrt{m}$	ksi $\sqrt{in}$
18 Ni Marage 200	A	1400	203	1500	218	10	60	155-240	140-220
18 Ni Marage 250	A	1700	247	1800	260	8	55	120	110
18 Ni Marage 300	A	2000	290	2050	297	7	40	80	73
18 Ni Marage 350	B	2400	348	2450	355	6	25	35-50	32-45
18 Ni Marage Cast	C	1650	240	1750	255	8	35	105	95

(a) Heat treatment: A, 815 °C (1500 °F), 1 h + 480 °C (900 °F), 3 h; B, 815 °C (1500 °F), 1 h + 480 °C (900 °F), 12 h; C, 1150 °C (2100 °F), 1 h + 595 °C (1100 °F), 1 h + 815 °C (1500 °F), 1 h + 480 °C (900 °F), 3 h

Table 7 Comparison of the longitudinal, room-temperature mechanical properties of standard, cobalt-free, and low cobalt-bearing 18 Ni Marage 250 steels

Specimen[(a)] grade	0.2% yield strength		Tensile strength		Elongation in 25mm (1 in.), %	Reduction in area, %	Charpy V-notch impact		L-S plane-strain fracture toughness (K_{Ic})[(b)]	
	MPa	ksi	MPa	ksi			J	ft · lbf	MPa $\sqrt{m}$	ksi $\sqrt{in}$
18 Ni Marage 250	1825	265	1870	271	12	64.5	37	27	138	125
Cobalt-free 18 Ni Marage 250	1825	265	1895	275	11.5	58.5	34	25	127	115
Low-cobalt 18 Ni	1780	258	1835	266	11	63.5	43	32	149	135

(a) Testing was conducted on 63.5 × 88.9 mm (2.50 × 3.50 in.) billets produced from 200 mm (8.0 in.) round vacuum induction melted/vacuum arc remelted ingots. Heat treatment: 815 °C (1500 °F), 1 h, air cooled + 480 °C (900 °F), 5 h, air cooled.

(b) L-S orientation (that is, tensile load applied along longitudinal axis and crack propagation along the short transverse axis)

Temperature and time exert a significant influence on the properties that are developed in maraging steels during age hardening. These effects are clearly illustrated by the graphs in Fig. 9(a) and 9(b) for 18 Ni Marage 250. Hardening is initially very rapid as shown by the substantial increases in hardness and tensile strength that occur after only a few minutes at the age-hardening temperature. As aging time increases, eventually a point is reached where hardness and strength begin to decrease due to coarsening of the precipitates and formation of reverted austenite. Reverted austenite

generally begins to form as rather small particles at prior austenite grain boundaries and at packet and lath martensite boundaries. As shown in Fig. 9(a) and 9(b), the time at which overaging begins to occur is a function of temperature and generally obeys known time/temperature kinetic relationships such as the familiar Larson-Miller parameter. Figure 9(a) also indicates that significantly higher-aged hardness levels can be achieved in 18 Ni maraging steels by aging at lower than normal temperatures for extended periods. Unfortunately, the times associated with aging temperatures in the 400 to 425 °C (750 to 800 °F) range are on the order of 300 to 1000 h and generally are not viable for commercial production.

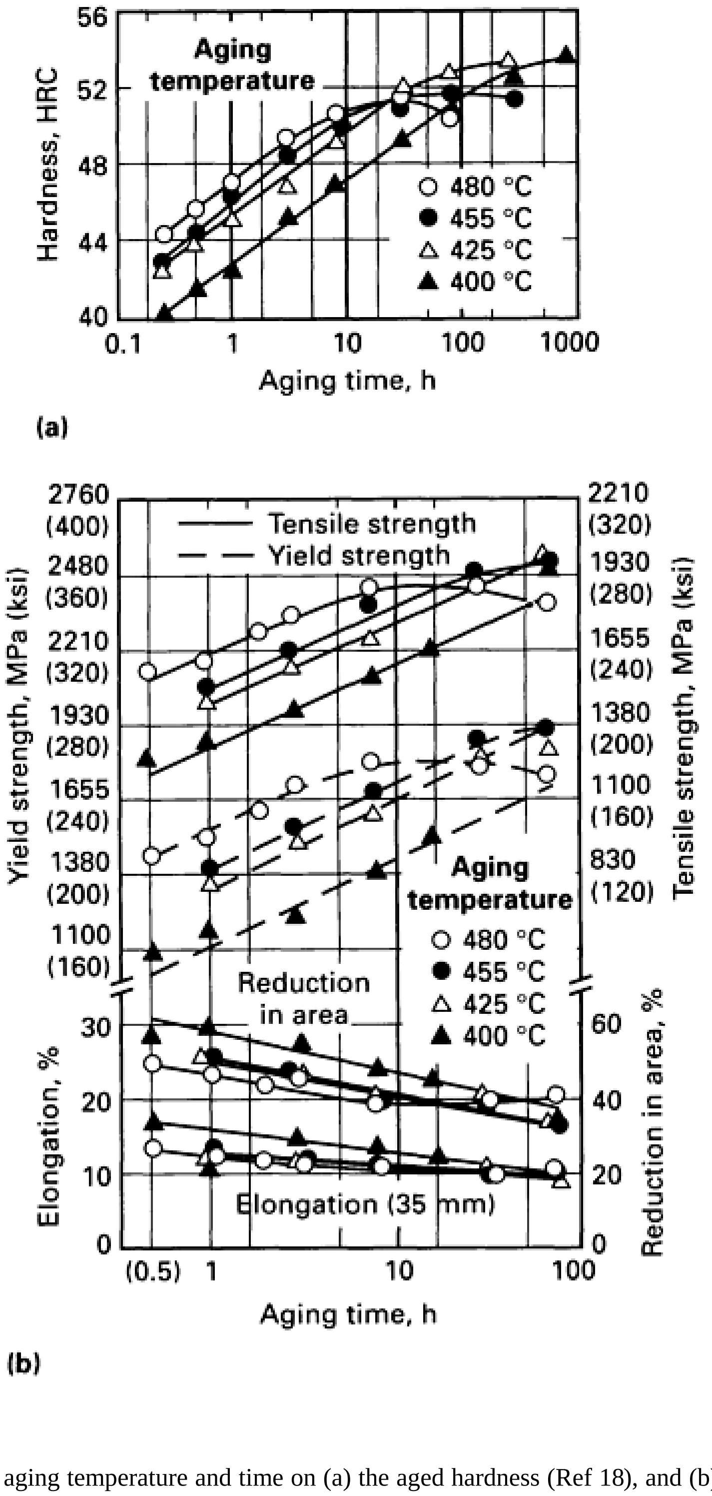

Fig. 9 Graphs showing the effect of aging temperature and time on (a) the aged hardness (Ref 18), and (b) the longitudinal tensile properties (Ref 37) of 18 Ni Marage 250 air-melted plate. Heat treatment: Solution heat treated at 815 °C (1500 °F) for 1 h, air cooled, and aged

Overaging. Great effort has been devoted to examining the properties of overaged maraging steels. The general belief is that an overaged microstructure should have good resistance to both fracture and stress-corrosion cracking (scc) as a result of the inherent lower strength and the potential crack-blunting ability of finely distributed austenite particles. In many instances this has been found to be so, and impressive improvements in plane-strain fracture toughness (K_{Ic}) or

threshold stress intensity for stress-corrosion cracking (K_{Iscc}) have been achieved with only modest reductions in yield strength of an overaged structure (Fig. 10). Unfortunately, however, there appears to be more heat-to-heat variability when overaging heat treatments are used. This variability is the result of a greater sensitivity of austenite formation to minor changes in composition and processing. Even the most homogeneous-looking structures contain minor alloy segregation that is manifested in the form of alloy-rich and alloy-lean bands. The alloy-rich bands tend to overage more rapidly than their alloy-lean counterparts. It is therefore difficult to recommend specific overaging heat treatments that will produce consistent mechanical properties. Generally, if a specific yield strength is required, it is better to use a maraging steel in which the required strength can be produced by conventional aging than to use an overaged steel of higher strength.

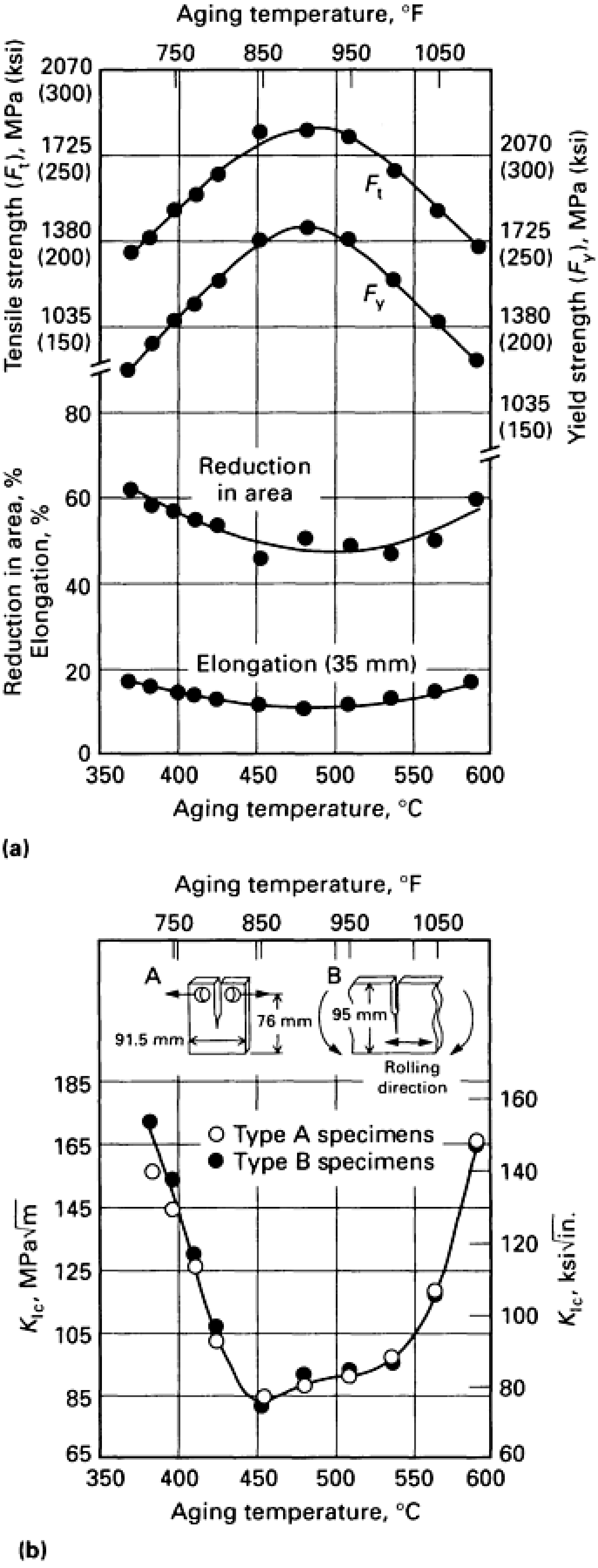

Fig. 10 Effect of aging temperature on (a) the longitudinal tensile properties, and (b) the plane-strain fracture toughness (L-T orientation) of 18 Ni Marage 250 consumable vacuum-melted plate. Heat treatment: Solution heat treated at 815 °C (1500 °F) for 1 h, air cooled, and aged

at indicated temperatures for 6 h. Sources: Ref 10, 38

Cold Working and Aging. The yield and ultimate tensile strengths of maraging steels can be increased by up to 15% by cold working prior to aging (see Table 8). This is accomplished by cold working previously solution-annealed material with up to a 50% reduction prior to aging. There is a concurrent loss in ductility and toughness. Some directionality of properties also occurs, with ductility being downgraded slightly more in the direction perpendicular to cold working. Cold reductions in excess of 50% should be avoided because delamination of the product may occur.

Table 8 Effect of cold work on Marage 250 fasteners

Alloy	Cold work, %	Yield strength		Tensile strength		Shear strength[a]		Elongation in 25 mm (1 in.), %	Reduction in area, %
		MPa	ksi	MPa	ksi	MPa	ksi		
18 Ni Marage 250	0	1800	261	1820	264	1025	149	8.6	57
	25	1875	272	1910	277	1070	155	6.5	49
	50	2020	293	2055	298	1140	165	5.2	44
20 Ni Marage 250	0	1750	254	1850	268	1040	151	9.2	56
	25	1903	276	1937	281	1062	154	6.7	48

(a) Double-shear-type test

Nitriding. Considerable surface hardening can be achieved by nitriding maraging steels in dissociated ammonia. Hardness levels equivalent to 65 to 70 HRC can be achieved at depths up to 0.15 mm (0.006 in.) after nitriding for 24 to 48 h at 455 °C (850 °F). Nitriding at this temperature allows simultaneous age hardening to occur. Salt bath nitriding for 90 min at 540 °C (1000 °F) has also been performed successfully; however, such treatment must be very carefully controlled to avoid excessive overaging. Both the fatigue strength and the wear resistance of maraging steels are improved by nitriding.

Postweld Heat Treatment. Welding exposes base metal to a range of temperatures, from molten metal within the weld, to ambient temperature some distance away. The area adjacent to the weld tends to be coarse grained as a result of the grain growth that accompanies the high temperatures in this portion of the heat-affected zone. Further away, the region that was heated between 595 and 745 °C (1100 and 1375 °F) tends to be overaged. Mechanical properties can be recovered for the most part by reaging the component. This should be considered a minimum requirement. Better properties can be obtained if the component is resolution annealed and aged; however, this may lead to distortion of the part. The most common practice is to simply reage after welding.

Baking is a low-temperature thermal exposure in the 150 to 200 °C (300 to 400 °F) range for hydrogen removal. Hydrogen embrittlement can occur in maraging steels when they are exposed to electrochemical operations such as plating. Because hydrogen pickup is difficult to detect, components exposed to such an environment should be baked for a period of 3 to 10 h. Mechanical properties, other than those that are deleteriously affected by hydrogen embrittlement, will not be affected by this low-temperature treatment.

Surface Treatment. Grit blasting is the most efficient technique for removing heat-treat oxide. Maraging steels can be chemically cleaned by pickling in sulfuric acid or by duplex pickling in hydrochloric acid and then in nitric and hydrofluoric acid. As with conventional steels, care must be taken to avoid overpickling. The sodium hydride cleaning of maraging steels should be avoided to minimize problems with crack formation. Grease and oils can be removed by cleaning in trichloroethane-type solutions.

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Heat Treating of Powder Metallurgy Steels

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Introduction

ATTAINING CONSISTENT RESULTS has always been a challenge in the heat treatment of sintered powder metallurgy (P/M) steel components. Unlike hardenability in wrought steel, where the response is controlled primarily by chemistry and grain size, hardenability in P/M steel is significantly influenced by interconnected porosity. Interconnected porosity is a network of connecting pores in a sintered object that permits a fluid or gas to pass through the object; also referred to as interlocking or open porosity. Because P/M is a net-shaped process, dimensional change or distortion occur that may affect the function or fit of the part. If a P/M part has been slack quenched, to reharden it without degrading the strength and toughness of the part is difficult.

In P/M, hardenability is influenced not only by porosity but also by prior processing variables such as graphite segregation and the degree of sintering. When P/M parts are quenched from the austenitic range, the external surfaces may be exposed to much higher cooling rates than are the interior surfaces, resulting in mixed microstructures and inconsistent hardness readings. These variations increase with the part design complexity. The next section briefly reviews the relationship between porosity and properties.

Effect of Porosity on Material Properties

The mechanical properties of wrought, fully dense steel are determined by chemical composition, microstructure, and surface characteristics. When porosity is uniformly distributed throughout a metal, the response to external stress can affect other physical, mechanical, and electrical properties. The degree of porosity in a metal affects the following material properties:

- Density
- Conductivity (thermal and electrical)
- Magnetic permeability
- Saturation induction
- Tensile strength, yield strength, and elongation
- Fatigue impact strength
- Modulus of elasticity
- Poisson's ratio
- Apparent hardness

- Hardenability
- Surface roughness

Approximate mathematical relationships [per Metal Powder Industries Federal (MPIF) Standard 35] between porosity and some physical properties are expressed as:

$$\textit{Density} = (\text{Theoretical density of metal}) \text{ x } \left(1\text{-}\frac{\%\text{porosity}}{100}\right)$$

$$\textit{Conductivity} = (\text{Theoretical conductivity of metal}) \text{ x } \left(1\text{-}2\frac{\%\text{porosity}}{100}\right)$$

Fatigue strength
= 0.40 × U.T.S., determined experimentally

$$\text{Modulus of elasticity of sintered steel} = (\text{Modulos of elasticity of wrought steel}) \text{ x } \left(1\text{-}\frac{\%\text{porosity}}{100}\right), \text{valid when \% porosity} < 50$$

Additional information is available in the article "Ferrous Powder Metallurgy Materials" in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.*

Relationship between Porosity and Hardenability

Maximum hardness is achieved in any steel composition with a fully martensitic microstructure. This microstructure can only be produced, however, if the diffusion-dependent transformation of austenite can be suppressed by sufficiently rapid cooling. A number of factors affect cooling rates throughout a given shape and the response of a given steel composition to those cooling rates. Hardenability for a wrought material can be defined as the capacity of the microstructure of a metal to be transformed from austenite to martensite at a given depth when cooled rapidly. The core hardenability depends directly upon the thermal conductivity of the steel to dissipate the heat content.

As has been shown, thermal conductivity in P/M parts is determined by the percent of porosity in the workpiece material. This porosity acts as an insulator and slows heat transfer. The quantity of heat (Q) (in kg-cal/kg) that can be removed from a porous steel upon quenching can be expressed by the relationship:

$$Q = M\,(1 - \varepsilon)\; C(\Delta T) \qquad \textbf{(Eq 1)}$$

where M (1 - ε) is the mass of the sintered steel with percent of porosity (ϵ), which has the same surface for heat exchange as a fully dense part of equal shape, and C is the average heat capacity of the material. This property is not influenced by the porosity. ΔT is the temperature differential occurring during cooling. Therefore:

$$\frac{Q}{M.\Delta T} = (1 - e)C \qquad \textbf{(Eq 2)}$$

As porosity approaches zero, hardenability increases linearly, as shown in Fig. 1. This figure shows the results of a series of Jominy tests in which test specimens made from atomized iron containing 0.90% graphite were pressed and sintered at various density levels. The lowest-density specimen contained 24% porosity, whereas the highest-density specimen contained approximately 9% porosity.

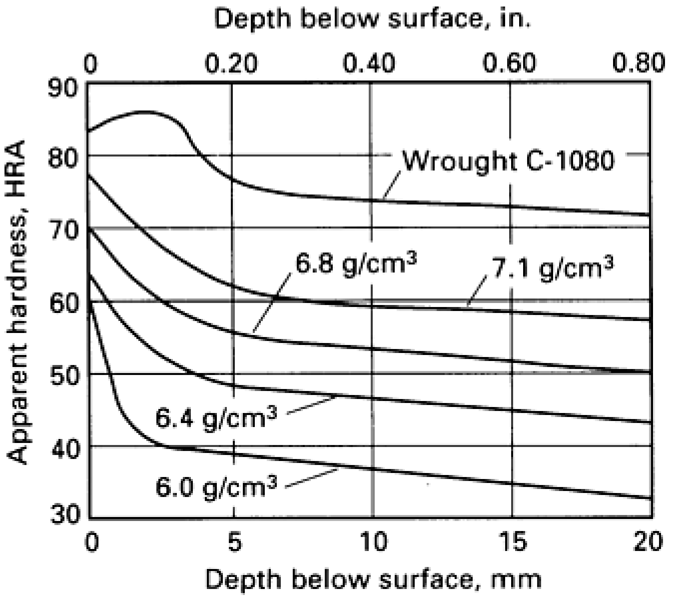


Fig. 1 Effect of metal powder density on the hardenability of P/M steels. The four test specimens, made from an atomized iron metal powder containing 0.90% graphite, had densities ranging from 6.0 g/cm^3 (0.217 lb/in.^{3}) (24% porosity) to 7.1 g/cm^3 (0.256 lb/in.^{3}) (9% porosity) and compositions similar to the wrought C-1080 with which they are being compared.

The test specimens, along with a test bar machined from wrought C-1080 steel having a composition similar to that of the P/M steel, were austenitized at 870 °C (1600 °F) for 30 min in a protective neutral atmosphere and then end quenched in a water column, according to the Jominy test described in ASTM A 255. Hardness readings were taken every 2.5 mm (0.10 in.) from the quenched end and plotted as shown in Fig. 1. This graph dramatically illustrates that the hardenability of P/M steels is limited by the influence of porosity on thermal conductivity.

Influences of Porosity on Case Depth

At porosity levels above 8%, the pores are interconnected by small channels. This allows gases to penetrate quite rapidly. Upon case hardening with gases containing a high carbon potential, this interconnected porosity allows diffusion of carbon into the internal pore surfaces as well as to the external surface of the part. If it is assumed that total porosity (ε_t) is the sum of both open porosity (ε_o) and closed porosity (ε_c):

$$\varepsilon_t = \varepsilon_o + \varepsilon_c \qquad \textbf{(Eq 3)}$$

The inverse of ε is a measure of the resistance to penetration of the gases, and the ratio:

$$R = \frac{1}{(e_0 - e_c)\, x\, e_0} \qquad \textbf{(Eq 4)}$$

is an indication of the maximum resistance that the gas can meet in its passage through the interconnected porosity. Plotting this resistance index (*R*) against total porosity, we see a curve as shown in Fig. 2. This curve can be verified by experiment.

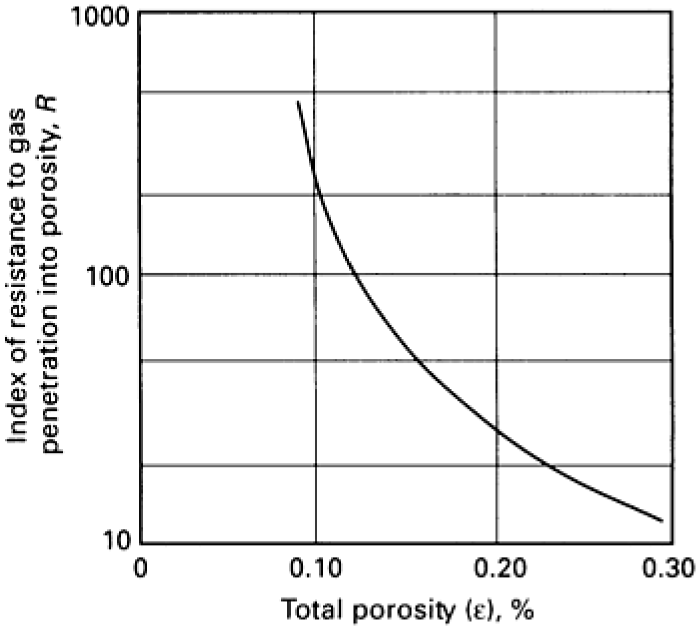


Fig. 2 Resistance to gas penetration of a P/M steel as a function of metal powder density

The photographs shown in Fig. 3 are microstructures of P/M test specimens that were carbonitrided. The 25 mm (1 in.) diam slugs were pressed and sintered to increasing density levels from atomized iron with 0.20% graphite added. Upon sintering, the chemistry of the P/M slugs approximated that of AISI/SAE C1018 carbon steel. A test specimen was also machined from C1018 bar stock, and all specimens were then carbonitrided at 870 °C (1600 °F) for 60 min and oil quenched. As is shown, increasing density was accompanied by a proportional decrease in carbon penetration, to approximately 7.0 g/cm^3 (0.253 lb/in.^{3}). At this point, the interconnected pores began to close off, preventing the gases from penetrating into the internal volume of the part.

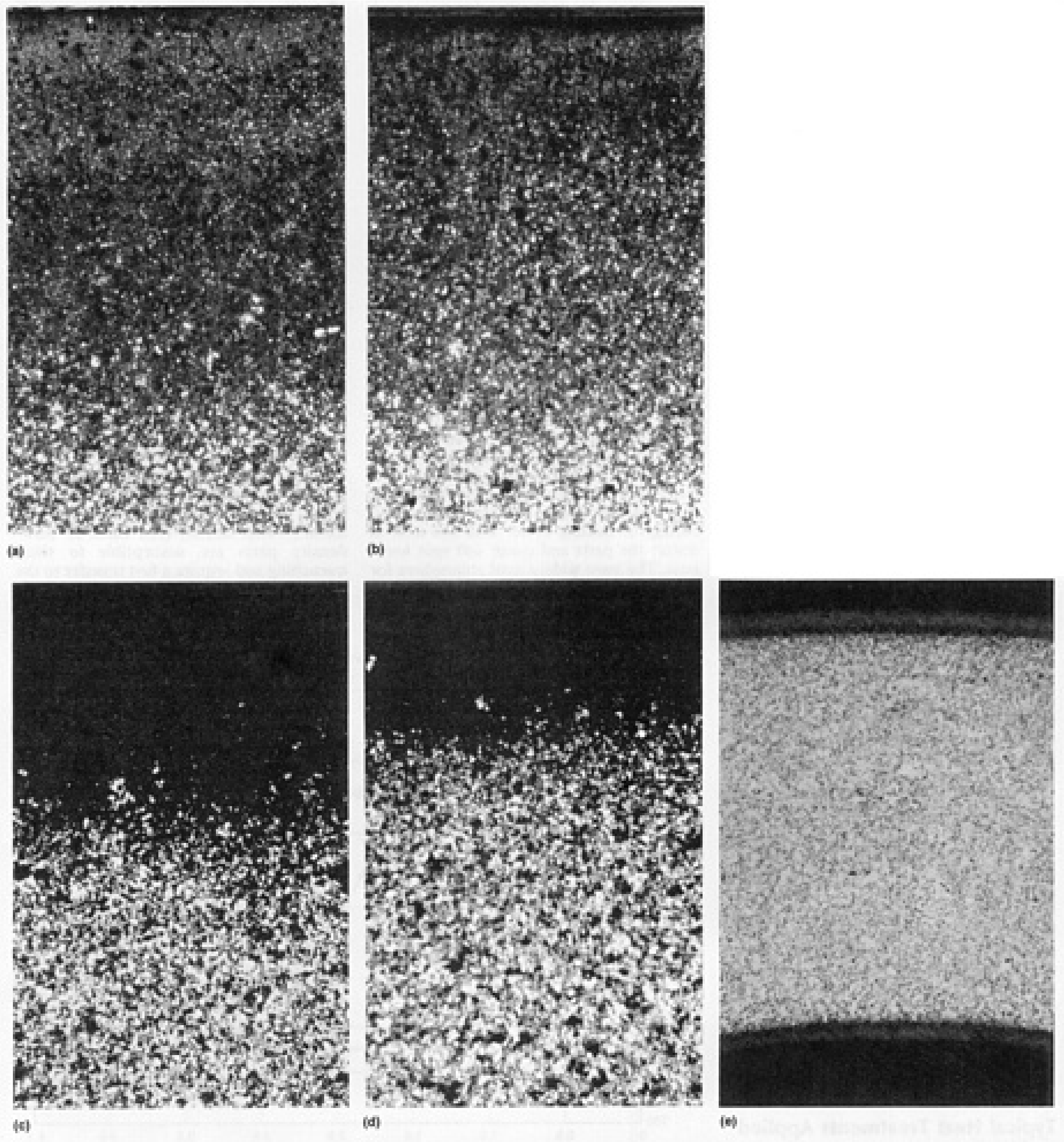


Fig. 3 Microstructures showing relationship of density to carbon penetration in carbonitrided P/M steels having composition similar to carbonitrided C1018 steel. (a) Density, 6.0 g/cm^3 (0.217 lb/in.^{3}); carbon penetration, 3.6 mm (0.140 in.). (b) Density, 6.4 g/cm^3 (0.231 lb/in.^{3}); carbon penetration, 3.3 mm (0.130 in.). (c) Density, 6.8 g/cm^3 (0.246 lb/in.^{3}); carbon penetration, 1.8 mm (0.070 in.). (d) Density, 7.0 g/cm^3 (0.253 lb/in.^{3}); carbon penetration, 1.0 mm (0.040 in.). (e) Density, 7.87 g/cm^3 (0.284 lb.in.^{3}) (wrought) C1018; carbon penetration, 0.3 mm (0.012 in.). All 25×

By plotting depth below surface against density (Fig. 4), it became evident that for optimum control of case-hardening processes, P/M parts should be specified at 7.0 g/cm^3 (0.253 lb/in.^{3}) or higher.

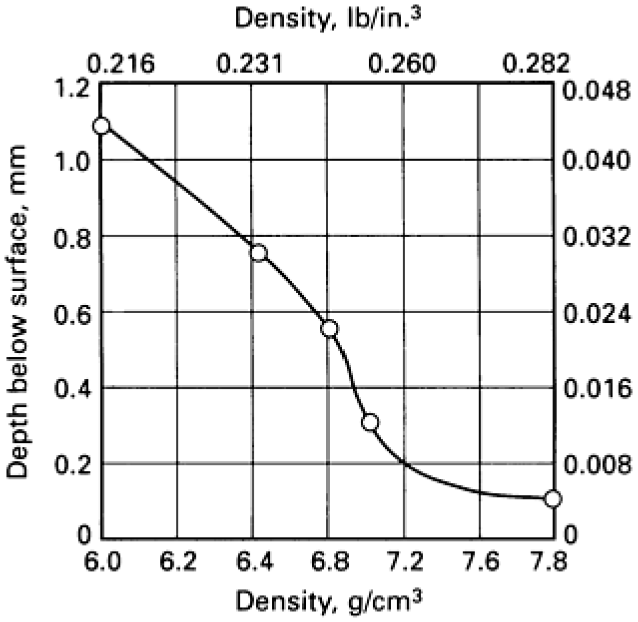


Fig. 4 Effect of metal powder density on the case depth of a carbonitrided P/M steel. Hardening sequence: carbonitrided at 70 °C (1600 °F) for 30 min, oil quenched, and tempered 1 h at 205 °C (400 °F)

These test specimens were then micro-hardness tested. From the graph shown in Fig. 5 it is apparent that many problems can occur when case hardening low-density parts. Because of the fast penetration of carburizing gases, a controlled carbon potential cannot be sustained at the surface of the part. This would allow soft spots to occur upon quenching.

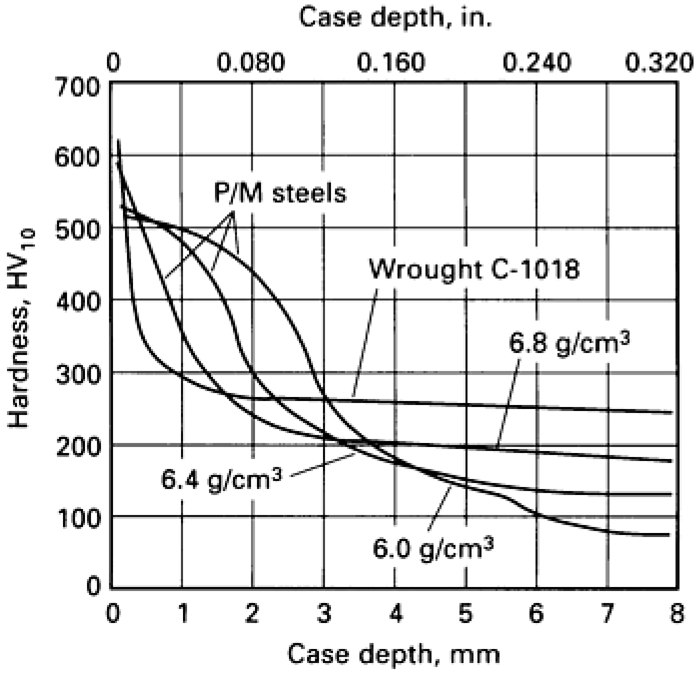


Fig. 5 Plot of hardness versus case depth as a function of metal powder density in P/M steels carbonitrided 30 min at 870 °C (1600 °F) and then oil quenched. P/M steel composition is similar to that of wrought C1018.

The primary purpose of case hardening low-carbon steels is to provide a hard, wear-resistant surface while maintaining a soft ductile core. This combination imparts optimum wear resistance and toughness properties to these materials. When

carbon penetration is uncontrolled, parts can exhibit extreme embrittlement and excessive dimensional distortion upon quenching.

Effect of Alloy Content on Hardenability

It is known that by increasing the carbon content of steel, tensile strength and hardness are gained in proportion to the added carbon. In wrought steel, this ratio is maintained to approximately 1.4% C.

In P/M steels, ultimate tensile strength is reached at the eutectoid composition of 0.9% C. By increasing carbon content above this level, carbide networks begin to form at grain boundaries and porosity channels. This causes embrittlement and loss of rupture strength. As alloying agents such as nickel, molybdenum, chromium, and copper are added, the optimum carbon content is lowered. These elements tend to reduce the critical cooling rate. In sintered steels, the most common alloying agents are copper and nickel.

Copper Content. Additions of copper increase both hardness and tensile strength in the sintered condition. Upon heat treatment, it increases depth of hardness but severely reduces toughness and elongation. The relationship existing among modulus of rupture, copper additions, and combined carbon is shown in Fig. 6. As carbon content increases, rupture strength increases proportionately to an optimum level and then begins to decrease.

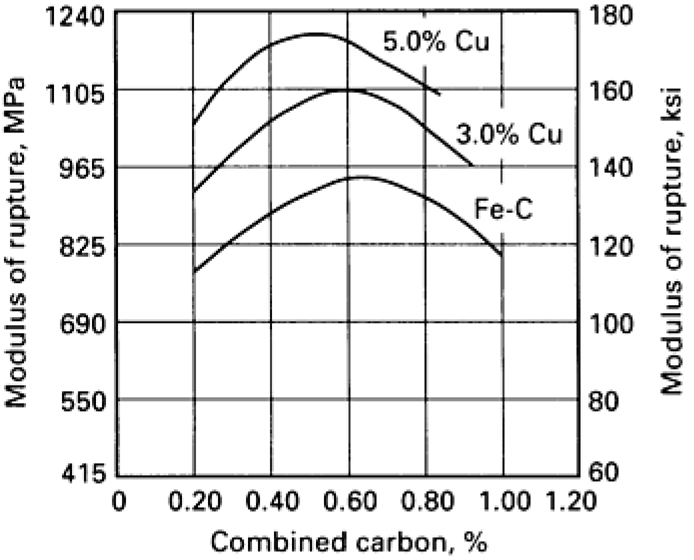


Fig. 6 Plot of combined carbon content versus modulus of rupture as a function of copper content (0 to 5%) in P/M steels. Metal powder density of steel is 6.6 g/cm^3 (0.238 lb/in.^{3}). Samples neutral hardened for 30 min at 870 °C (1600 °F)

In the plain iron-carbon compositions, peak strength occurs near the eutectoid composition in the as-sintered condition and at approximately 0.65% C in the heat-treated condition. By adding copper to the iron-carbon compositions, there exists a significant increase in strength with increasing copper content to approximately 5% Cu. Upon heat treatment however, optimum strength is found at a lower carbon content as the copper content is increased.

Nickel Content. Nickel increases tensile properties of as-sintered P/M steels approximately one-half as much as copper but provides significantly higher strengths after heat treatment due to higher hardenability. This is because of the heterogeneous nature of blended nickel alloys. Copper, which melts at approximately 1040 °C (1905 °F), forms a liquid phase upon sintering at 1120 °C (2050 °F), creating a homogeneous iron-copper alloy. Nickel, having a higher melting point than the sintering temperature, will alloy only by solid-state diffusion. This produces a duplex microstructure consisting of partially alloyed iron surrounding nickel-rich islands. Upon heat treatment the matrix transforms to martensite, but the nickel-rich areas remain austenitic. This results in a strengthening of the matrix with some ductility and toughness retained.

Nickel-Copper Content. Figure 7 shows the influence of increasing nickel and copper contents on hardenability of P/M steels. Here Jominy bars were made with increasing levels of copper and nickel, holding carbon content at 0.50%. All

bars were pressed to a 6.7 g/cm^3 (0.24 lb/in.^{3}) density and austenitized at 850 °C (1560 °F) for 2 h. By adding copper to the iron-carbon alloy, a dramatic increase in surface hardness is seen with a relatively small increase in hardenability. By adding nickel to the iron-copper-carbon alloy, we see a slight gain in surface hardness but a significant improvement in hardenability. Many components made today that require optimum heat-treated properties contain both nickel and copper additions to a low-carbon, high-density steel.

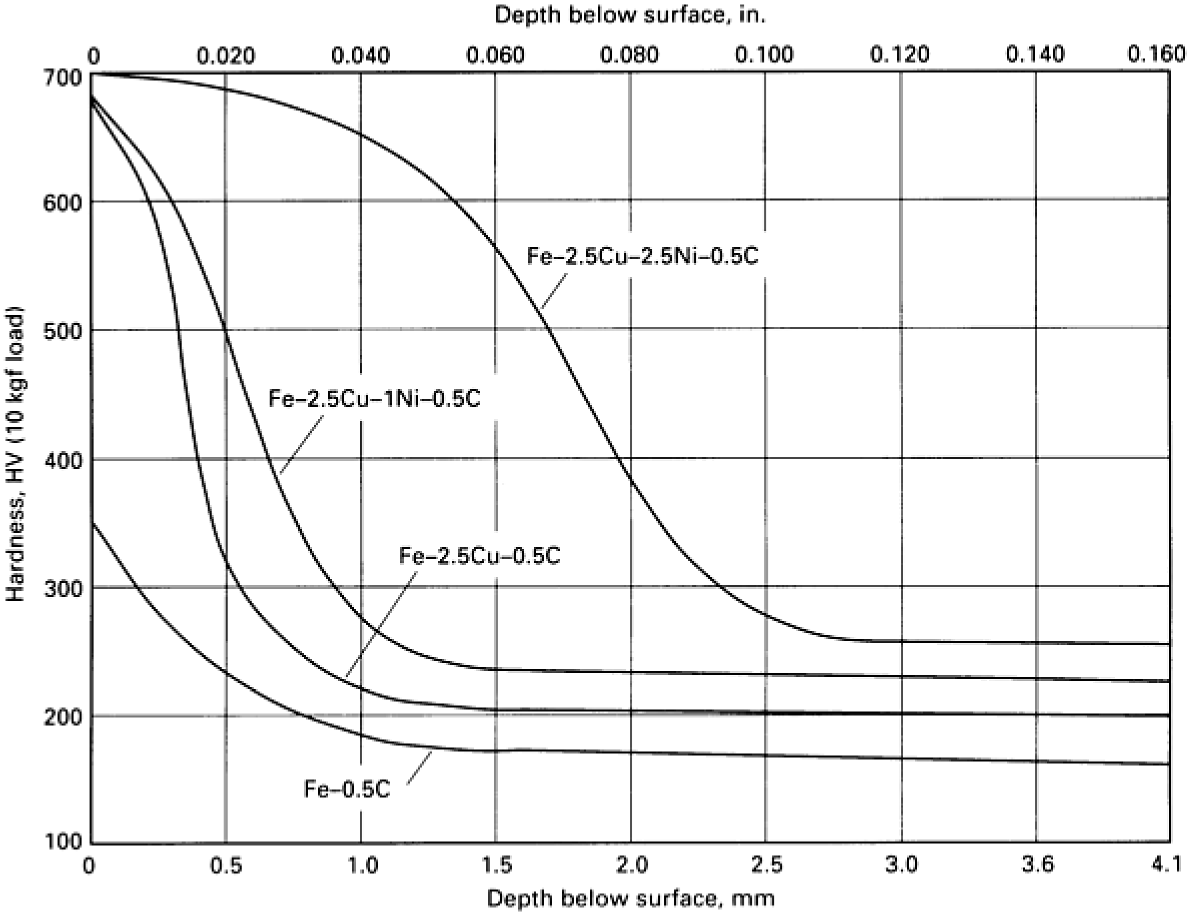


Fig. 7 Effect of copper and nickel additions on the hardenability of iron-carbon P/M steels. Metal powder density was 6.7 g/cm^3 (0.242 lb/in.^{3}). Specimens carburized 2 h at 850 °C (1560 °F)

Effect of Materials and Processing on Heat-Treated Properties

Conventional blended alloys as previously described with a single compaction at 410 to 620 MPa (30 to 45 tsi) and a conventional sinter at 1120 °C (2050 °F) provide typical heat-treated properties listed in Table 1. Further details of the range of properties obtainable by heat treating P/M copper and nickel steels made from elemental powders are given in Table 2.

Table 1 Comparison of the mechanical properties of conventional blended P/M alloys versus prealloyed P/M alloys

P/M alloy	Sintering temperature		Ultimate tensile strength		Yield strength		Elongation, %	Hardness, HRC	Fatigue strength		Impact resistance (Unnotched Charpy test)	
	°C	°F	MPa	ksi	MPa	ksi			MPa	ksi	J	ft · lbf

Conventional blended (410-620 MPa, or 30-45 tsi single compaction)	1120	2050	860	125	. . .	. . .	0.5	30	315	46	8-11	6-8
Prealloyed SAE 4600 type with 0.5% C												
Re-pressed [410 MPa (30 tsi) initial pressing; 550 MPa (40 tsi) re-pressing]	1120	2050	895	130	. . .	. . .	1.0	40	345	50	11-14	8-10
High-temperature sintering (also heat treated)	1260	2300	1170	170	1035	150	1.5	48	425	62	16-19	12-14

Table 2 Composition and mechanical properties of selected heat-treated iron-copper, iron-nickel, and nickel-molybdenum P/M steels

P/M alloy steel	MPIF material code[(a)]	Composition, wt%					Density		UTS		Transverse rupture strength		Apparent hardness, HRC	Impact strength	
		Fe	C	Cu	Ni	Mo	g/cm^3	lb/in.^{3}	MPa	ksi	MPa	ksi		J	ft · lbf
Mixed elemental powders based on ATOMET 1001 steel powder[(b)]															
Iron-copper	FC-0205-HT	97.5	0.5	2	. . .	. . .	6.8	0.246	786	114	1170	170	27	. . .	. . .
							7.0	0.253	869	126	1345	195	30	. . .	. . .
		96.5	0.5	3	. . .	. . .	6.8	0.246	765	111	1235	179	27	. . .	. . .
							7.0	0.253	883	128	1370	199	29	. . .	. . .
	FC-0208-HT	97.3	0.7	2	. . .	. . .	6.8	0.246	862	125	1360	197	35	. . .	. . .
							7.0	0.253	1030	149	1595	231	40	. . .	. . .
		96.3	0.7	3	. . .	. . .	6.8	0.246	848	123	1435	208	34	. . .	. . .
							7.0	0.253	979	142	1745	253	38	. .	. . .

														.	
Iron-nickel	FN-0205-HT	97.4	0.6	. . .	2	. . .	6.8	0.246	792	115	1235	179	36		6
							7.0	0.253	993	144	1545	224	41		8
							7.2	0.260	1165	169	1795	260	44		10
Based on 4201 and 4601 prealloyed low-alloy steel powders															
Nickel-molybdenum	FL-4205-HT	98.45	0.5	. . .	0.45	0.60	6.8	0.246	765	111	1480	215	34	. . .	. . .
							7.0	0.253	889	129	1780	258	38	. . .	. . .
							7.1	0.256	979	142	1930	280	40	. . .	. . .
	FL-4605-HT	97.15	0.5	. . .	1.8	0.55	6.8	0.246	876	127	1505	218	33	. . .	. . .
							7.0	0.253	1035	150	1795	260	39	. . .	. . .
							7.1	0.256	1150	167	1950	283	42	. . .	. . .

Source: Quebec Metal Powders Ltd.

(a) MPIF, Metal Powder Industries Federation.

(b) All mixes contained 0.5% zinc stearate [$Zn(C_{18}H_{35}O_2)_2$]; sintered in endogas at 1125 °C (2050 °F) for 30 min. Heat treatment: austenitized at 815 °C (1500 °F) for 15 min, quenched in oil at 65 °C (150 °F), tempered at 175 °C (350 °F) for 60 min.

Prealloyed Powders. To attain higher properties, special materials or processes must be employed. The first consideration is to use a prealloyed powder that provides more uniform hardenability. The most commonly used prealloy on the market is similar to the AISI/SAE 4600 composition. The nominal composition of this prealloy is 0.20% Mn, 1.8% Ni, 0.50% Mo, and a balance of iron.

Traditionally, prealloyed powders have been harder to compact than mixed elemental powders based on atomized iron. Recent improvements in compressibility of low-alloy steel powders have enabled higher densities to be reached with compaction pressures of 485 to 620 MPa (35 to 45 tsi). Properties of heat-treated nickel-molybdenum P/M steels (MPIF designations FL-4205 and FL-4605) for a wide range of densities are given in Table 2.

By alloying the iron prior to atomization, the hardenability can be significantly improved when compared to a similar blended alloy. However, this increases the particle hardness and reduces compressibility of the powder. To increase the hardenability of these materials, additional operations that would increase density need to be employed.

Re-pressing. Probably the most common method is re-pressing. Dependent on part shape, this can be done in tools similar to the compacting tools, allowing for size change upon sintering. A fully sintered 4600-type prealloy composition would require a 550 to 690 MPa (40 to 50 tsi) re-press to attain 90% of theoretical density. For complex-shaped parts, a process that includes pressing, presintering, re-pressing, and sintering is frequently used. This will provide density levels to approximately 94% of theoretical.

The improvement in hardenability of the 4600-type prealloy is shown in Fig. 8. Here it is compared to an iron-carbon and an iron-nickel-carbon blended alloy with equivalent carbon content and density. The Jominy bars were made by pressing the various alloys at 415 MPa (30 tsi) and sintering at 1120 °C (2050 °F). As shown, the prealloy density was slightly lower than the preblended alloys. The prealloy was then repressed at 550 MPa (40 tsi) to show the improvement in hardenability due to repressing. The 4600 prealloy with 0.50% combined carbon, sintered and re-pressed to 90% of theoretical density and heat treated in the same manner as the blended alloy shown above, will develop the typical heat-treated properties listed in Table 1.

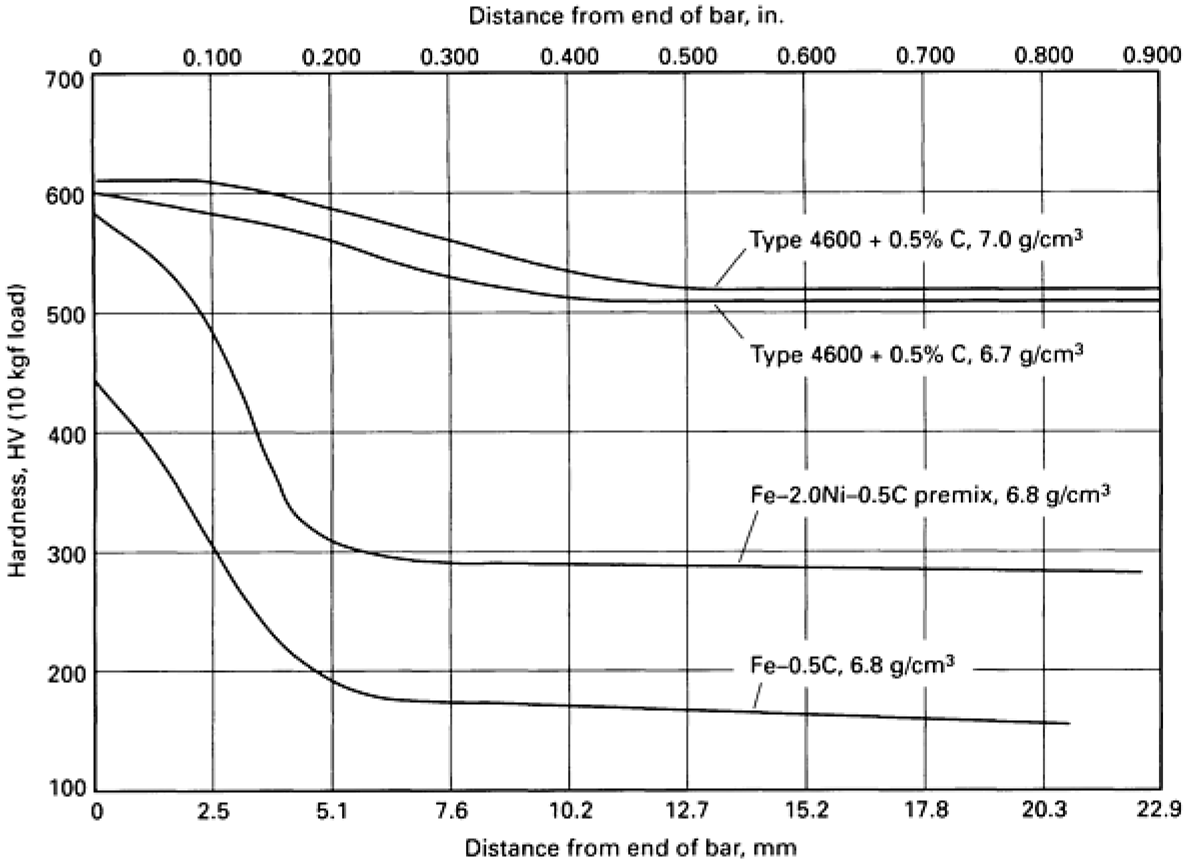


Fig. 8 Effect of prealloying on the hardenability of P/M steels. Two type 4600 prealloyed P/M steels with different metal powder densities are compared with two preblended P/M alloys having different compositions but identical densities. All four steels sintered at 1120 °C (2050 °F)

High-Temperature Sintering. Most P/M sintering is done in mesh belt furnaces with a temperature capability to 1150 °C (2100 °F) Special pusher- and walking-beam furnaces are now being used that can provide temperatures to 1380 °C (2515 °F) These temperatures can also be attained in batch-type vacuum furnaces. By sintering at higher temperatures, more uniformity in alloying is realized along with improved pore rounding and coalescence. This can provide added hardenability and more consistent heat-treating properties. Properties of an AISI/SAE 4600-type alloy with 0.5% C, sintered at 1260 °C (2300 °F) and subsequently heat treated, are listed in Table 1.

Typical Heat Treatments Applied to P/M Parts

Neutral Hardening. Many P/M parts heat treated today are neutral hardened. These alloys contain 0.50 to 0.80% C and have densities exceeding 88% of theoretical. They are hardened primarily for wear resistance and improved core strength.

These parts are normally hardened in belt-type or batch-type sealed quench furnaces. Because they are net-shaped parts, they must not touch or impinge upon one another during the heating cycle. This will tend to distort the parts and cause soft spot hardness. The most widely used atmosphere for these furnaces is endothermic gas, with both methane and air additions to control carbon potential (see the article "Furnace Atmospheres" in this Volume). Because these gases can rapidly penetrate the porosity, carbon diffusion is quite rapid. Therefore, short time cycles at relatively low temperatures are used.

Metal Powder Density Determines Hardening Variables. A general rule of thumb for selection of hardening cycles when maximum wear resistance and core strength are desired is to determine the heat-treating cycle on the basis of the metal powder density (see Table 3). Low-density parts are susceptible to slack quenching and require a fast transfer to the quench. The ideal furnace for these parts would be a mesh belt or shaker hearth where the parts can fall freely into the quench. In these furnaces, it is recommended that a high temperature and a slightly carburizing atmosphere be used to counterbalance the loss of control at the quench end of these furnaces.

Table 3 Recommended P/M steel hardening cycles for obtaining maximum combination of wear resistance and core strength based on metal powder density

Density		Quenching					Tempering temperature	
		Temperature		Time at temperature, min	Transfer time, s	Medium		
g/cm^3	lb/in.^{3}	°C	°F				°C	°F
6.4-6.8	0.231-0.246	870-890	1600-1635	30-45	<8	Fast oil	. . .	. . .
6.8-7.2	0.246-0.260	850-870	1560-1600	45-60	<12	Fast oil	150-180	300-355

Medium- to high-density parts suited to batch-type sealed quench furnaces where temperature uniformity and carbon content of the atmosphere are better controlled. Here lower temperatures can be used that minimize part distortion, and atmosphere carbon content can be neutral to the part. The one drawback to batch-type furnaces is the longer transfer time to the quench. Many of the new batch furnaces on the market have automated internal handling equipment to transfer the hot load to the quench. These are not suitable for many P/M parts because of the excessive time delay in reaching the quench.

Quenching Mediums. Also recommended is a fast oil, an oil defined as having a General Motors' quenchometer rating of 10 s or less. Load size is also a critical factor in attaining uniform hardness upon quenching. Most sealed quench furnaces are designed to quench out 0.5 kg (1 lb) of parts per gallon of quench oil. For P/M parts it is recommended that 0.5 kg (1 lb) of parts require 11 to 15 L (3 to 4 gal) of quench oil.

Overloading is probably the most common problem in attaining uniform heat-treated properties. When these parts are quenched, the gases entrained in the porosity are rapidly expelled, creating an extended vapor phase around the parts and thereby reducing the critical cooling rate.

Carburizing is normally specified in parts with a large cross-sectional thickness to attain maximum fatigue and impact properties. The material usually specified for carburizing contains hardenability agents such as nickel, molybdenum, and copper with relatively low carbon content. To develop optimum dynamic properties at porosity levels between 10 to 15%, a combined carbon level of 0.30 to 0.35% is recommended. As porosity is reduced below 10%, combined carbon can be reduced to 0.15 to 0.25% C. Because improved dynamic properties are also associated with high densities, it is recommended that combined carbon be adjusted to a level best suited for re-pressing after sintering Additional information is available in the articles "Gas Carburizing," "Pack Carburizing," "Liquid Carburizing and Cyaniding," and "Vacuum Carburizing" in this Volume.

Wrought Steel. In wrought steel, carburizing is normally characterized by a surface hardness range and an effective case depth. Microhardness measurements can accurately show the hardness profile in wrought steel but can be erratic when used on P/M steels.

P/M Steels. Here subsurface porosity can influence the microhardness readings, resulting in false hardness readings. It is recommended that at least three hardness readings be taken at each level below the surface and averaged to determine effective case depth.

Carburizing of P/M steels is usually done at temperatures between 900 to 930 °C (1650 to 1705 °F). Time cycles are normally short because of the rapid diffusion of carbon through the interconnected porosity. Therefore, atmosphere carbon potentials need to be somewhat higher than those required for wrought steels of similar composition.

Carbonitriding is probably the more common case-hardening treatment used on P/M parts. Here process temperatures are lower (800 to 850 °C, or 1470 to 1560 °F) and ammonia additions to approximately 10% are made. Ammonia dissociates on the parts, allowing nitrogen to diffuse into the surfaces. This retards the critical cooling rate upon quenching and provides a more consistent martensite transformation. It also produces a more consistent surface hardness, which improves wear resistance and toughness of the P/M steel. Because lower temperatures can be used, carbonitriding provides better control of distortion compared to carburizing. Care must be taken when adding ammonia, however, since excessive nitrogen diffusion into the internal pore surfaces can cause embrittlement.

Carbonitriding is a shallow case-hardening treatment. Case depths greater than 0.51 mm (0.020 in.) deep are seldom specified. For this reason, cycle times are relatively short, usually on the order of 30 to 60 min. As in neutral hardening, carbon control is a critical aspect of the treatment. Normally carbon potentials of 1.0 to 1.2% are specified to maintain the carbon profile in the part. Additional information is available in the article "Carbonitriding" in this Volume.

Tempering is usually required after case hardening when densities exceed 90%. In this case, significantly high stresses that could initiate cracking are developed upon quenching. As porosity increases, this stress level is reduced to a level at which a posttemper is not necessary. However, judgment should be used when deciding whether tempering is required. If a substantial amount of retained austenite is formed upon carbonitriding, a temper is advisable.

If the part has thin cross sections, sharp corners, or undercuts that would act as stress raisers, then tempering would also be advisable. Recommended tempering temperatures for P/M parts range from 105 to 200 °C (220 to 390 °F). Above this temperature, entrained quench oil can ignite, creating a hazardous condition in the furnace. Tempering above 200 °C (390 °F) will result in improved toughness and fatigue properties of the heat-treated P/M steel. However, furnaces will need special adaptations to handle the high volume of smoke created by the ignition of the quench oil. Additional information is available in the article "Tempering of Steel" in this Volume.

Induction Hardening. Spur gears, bevel gears, splined hubs, and cams are ideal components to utilize P/M production techniques. These parts usually require hard wear-resistant surfaces in some areas, with the retention of the ductility of the sintered matrix in the remainder of the part. Induction hardening is commonly specified for these applications.

This process can be placed in an automated machining line that can reduce handling and be a cost-effective hardening treatment when high volumes of parts are being produced. Because the inductance of P/M materials is typically reduced due to porosity, a higher power setting is normally required to reach a given depth of hardening compared to that used for a wrought material of similar composition. Furthermore, because the heat is rapidly dissipated, a rapid transfer to the quench is mandatory.

As with wrought steels, the response to hardening by induction is dependent upon combined carbon content, alloy content, and surface decarburization. This latter variable can be a major concern with P/M parts. With today's conventional belt-type sintering furnaces using an Endogas atmosphere, decarburizing can occur as the parts leave the hot zone and cool slowly through the 1100 to 800 °C (2010 to 1470 °F) temperature range.

In most cases, P/M parts are quenched in a water-based solution containing some type of rust preventative to forestall internal corrosion. In those applications where induction hardening is considered, densities above 90% should be specified. With a decrease in density, the resistivity of the steel increases and permeability decreases. For this reason, integral quench coils using a high-velocity spray quench are generally used to attain maximum surface hardness in the P/M part. Additional information is available in the article "Induction Heat Treating of Steel" in this Volume.

Nitrocarburizing. This process is rapidly growing in popularity as a treatment for P/M parts. Here, nitrogen is diffused into the surfaces of the steel in sufficiently high concentration to form a thin layer of ε iron nitride on the surface of the part. This is done at temperatures ranging from 570 to 600 °C (1060 to 1110 °F). At these temperatures no austenite transformation occurs, thereby significantly reducing the dimensional changes and distortion.

The process uses conventional integral quench atmosphere furnaces. The atmosphere usually consists of a 50/50 mixture of endothermic gas and anhydrous ammonia. Control of the nitrided layer thickness, as with the other treatments, is dependent on density. If the nitrided layer is allowed to form on the internal pore surfaces to any significant extent, a volume expansion can occur. For this reason, density of the P/M part should be above 90% of theoretical. This nitrided layer, when properly applied, can reduce the coefficient of friction at the surface of the part and provide improved wear resistance compared to conventional hardening to martensite. This process is best applied to applications where sliding wear and fretting are involved.

Because the hard nitrided layer is relatively thin, this process should not be applied where high indentation or impact loading is involved. The ε nitride layer that is formed can attain a file hardness in excess of HRC 60, depending upon alloy content of the steel. Indentation hardness testing is not recommended when evaluating this process. Since no transformation occurs, the P/M parts can be air cooled without loss of surface hardness. Also, no oil absorption occurs, which leaves the porosity open for impregnation if desired.

Nitrocarburizing also provides improved strength and reduced notch sensitivity in P/M parts. Figure 9 shows the fatigue improvement of two low-carbon P/M steels after nitrocarburizing. A typical nitrocarburized microstructure of an iron-copper-carbon P/M steel is shown in Fig. 10. Additional information is available in the article "Gaseous and Plasma Nitrocarburizing" in this Volume.

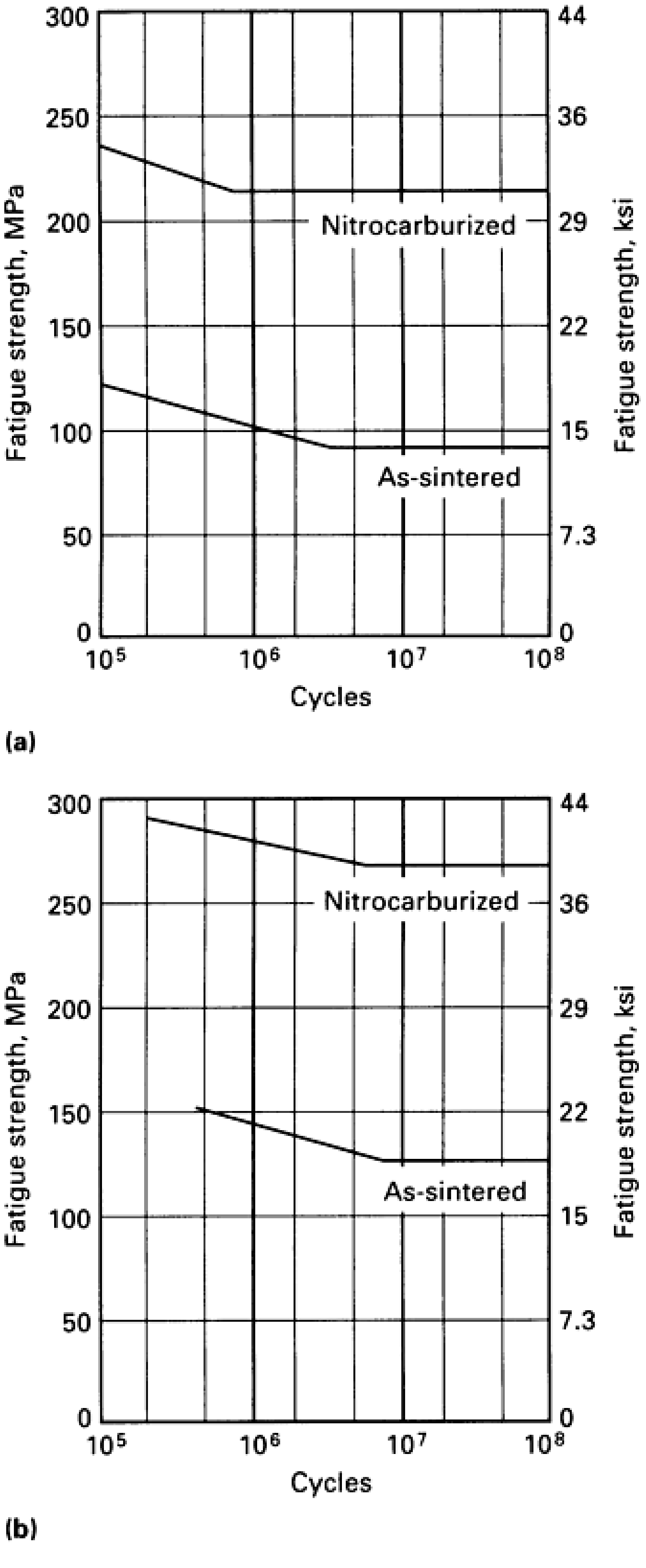


Fig. 9 Increase in the notched axial fatigue strength of sintered low-carbon P/M steels after nitro-carburizing for 2 h at 570 °C (1060 °F). (a) F-0000 carbon steel. (b) FC-0205 copper-carbon steel. Metal powder density was 7.1 g/cm^3 (0.256 lb/in.^{3}).

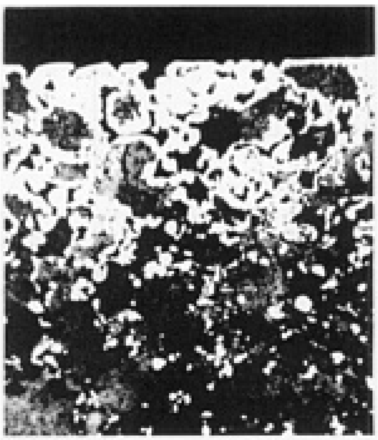


Fig. 10 Typical microstructure in a sintered ferritic nitrocarburized iron-copper-carbon P/M steel. 100×

Steam Treating. P/M parts have traditionally been steam treated for improved wear resistance, corrosion resistance, and sealing capacity. Here, P/M parts are heated in a specific manner under a steam atmosphere at temperatures between 510 to 595 °C (950 to 1100 °F) to form a layer of black iron oxide (magnetite, or ferrous-ferric oxide, $FeO \cdot Fe_2O_3$) in the surface porosity according to the chemical reactions:

$$3Fe + 4H_2O \text{ (steam) } Fe_3O_4 + 4H_2 \text{ (gas)} \qquad \textbf{(Eq 5)}$$

Steam treating cannot truly be described as a heat treatment because no structural changes occur in the matrix. In this process, magnetite (Fe_3O_4) is formed at the interconnecting surface porosity, filling the porosity with a second phase. Magnetite has a microhardness equivalent to HRC 50.

The process itself is straightforward, the primary variables being temperature, time, and steam pressure. Caution must be used to prevent the formation of hydroxides and lower oxides such as ferrous oxide (FeO) and ferric oxide (Fe_2O_3), which is red rust.

The recommended procedure for steam treating is:

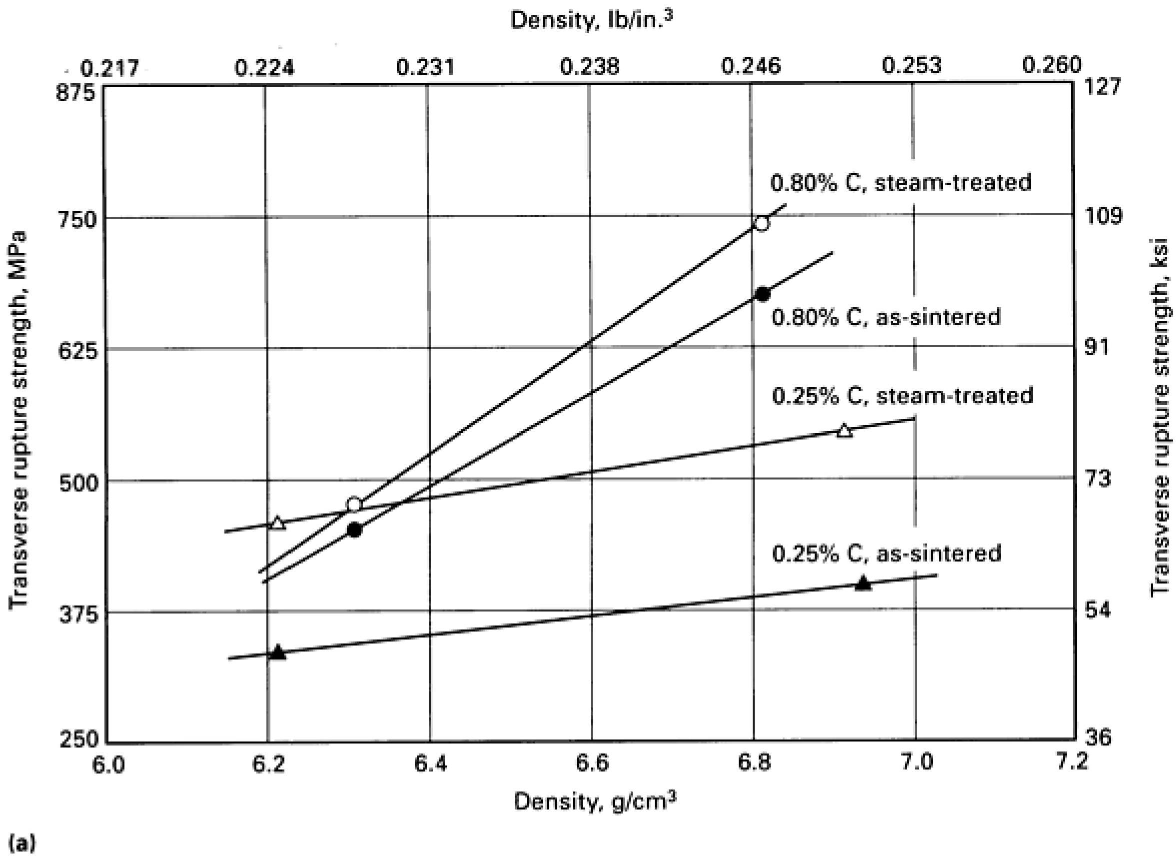
- Preclean parts to remove any oil or lubricants that may have been absorbed into the porosity from prior machining, sizing, or finishing operations
- Load clean sintered parts in loosely packed baskets and place fixture into a furnace preheated to 315 °C (600 °F)
- Heat parts in air until the center of the load has stabilized at the set temperature
- Introduce superheated steam at a line pressure of 35 to 105 kPa (5 to 15 psi) and allow furnace to purge for at least 15 min
- Increase furnace temperature to desired set point and hold for no longer than 4 h at heat
- Upon completion of cycle, reduce furnace temperature to 315 °C (600 °F). When parts reach this temperature, the steam can be shut off and the parts unloaded

Caution should be used when opening the furnace door after the steam cycle. As shown in Equation 5, hydrogen is produced during this process and can ignite. It is recommended that a nitrogen purge be applied prior to unloading. This process, when correctly applied, can impart improved surface properties, and, depending upon steel composition, increased compressive yield strength.

In all steam-treated P/M steels, the ductility is significantly reduced due to the internal stresses created by the formation of the iron oxide. Care must be taken when treating high-carbon P/M steels because these internal stresses can initiate microcracking and cause severe loss of ductility. Many cases have been reported in which parts were accidentally

dropped on the floor after being steam treated, and the parts subsequently shattered like glass. The best recommendation for preventing such an incident is to specify a 0.5% C (max) content on materials that are to be steam treated.

Figure 11(a) shows that transverse rupture strength increases proportionately with sintered density. Upon steam treating, low-carbon P/M steels exhibit a uniform increase in strength, whereas the higher-carbon P/M steels show only a small incremental increase in strength.



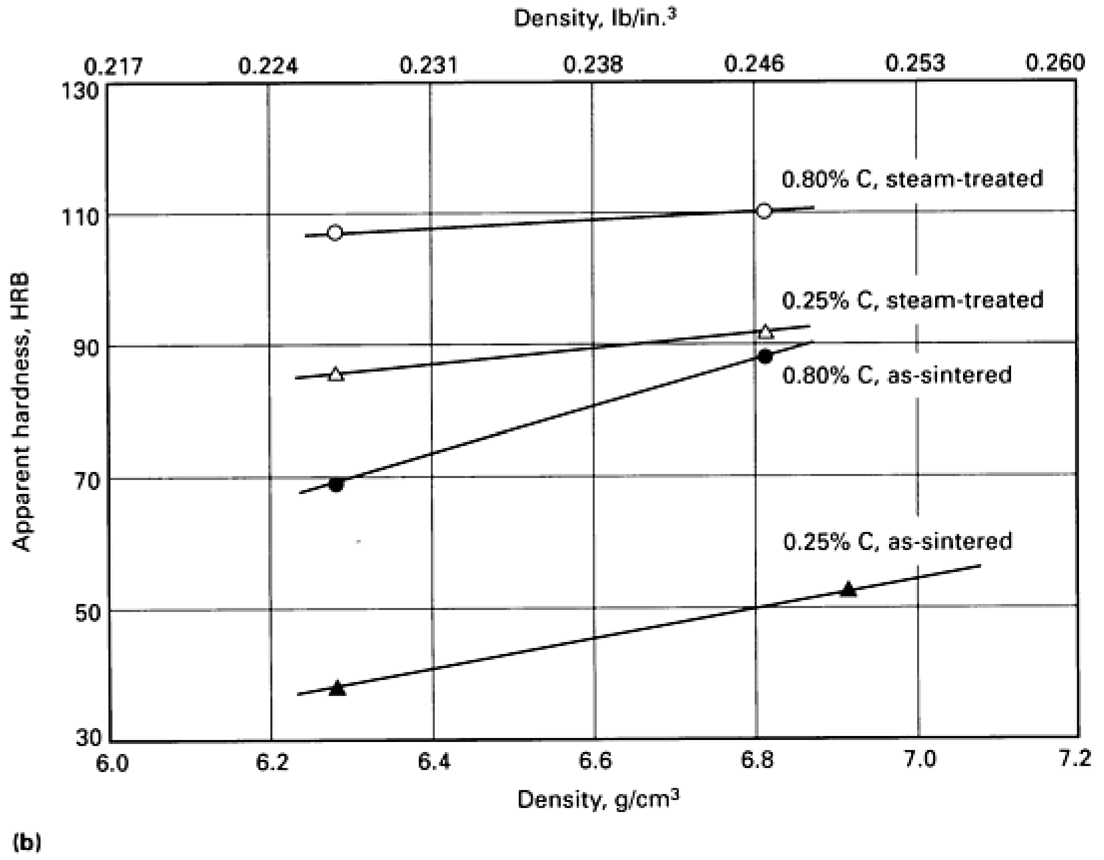


Fig. 11 Effect of steam treating on the mechanical properties of sintered carbon P/M steels as a function of density. (a) Transverse rupture strength. (b) Apparent hardness

Apparent hardness also is improved as shown in Fig. 11(b). By filling the porosity with a hard second phase, the P/M steel can offer better support to an indentation hardness test. As with rupture strength, the incremental increase in hardness of high-carbon steels is less than that of low-carbon steels.

Guidelines to Heat Treating P/M Parts

Whether this secondary operation is done in-house or sent out to a commercial heat treater, some guidelines need to be considered to ensure that parts get properly treated. In the past, a heat treatment was specified primarily to improve wear resistance. With the advent of high-compressibility powders and high-temperature sintering, heat treatments are added to provide improved dynamic properties as well. The following is a list of recommendations when heat treating porous P/M parts:

- Always degrease parts prior to heat treating. In many manufacturing plants, P/M parts are dipped in a rust preventative after sintering. Also, many P/M parts are machined prior to heat treatment and can retain some of the lubricant. These oils can contaminate the heat-treating atmosphere and cause discoloration
- Do not use dense loads. Overlapping parts can cause soft spots and distortion. For best results, parts should be single spaced in layers
- Use highly agitated quenching oil with a quench severity rating (*H*) of 0.7 to 1.5
- When tempering, hold at 205 °C (400 °F) for 2 h before proceeding to higher temperatures. This is to minimize the evolution of smoke and to prevent ignition

If it is planned to send parts outside to a commercial heat treater, a technical review of the part requirements and prior processing history is recommended. Many commercial shops have had bad experiences with P/M because they do not fully understand the implication of porosity and tend to treat parts as they would wrought steels. It is important that you establish a good communication network with your heat treater to alert him to any structural changes in your part caused by changes in powder lot, tooling, or sintering cycle.

A good procedure is to send sample lots to the heat treater for him to establish process capability. After he has met the print requirements, he should be requested to run the parts in the same furnace under the exact conditions as were established. As a parts fabricator, it would be wise to give as much consideration to the heat-treating process as would be given to the primary processes. Reworking because of improper heat treatment can not only add more cost but can also significantly affect the physical properties of the P/M part.

Thermomechanical Processing of Steels

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Introduction

ECONOMIC AND TECHNICAL DEMANDS of the last three decades have forced the global steel industry to undergo a series of important changes. These changes were made imperative by the need of the steel industry to maintain a competitive and leadership position in relation to other engineering materials. Significant advances have been made in both process metallurgy and product metallurgy. These advances have transferred the steel industry into a modern, cost-effective, and high-quality manufacturing force in the world marketplace. The improvements in steelmaking, ladle refining, and continuous casting practices have been matched with other advances in the science and technology of microstructural control in the final product. It is this ability to control microstructure during processing that has allowed significant and cost-effective improvements in the final properties of steel to be achieved. Central to the concept of controlled processing is thermomechanical processing (TMP).

It is now possible to produce as-rolled steels with final properties tailored to the requirements of the final application. The concept of tailored final properties is possible primarily through the ability of the heat treater to control the final microstructure in a predictable manner. This control of the final microstructure is based on an understanding of the way that steels respond to hot processing and how that response can be altered through alloying.

It is well known that the control (that is, refinement) of final microstructure begins during solidification and proceeds during reheating, hot rolling, and final transformation. Because the final transformed microstructure reflects the microstructure and composition of the austenite prior to transformation, it is obvious that the refinement of this final austenite is critical to obtaining the optimum final microstructure and properties. One of the key processing elements used to obtain the proper austenite microstructure is known as thermomechanical processing, which, as will be shown later, is a special type of hot deformation process (for example, rolling, forging, piercing, and so on). The most common form of thermomechanical processing in use today is called controlled rolling (Ref 1). During controlled rolling, it is the as-rolled austenite microstructure that is being controlled.

Because the goal of thermomechanical processing is the refinement of the austenite grain structure, the control of recrystallization and/or grain coarsening during processing are among the metallurgical techniques available. The presence of minute quantities of elements such as niobium, titanium, and vanadium have been shown to be particularly useful during thermomechanical processing because of the change in the solubilities of their carbides/carbonitrides/nitrides in austenite as a function of temperature. These elements are known as microalloying elements (MAE) because they are generally present at levels at or below 0.1 wt%. Hence, the use of these microalloying elements enables the goal of thermomechanical processing to be easily achieved because these elements permit forces retarding recrystallization and grain coarsening to be governed by controlled precipitation during processing. It is, therefore, normal to have microalloyed steels mentioned in discussions of thermomechanical processing. The discussion that follows is a review of various aspects of thermomechanical processing, including its justification, history, underlying physical metallurgy, methods of application, beneficial effects on properties, and current and future applications.

Acknowledgement

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Effect of Microstructure on the Mechanical Properties of Ferrite-Pearlite Steels

Engineering steels require a range of properties in order to be technologically and economically successful. The principal properties of interest in these steels are strength, toughness, ductility, and weldability. Prior to the mid-1960s, structural steels were available in essentially two forms. The first were simple carbon-manganese-silicon steels which were available in either the as-rolled or as-normalized condition. These steels exhibited ferrite-pearlite (F-P) microstructures with yield strengths generally less than 350 MPa (51 ksi). Alternatively, higher-strength steels were available through the heat treatment of these and, more likely, the low-alloy steel grades. These steels exhibited tempered martensite structures with yield strengths generally in excess of 560 MPa (81 ksi). The technological demands of the 1970s in the transportation, energy, and construction industries required large quantities of higher strength, cost-effective steels. Because these demands could not be satisfied by either the existing hot-rolled steels or the existing heat-treated steels due to factors such as insufficient strength and excessive cost, respectively, new steels were clearly required. This demand was ultimately satisfied by the parallel development of microalloyed (MA) steels on the one hand and thermomechanical processing on the other. As discussed later in this section, the synergistic effect of microalloy additions to simple steels and thermomechanical processing together led to improvements in strength, toughness, and weldability. Hence, where it was once possible to have both high strength and toughness only in heat-treated steels, it is now possible to have similar properties in as-processed steels without the need of final heat treatment.

Effect of Microstructure on Yield Strength. Let us begin by discussing the yield strength of hot-rolled microalloyed low-carbon F-P steels. This strength is often expressed as an expanded Hall-Petch equation (Ref 2, 3):

$$\sigma = \sigma_o + \Delta\sigma_S + \Delta\sigma_T + \Delta\sigma_P + \Delta\sigma_D + \kappa_y d_F^{-\frac{1}{2}} \quad \textbf{(Eq 1)}$$

where σ is the observed yield strength, σ_o is the lattice friction stress, and $\Delta\sigma_S$, $\Delta\sigma_T$, $\Delta\sigma_P$, and $\Delta\sigma_D$ are strengthening increments caused by solid solution, texture, precipitation and dislocation effects, respectively. The last term, $\kappa_y d_F^{-\frac{1}{2}}$, is the contribution to strength by the ferrite grain size. More detailed information concerning the contribution of each term to the observed yield strength is given in Table 1.

Table 1 Contributions of microstructure to the yield strength of steel

Strength component	Description of strength variable	Definition or value	Ref
σ_o	Lattice friction	Constant	. . .
$\Delta\sigma_S$	Solid solution	$\approx k_1(C_S)^{\frac{1}{2}}$ (b) $\approx k_1 C_S$ (dilute)	Pickering (4)
$\Delta\sigma_T$	Texture	(hkl)<uvw>	Gladman (5) Backofen (6)
$\Delta\sigma_P$	Precipitation	$\approx f^{\frac{1}{2}}/r$ (c)	Gladman (5)
$\Delta\sigma_D$	Dislocation	$\approx k_2 d_D^{\frac{1}{2}}$ (d)	Dieter (7)
$\kappa_y d_F^{-\frac{1}{2}}$ (a)	Grain size	. . .	Pickering (6)

(a) κ_y, Hall-Petch constant; d_F, ferrite grain diameter.

(b) C_S, solute concentration; k_1, a constant.

(c) *f*, precipitate volume fraction; *r*, precipitate radius.

(d) d_D, dislocation density; k_2, a constant

As shown in Table 1, the lattice friction stress, for a given crystal structure, is a constant (Ref 8). Theoretically, the solid solution strengthening component should vary with the square root of the solute content, but $\Delta\sigma_S$ has been found to vary approximately linearly in dilute solutions (Ref 4). The texture component, $\Delta\sigma_T$, originates in the Schmid factor and, hence, would vary with the nature, sharpness, and intensity of the crystallographic texture exhibited by the ferrite grains (Ref 5, 6). The precipitation hardening increment, $\Delta\sigma_P$, varies with the square root of the volume fraction of precipitation, *f,* and inversely with precipitate size, *r,* while the dislocation strengthening increment, $\Delta\sigma_D$, increases with the square root of the excess dislocation density, d_D (Ref 5, 7). Finally, the strength also increases with the inverse square root of the ferrite grain size, d_F (Ref 4).

These contributions to yield strength are shown in Fig. 1. Superimposed on Fig. 1 are grain sizes typical of hot-rolled carbon steels and controlled-rolled MA steels. Note that these two steels differ in grain size and the presence of a precipitation hardening increment ($\Delta\sigma_P$ in Eq 1) in the MA steel. This combination of extra grain refinement and precipitation hardening renders the controlled-rolled MA steel approximately twice as strong as the hot-rolled carbon steel. A concrete example of these effects, shown in Fig. 2, compares the as-rolled behavior of a hot-rolled carbon steel

with a controlled-rolled MA steel. The presence of the niobium has led to finer grain sizes and higher-strength levels, all because of the synergism that exists between microalloying elements and thermomechanical processing.

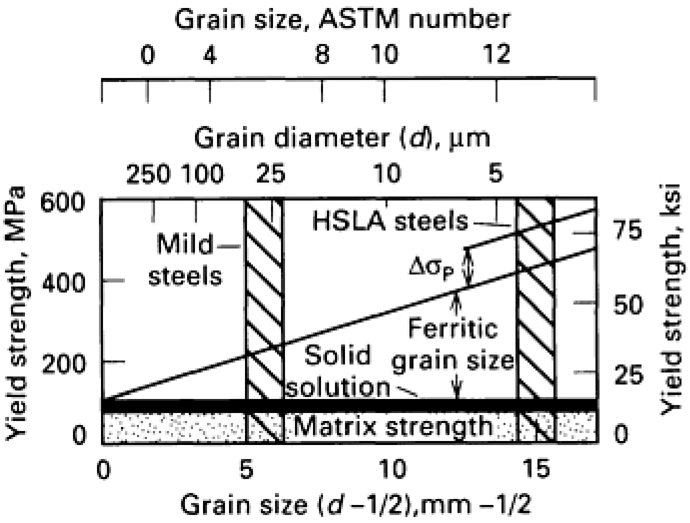

Fig. 1 Plot of yield strength versus grain size showing possible strengthening mechanisms operative in low-carbon steels. HSLA, high-strength low-alloy. Source: Ref 9

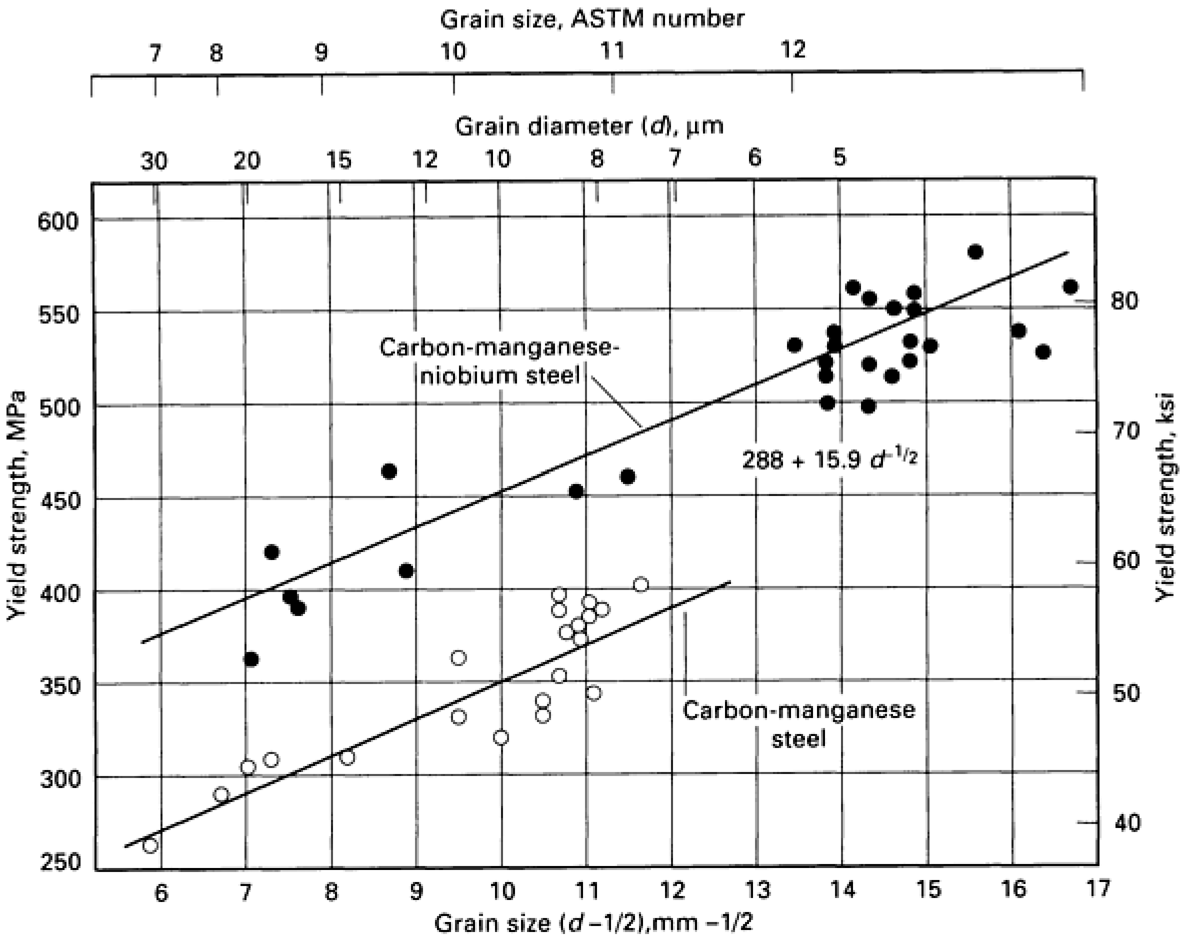

Fig. 2 Experimental Hall-Petch relationships as determined by quantitative metallography for carbon-manganese and carbon-manganese-niobium steels. Source: Ref 10

Of prime importance here is that, with the exception of the lattice friction term and solid solution strengthening by non-precipitating solutes, every component of the final strength of a given MA or high-strength low-alloy (HSLA) steel is affected, directly or indirectly, by not only the bulk microalloy composition but also by the hot-rolling process.

Resistance to Brittle Fracture. Another property of importance in hot-rolled material is the resistance to brittle fracture. This, of course, differs from the resistance to ductile fracture, which is controlled to a large extent by the cleanliness of the steel and its strength level. Clean steels typically have high Charpy shelf energies, high tensile ductilities, and excellent formabilities. The resistance to brittle fracture is usually measured in a Charpy V-notch impact test. This resistance is quoted either as a ductile-to-brittle transition temperature (DBTT) or as a test temperature corresponding to a given fracture energy (Ref 6, 8). In general, however, any index of the resistance to brittle fracture is improved with ferrite grain refinement and is deteriorated by increases in any of the other strengthening mechanisms. These relationships are shown in Fig. 3. Hence, the production of hot-rolled steels with good resistance to low-temperature brittle fracture is dependent on achieving a fine ferrite grain size in the final product. Furthermore, because grain refinement is the only strengthening mechanism that simultaneously improves both strength and toughness, it is the mechanism that assumes paramount importance in the design of strong and tough microstructures.

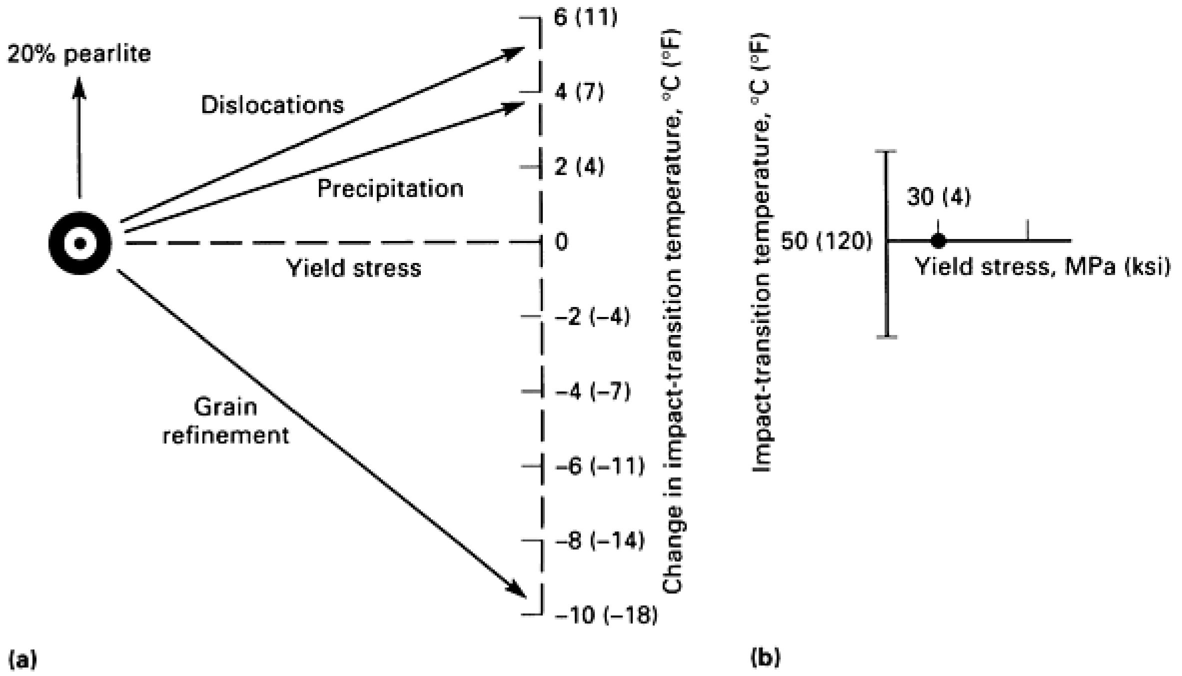

Fig. 3 Two methods of determining resistance to brittle fracture by Charpy V-notch impact testing. (a) Effect of ductile-to-brittle transition temperature on yield stress. (Ratios indicate the change in transition temperature per 15 MPa, or 2.2 ksi, increase in yield strength.) (b) Test temperature corresponding to given fracture energy. Source: Ref 3

The role of grain refinement in resisting brittle fracture extends beyond F-P steels to the acicular and bainitic steels as well. While the resistance to brittle fracture in F-P steels is controlled largely by the final ferrite grain size, the resistance to brittle fracture in fully acicular or bainitic steels is controlled by the prior-austenite grain size. In a recent study of the various contributions to the resistance to brittle fracture, several factors were found (Ref 11):

- Grain size ($D\gamma$) of the parent austenite
- Cleanliness of the steel (total projected inclusion length, $\sum b$)
- Strength level, YS

The influence of these factors is illustrated in Fig. 4. These data indicate that the effective grain size of the austenite is the most important factor, followed by the steel cleanliness, and the strength level in order of importance in increasing the resistance to brittle fracture.

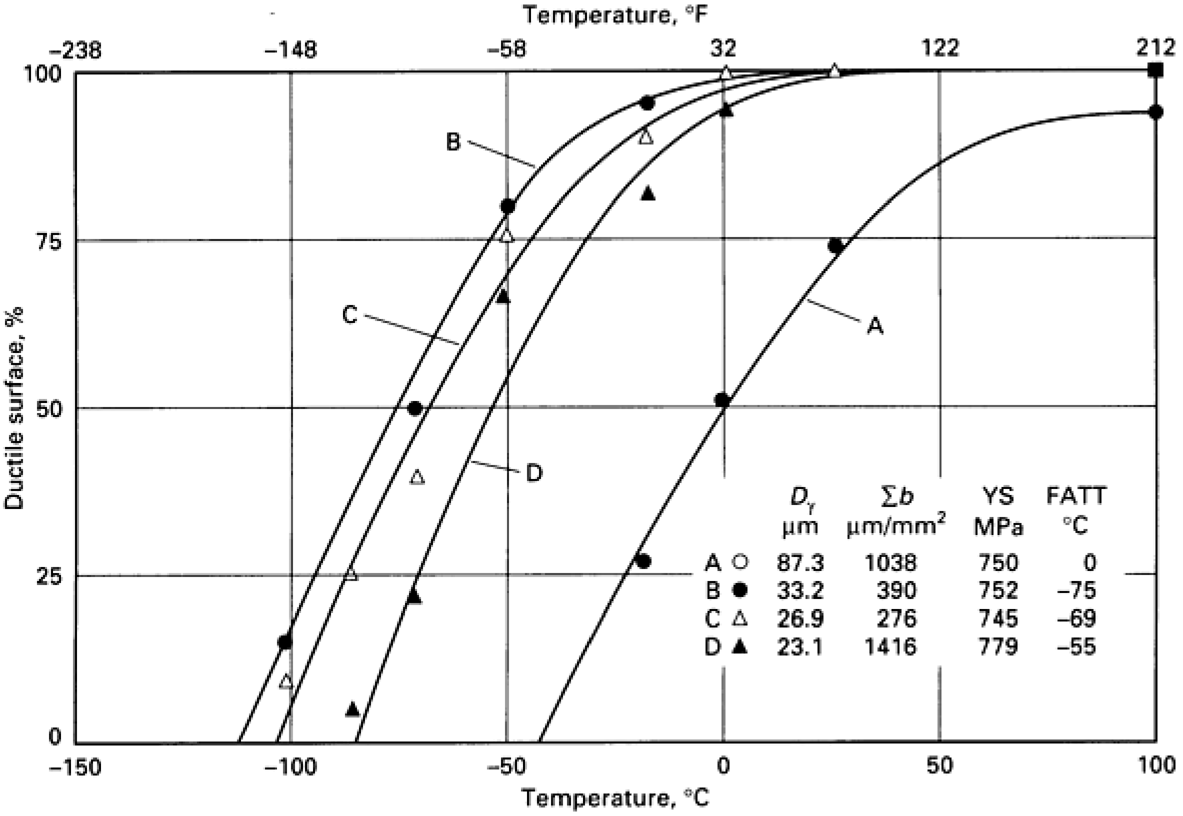

Fig. 4 Factors that affect the ductile-to-brittle transition in Charpy V-notch impact tests of ultralow carbon bainitic steels (ULCB). *Dγ*, average austenite grain size; $\sum b$, total projected length of inclusions per unit area; YS, yield strength; FATT, fracture-appearance transition temperature. Source: Ref 11

Whereas the texture contribution to strength in hot-rolled steels is rather small, on the order of a few percent (Ref 5), crystallographic texture can strongly influence other important properties such as through-thickness ductility in plate (that is, the phenomenon of splitting or separation) (Ref 12) and the deep drawability of cold-rolled and annealed steels (Ref 13). Finally, the weldability of the steel, taken here to mean the resistance to cold or underbead cracking, has been shown to be controlled chiefly by its composition (for example, its carbon content and its carbon equivalent value) (see Fig. 5).

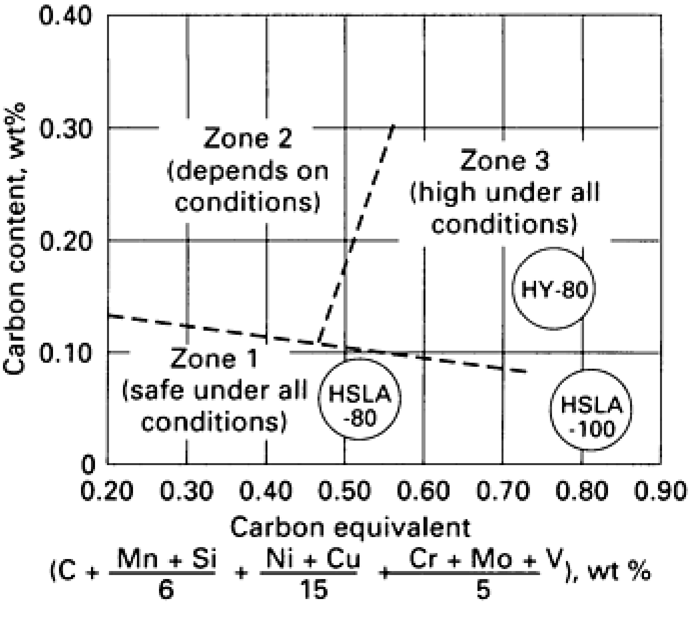

Fig. 5 Effect of steel composition on the susceptibility of the heat-affected zone (HAZ) to cold cracking for HY-80, HSLA-80, and HSLA-100 steels. Source: Ref 14

In summary, a properly designed and hot-rolled steel should exhibit the minimum required strength and the maximum resistance to brittle fracture. In the discussion that follows, an attempt will be made to explain how the proper microstructure and optimum properties can be obtained through the proper synergism of alloy design and thermomechanical processing.

Property Improvements Achieved through Thermomechanical Processing. As discussed above, the thermomechanical processing or controlled rolling of MA steel leads to enhanced grain refinement when compared with hot-rolled carbon steels. Furthermore, the presence of microalloying elements can lead to the precipitation hardening of ferrite. Together, these effects would be expected to lead to stronger and tougher steels. A good example of the benefits of thermomechanical processing regarding mechanical properties is illustrated in Fig. 6, which shows schematically the strength-toughness balance in linepipe steel. In Fig. 6, the strength is given by the American Petroleum Institute (API) grade which indicates the yield strength in ksi (for example, API X70 has a yield strength of 70 ksi). As shown in Fig. 6, X60 steel represented the technology from the mid-to-late 1960s and was represented by hot-rolled and normalized F-P steels. About ten years later, these steels were replaced by thermomechanically processed steels (labeled TM-treated in Fig. 6) that were able to attain both API X70 strength levels and higher levels of toughness. Further discussions including data are available in the literature (Ref 16, 17). A further example of the benefits of thermomechanical processing is given in Fig. 7 which shows the strength and toughness (that is, ductile-to-brittle transition temperature) of 30 mm ($1\frac{3}{16}$ in.) thick MA plate steel processed in several different ways. The processing variables examined in Fig. 7 include the type of rolling with or without subsequent normalizing. Normal hot-rolling and controlled-rolling schedules were used. An examination of the hot-rolled properties indicates very poor toughness. In order for these plates to be used, they would have to be normalized after rolling. However, while the normalizing treatment improves the toughness, it does so at the expense of strength. In comparison, the controlled as-rolled properties indicate that both high strength and high toughness are possible without the need of post-rolling normalizing. The data of Fig. 6 and 7 are intended as examples to show the improvement in mechanical properties attainable through the use of thermomechanical processing or controlled rolling.

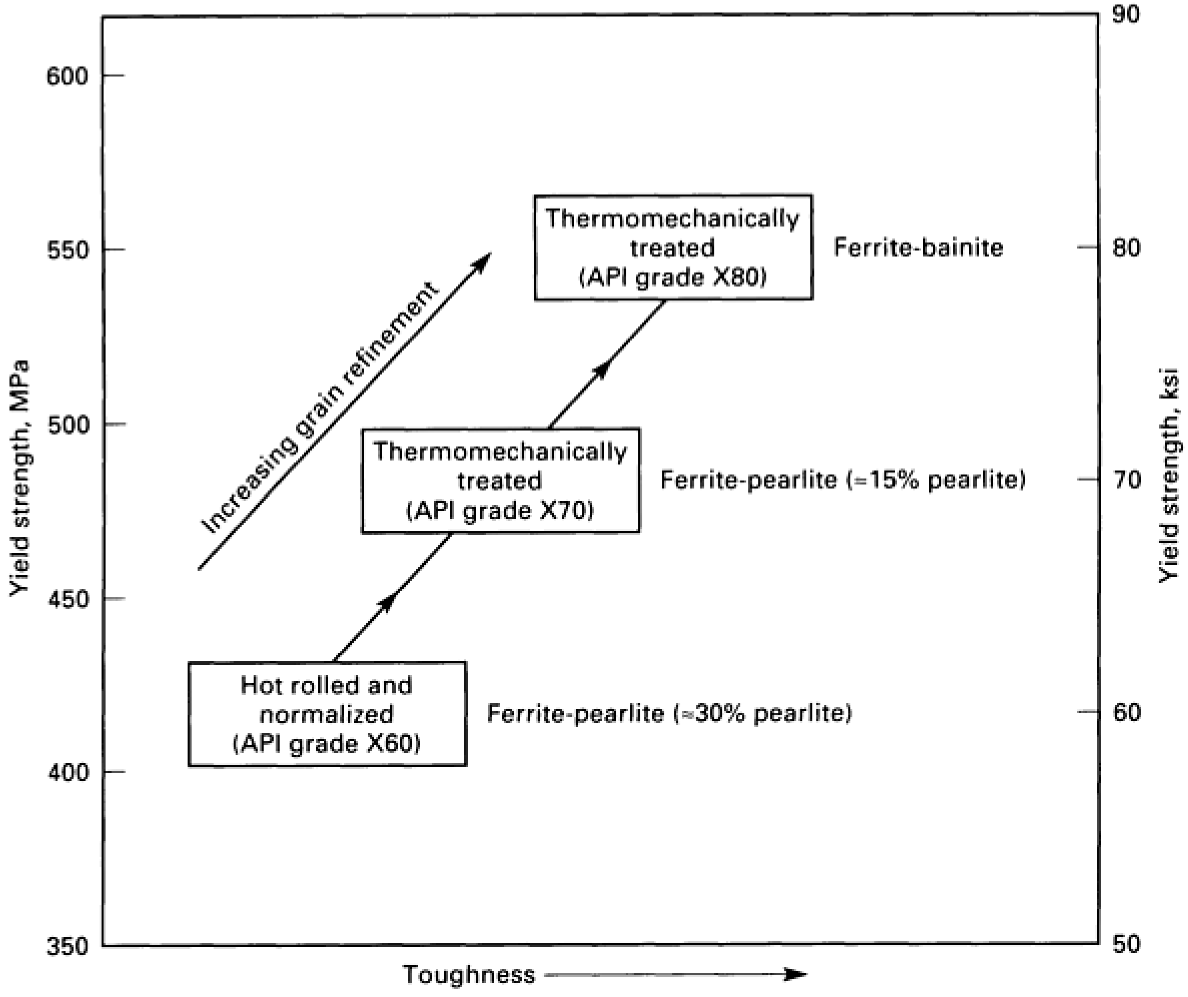

Fig. 6 Effect of microstructure and production process on the mechanical properties of linepipe steels. Source: Ref 15

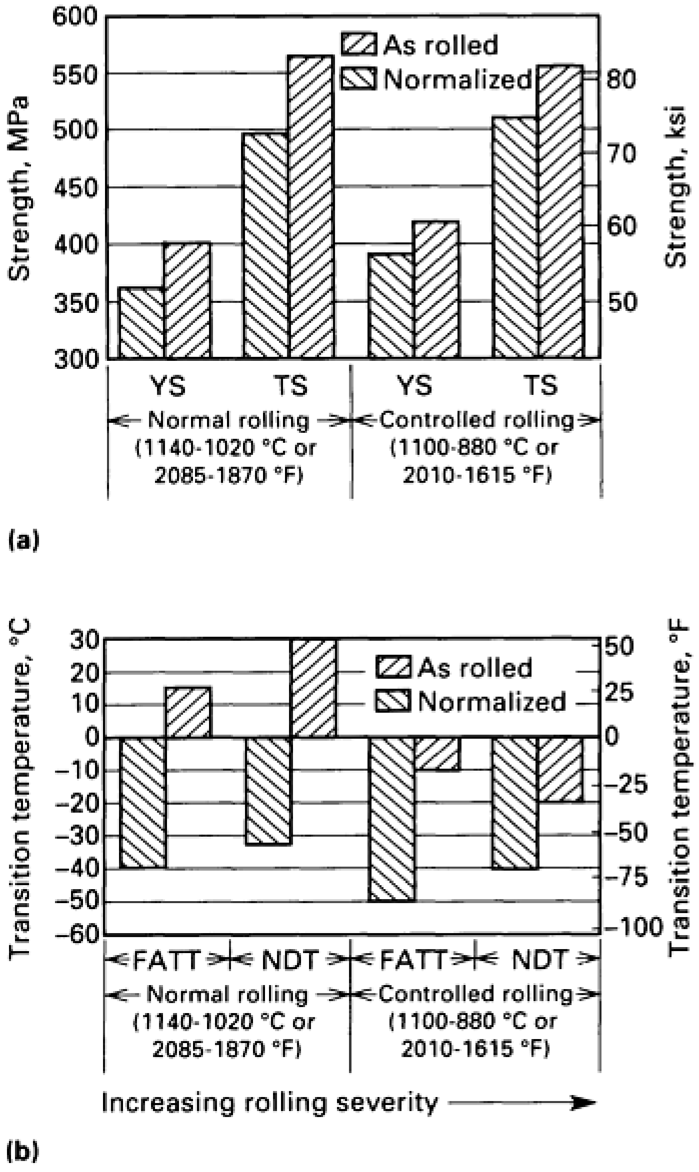

Fig. 7 Effect of normalizing on the properties of as-rolled 30 mm ($1\frac{3}{16}$ in.) thick structural steel (0.15C-0.25Si-1.35Mn-0.04Nb) plates that were produced using both conventional hot-rolling and controlled-rolling procedures. (a) Yield and tensile strength properties. (b) Transition temperature properties. FATT, fracture-appearance transition temperature; NDT, nil-ductility temperature. Source: Ref 18

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Fundamentals of Thermomechanical Processing

In his 1981 review of controlled rolling, Tanaka (Ref 19) pointed out that by 1924 the advantages of grain refinement to the mechanical properties of steel were already appreciated. Later, the beneficial effects of low finish rolling temperatures to the mechanical properties of steels were first realized (Ref 20, 21). Simultaneously, the relationship between low-temperature rolling of the austenite and the effect of ferrite grain size was being discussed (Ref 22). It is interesting to note that this early work was conducted in Europe on non-microalloyed steels. Perhaps the first indication of the benefits of microalloying to the as-rolled structure and properties of carbon and low-alloy steels was presented in the early 1940s (Ref 23, 24). In this work, attention was focused on the increased strength and toughness obtained with decreased grain size that were associated with the presence of small amounts of niobium.

From the early 1960s through to the present, research on thermomechanical processing has been centered on the controlled rolling of plate. Since a large portion of this research has been presented in several international symposia (Ref 25, 26, 27, 28, 29, 30, 31, 32), only a few of the important highlights will be reviewed at this time. It should be mentioned that a majority of the research on controlled rolling was performed in Europe during this period (Ref 33, 34). This was in contrast to the research conducted in the United States at the same time (late 1950s through early 1970s) on high-strength quenched and tempered steels. The unusually high strengths in these steels were developed either by an ausforming process or by direct quenching followed by a tempering treatment (Ref 4, 35).

The results from early research on controlled rolling indicated the importance of the synergism which exists between thermomechanical processing and the microalloying elements. Two major results from these investigations were:

- It was very difficult to thermomechanically process steels that did not contain microalloying elements. Hence, it was difficult to achieve the benefits in mechanical properties of thermomechanical processing without the microalloying elements
- Steels with microalloying elements, but without thermomechanical processing, displayed a lower toughness than their plain-carbon steel counterparts

This second point is clearly observed in Table 2, which shows the lower yield stress and fibrous transition temperature for a plain-carbon and a MA steel that were both deformed at two different temperatures (Ref 34). Table 2 illustrates that with suitable thermomechanical processing (that is, deforming at 860 °C, or 1580 °F, and below the recrystallization stop temperature of austenite), the MA steel was able to lower its fibrous transition temperature by approximately 60 °C (110 °F), while simultaneously maintaining a similar yield stress. The key point to be made is that if the austenite is not grain-refined by thermomechanical processing, the large austenite grains will lead to the combination of large ferrite grains in addition to the potential for low-temperature transformation products (which contain high carbon concentrations) to be

present in the centers of the large, prior austenite grains. This, coupled with the higher strength imparted by the microalloying elements, all act to deteriorate the toughness of the steel.

Table 2 As-deformed mechanical properties of plain carbon steel and steel microalloyed with 0.03% Nb at 860 °C (1580 °F) and 950 °C (1740 °F)

Material	Deformation temperature		Mechanical properties			
			Lower yield stress		Fibrous transition temperature	
	°C	°F	MPa	ksi	°C	°F
Plain carbon steel (0% Nb)	860	1580	217.7	31.57	-21	-5.8
	950	1740	206.7	29.97	-20	-4.0
Microalloyed steel (0.03% Nb)	860	1580	364.5	52.85	-48	-54
	950	1740	349.3	50.65	13	55

Physical Metallurgy

Our understanding of the relationship between the microstructure and the properties in F-P steels has led us to very different views concerning the origins of strength and the origins of toughness. For example, it is apparent that high strengths can be obtained in a simple manner (for example, through the addition of solute strengthening or precipitation hardening elements). Resistance to brittle fracture, on the other hand, cannot be achieved through alloy additions but must be achieved through the control of the final microstructure. It is now known that tough microstructures exhibit fine ferrite grain sizes and a minimum amount of lower temperature transformation products that contain cementite (for example, upper bainite). Hence, obtaining large amounts of fine ferrite grains and small amounts of pearlite are among the principal goals of thermomechanical processing.

The key question then becomes how these two goals may be achieved. It is now clear that both of these goals can be achieved when the austenite itself, at the point of transformation, exhibits a fine grain size. The as-rolled austenite can show three types of microstructures:

- Fully recrystallized
- Partially recrystallized
- Fully unrecrystallized

While the grain size of fully recrystallized austenite is a simple matter to comprehend and determine, the determination of a fully unrecrystallized microstructure is not. In order to specify the grain size of fully recrystallized austenite, only an average grain diameter is required; this fully describes the grain boundary area per unit volume. In the case of fully unrecrystallized austenite, both the starting grain size and the aspect ratio of the deformed grains are required to determine the grain boundary surface per unit volume. In general, because the ferrite grain size is related to the number of sites for ferrite nucleation and since this number is related to the grain boundary area per unit volume, the ferrite grain size will decrease as this boundary area increases. Furthermore, finer austenite grains reduce the chances of forming upper bainite during transformation because the austenite grain volume can be completely consumed by the ferrite and pearlite reactions. Although both of the issues were qualitatively recognized in the 1960s (for example, ferrite grain size was

reduced by lowering the finish rolling temperature of austenite), it was not until the mid-1970s that effects such as these could be quantitatively assessed.

Significance of S_v in Ferrite Grain Refinement. The understanding of the hot deformation of austenite in general and its influence on final ferrite grain size was improved dramatically in the mid-1970s through the research of Kozasu *et al.* (Ref 36), Tanaka (Ref 37), Sekine and Maruyama (Ref 38), and Morrison and Chapman (Ref 39), and others. A summary of this work was presented in the review by Tanaka (Ref 19). Kozasu *et al.* (Ref 36) for example, showed that the key to understanding the process by which austenite links alloying and hot rolling with the final ferrite grain size was based on quantitatively assessing the number of preexisting or strain-induced heterogeneities introduced into the austenite during rolling that could act as sites for ferrite nucleation. Earlier research using quantitative metallography led Underwood (Ref 40) to define a parameter S_v that attempted to account for all the near planar crystalline defects which may exist in a polycrystalline aggregate. The parameter S_v has units of mm^{-1} or equivalently area (mm^2) per unit volume (mm^3). Kozasu *et al.* (Ref 36) applied the parameter S_v, which they defined as the total effective interfacial area per unit volume, to the problem of quantitatively assessing the number of sites in thermomechanically processed austenite for potential nucleation of ferrite and developed the correlation shown in Fig. 8.

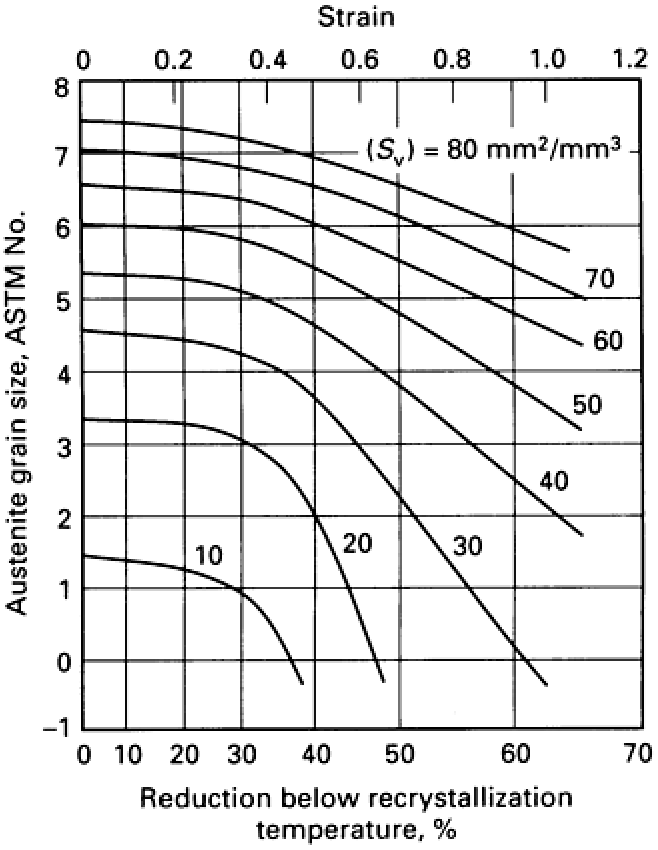

Fig. 8 Variation of effective austenite interfacial area (S_v) with initial grain size and amount of reduction below the recrystallization stop temperature for a 0.03 wt% Nb steel. Source: Ref 36

Attempts to quantify the influence of S_b on final ferrite grain size have been made by several groups. For example, Kozasu *et al.* (Ref 36) and later Roberts *et al.* (Ref 41) and Cuddy (Ref 42) have shown that the ferrite grain size decreases continuously with increases in S_v. There is still some disagreement over the exact relationship, but the general form has been well defined (see Fig. 9). Hence, from the standpoint of ferrite grain refinement, a well-conditioned austenite is one which exhibits a large S_v.

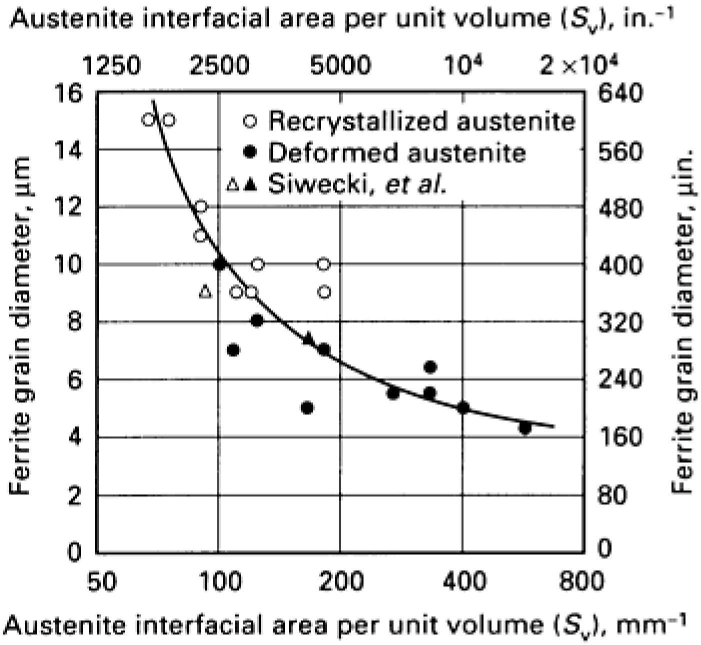

Fig. 9 Ferrite grain sizes produced from recrystallized and unrecrystallized austenite at various S_v values. Source: Ref 43

Methods of Obtaining Large S_v. As indicated in Fig. 9, ferrite grain refinement depends on obtaining a high S_v in the austenite prior to transformation. The discussion which follows suggests methods that achieve high S_v values through the proper combination of alloy design and thermomechanical processing.

In the extreme, a given as-reheated austenite grain structure can be hot rolled to two very different microstructures. If the rolling takes place above the recrystallization temperature of the austenite, then the original, equiaxed, recrystallized austenite grains are replaced with a different set of equiaxed grains that differ from the original chiefly in size. Because for equiaxed grains:

$$S_v = \frac{3}{D_g} \qquad \textbf{(Eq 2)}$$

where $D\gamma$ is the diameter of the austenite grains, a reduction in grain size by hot rolling will lead to an increase in grain boundary area and, hence, an increase in S_v (Ref 40).

The hot-rolling process, which leads directly to fine equiaxed grains, has been labelled recrystallization controlled rolling (RCR) (Ref 41, 44). This form of thermomechanical processing involves repeated recrystallization of austenite during deformation above the recrystallization temperature leading to a fine equiaxed austenite exhibiting a high S_v. The success of this technique depends on both achieving and maintaining a fine austenite grain size. While the origin of the grain refinement is based on repeated recrystallization, maintaining that grain size requires the use of grain coarsening inhibition mechanisms. Traditionally, successful mechanisms have involved the use of either stable precipitates or solute drag that can retard grain coarsening.

If the hot rolling takes place below the recrystallization temperature, the austenite grains become highly elongated and, at a sufficiently large strain, become filled with intragranular defects such as deformation bands and twins. This represents the wellknown and most popular variant of thermomechanical processing, controlled rolling (Ref 36, 37). Controlled rolling means rolling to control the microstructure of austenite (for example, pancaked grains containing intragranular crystalline defects). Obviously, not all hot-rolling practices which are under strict temperature and deformation control will lead to controlled-rolled microstructures and, hence, are not considered controlled-rolling practices. In controlled rolling, the final S_v is comprised of two terms, one describing the grain boundary surface area per unit volume and the other describing the surface area of the deformation bands and twins contained within the elongated grains. The S_v expression to be used in this case is (Ref 43):

$$S_v = S_v(\mathrm{GB}) + S_v(\mathrm{IPD}) \quad \textbf{(Eq 3)}$$

where S_v is the total effective area per unit volume, mm^2/mm^3; S_v(GB) is the grain boundary contribution to S_v; and S_v(IPD) is the intragranular planar defect contribution to S_v.

The quantity S_v can also be expressed as:

$$S_v = 0.429 N_{LR} + 2.571 N_{LZ} - N_{LT} + \frac{N_{DB}}{\sin q} \quad \textbf{(Eq 4)}$$

where N_{LR}, N_{LZ}, and N_{LT} are the grain boundary intercept number per unit length along the rolling, thickness, and transverse directions, respectively; N_{DB} is the number of intragranular planar defects (IPD) per unit area, mm/mm^2; and θ is the angle between the intergranular planar defect and the plate thickness direction.

Although the variation in S_v with alloying and processing has not been defined completely, the most important parameters have been shown to be the extent of deformation below the recrystallization temperature and the grain size of the austenite prior to pancaking (Ref 43, 44, 45). This work has been summarized by Speich *et al.* (Ref 43) and is illustrated in Fig. 10 and 11. Speich *et al.* calculated the variation of S_v for a hypothetical array of cube-shaped grains of variable initial size which were subjected to various plane strain deformations, all to simulate the behavior of grains during controlled rolling (Ref 43). A major contributor to S_v is the grain boundary area per unit volume. Under the assumptions of a cubical grain shape and plane strain deformation, the contribution of the grain boundary area to the total S_v will vary with reduction as follows (Ref 43):

$$S_v^{GB} = \frac{1}{D}\left(1 + \frac{1}{R} + R\right) \quad \textbf{(Eq 5)}$$

where D is the cube edge length and R is the rolling reduction ratio (original to final thickness). The variation of the contribution of the initial grain boundaries to S_v is shown in Fig. 11. Ouchi *et al.* (Ref 46) have shown that the intragranular defects, such as deformation bands and twin boundaries, contribute to the S_v as follows:

$$S_v^{GB} = 0.63\ (\%\ \mathrm{Reduction} - 30)\ \mathrm{mm}^{-1} \quad \textbf{(Eq 6)}$$

Equation 6 indicates that no deformation bands form during controlled rolling until a reduction of 30% has been reached, and then the band density increases linearly with additional strain. When S_v^{GB} and S_v^{DB} are plotted individually and added together, the sum, $S_v^{GB} + S_v^{DB}$, versus strain below the recrystallization temperature is as shown in Fig. 11. It is clear from Fig. 10 and 11 that both the grain size prior to pancaking and the amount of reduction below the recrystallization temperature play important roles in controlling the magnitude of S_v.

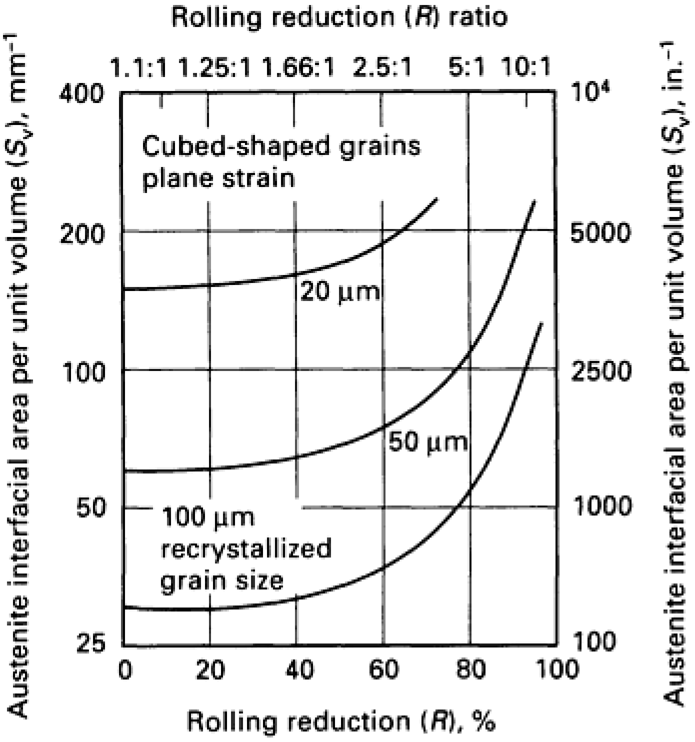

Fig. 10 Effect of rolling reduction on S_v for cube-shaped austenite grains. Source: Ref 43

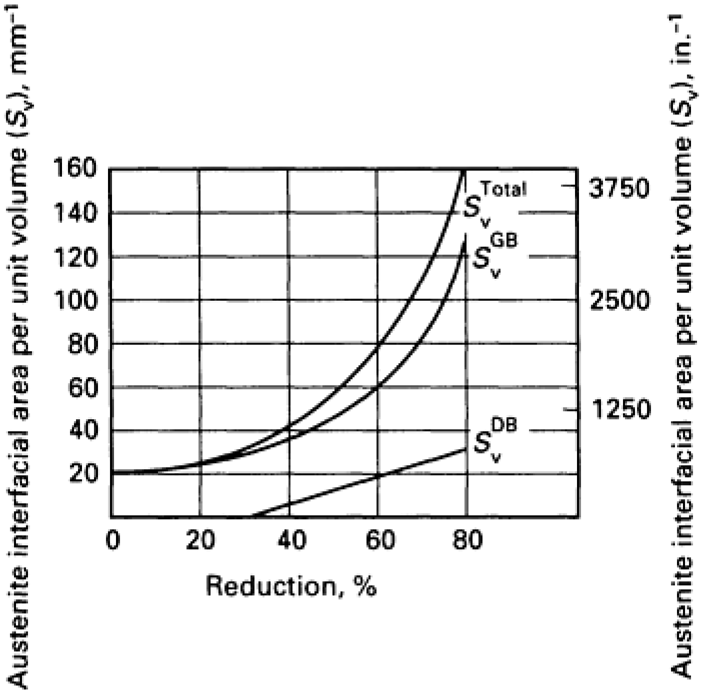

Fig. 11 Increase in S_v because of deformation bands. Austenite grain diameter, $D\gamma$ = 100 μm (0.004 in.); $S_v^{total} = S_v^{GB} + S_v^{DB}$; S_v^{GB}, grain boundary planar-linear model; S_v^{DB}, deformation band. Source: Ref 43

Forces that Activate Microstructural Restoration in Austenite. As shown in Fig. 9, the ferrite grain size was strongly influenced by the magnitude of S_v. Simultaneously, it was shown in the section "Methods of Obtaining Large S_v" that the magnitude of S_v is dependent upon the microstructural condition of the austenite at the point of transformation. The

metallurgical condition of the austenite at the transformation temperature is dependent on a complex interplay between the stored energy of deformation on one hand and retarding forces on the other hand. The stored energy of deformation is the driving force for any restoration process [that is, recovery (Ref 47) and recrystallization (Ref 48)) to occur. In this context, restoration means achieving a metallurgical condition that is energetically comparable to or lower than the condition existing before deformation. Hence, through the operation of the recovery and recrystallization processes, the predeformation condition is essentially restored. Clearly, when the driving force for a restoration process exceeds all retarding forces, the process will proceed. However, when the retarding forces exceed the driving force, the restoration processes will not occur, and the as-deformed condition will prevail.

Driving Forces for Restoration. The driving force for recovery and recrystallization has been shown to be equal to the difference in dislocation density that is present between strained and strain-free local volumes (Ref 49, 50, 51, 52). This driving force has been estimated and, based upon the area under the flow curve (Ref 53, 54), is expressed by the following equation:

$$\Delta\sigma = 0.2\mu\mathbf{b}\sqrt{\Delta r} \qquad \textbf{(Eq 7)}$$

where $\Delta\sigma$is the increment in flow stress due to work hardening, $\mu$is the shear modulus, **b** is the Burgers vector, and $\Delta\rho$is the excess dislocation density.

In addition to recovery and recrystallization, other types of restoration processes can exist. One familiar process is grain coarsening. The driving force for grain coarsening is the minimization of grain boundary energy (or area) per unit volume (Ref 47).

Retarding Forces for Restoration. Up until this point, only driving forces for restoration have been considered. Attention will now be turned towards the forces that resist the progress of restoration. The two major retarding forces are solute drag and particle pinning. The influence of solutes (Ref 55) and particles (Ref 56) on the mobility of grain boundaries were recognized as early as 1949. The effectiveness of solute drag has been shown to be related to differences in size and valence between the solute and solvent atoms (Ref 57, 58, 59). Hence, the level of solute drag depends on the nature of the solute and its concentration in solid solution. While solute drag has been discussed extensively in the literature (Ref 60, 61, 62, 63, 64), there is no acceptable quantitative expression of this effect currently available.

Particle pinning, on the other hand, has been subjected to a more quantitative treatment. The first attempt to treat the retarding effects of second-phase particles on a migrating grain boundary was made by Zener (Ref 56). He indicated that when particles were present in the vicinity of a grain boundary, the effective energy of the grain boundary would be lowered. The reduction in grain boundary energy occurs because the surface area of second-phase particles would replace part of the grain boundary. Therefore, the movement of a grain boundary away from particles would require work as the effective grain boundary area is increased (Ref 65). Zener's original theory was later quantified by Gladman (Ref 66) who assumed the rigid motion of grain boundaries through a regular array of spherical particles. It was shown that the pinning force for each particle (F) and the particle radius (r) were related by:

$$F = 4r\sigma \qquad \textbf{(Eq 8)}$$

where σ is the interfacial energy per unit area of boundary. Gladman (Ref 66) subsequently derived an expression for the critical particle size, r_c, below which grain boundaries are pinned:

$$r_c = \frac{6R_0 f_v}{p} \cdot \left(\frac{3}{2} - \frac{2}{z}\right)^{-1} \qquad \textbf{(Eq 9)}$$

The relationship shown by Eq 9 was obtained by equating the rates of the grain boundary energy increase during grain growth and the particle pinning force. In this expression, R_o is the mean radius of the matrix grain and f_v is the volume fraction of second-phase particles. The term z represents the ratio of the radii of growing and matrix grains. Hillert (Ref 67) has deduced that z can range in value between $\sqrt{2}$ to 2 throughout the grain growth process. The important point to be realized from Eq 9 is that a high volume fraction of small particles will inhibit boundary migration.

Equation 8 can be expanded to account for the total pinning force, F_{PIN}, that a number of particles per unit area (N_s) exert on a migrating boundary. This total pinning force is expressed as:

$$F_{PIN} = 4r\sigma N_s \qquad \textbf{(Eq 10)}$$

Three models have been postulated to explain how microalloy precipitates suppress austenite recrystallization (Ref 60, 65, 68, 69, 70, 71). All of these models are based upon the general form of Eq 10. Their differences arise from the method by which N_s is calculated. The first of these models was an extension of Gladman's (Ref 66) work. This model is often referred to as the rigid boundary model because it assumes the motion of a rigid grain boundary which is capable of interacting with those particles lying within $\pm r$ of the boundary plane (Ref 56, 60, 65, 66, 68). Under this set of conditions, N_s is defined by:

$$N_s = 2rN_v \qquad \textbf{(Eq 11)}$$

where N_v is the number of particles per unit volume. Again, assuming spherical particles having radius r and volume fraction f_v, N_v is defined by the following expression (Ref 66, 68):

$$Nv = \frac{3f_v}{4p\,r^3} \qquad \textbf{(Eq 12)}$$

Combining Eq 11 and 12 yields the number of particles per unit area assuming a rigid boundary model, N_s^R:

$$N_s^R = \frac{3f_v}{2p\,r^2} \qquad \textbf{(Eq 13)}$$

The rigid boundary model, however, was rather simple and unrealistic since it did not account for any flexibility of the austenite grain boundaries (Ref 65).

Cuddy (Ref 53, 72) proposed a model that was at the opposite extreme of the rigid boundary model. This model was termed the flexible boundary model. It assumed that an infinitely flexible boundary was capable of interacting with every particle in the three dimensional array until it is fully pinned (Ref 53). This led to the relationship:

$$N_s = rf_v^{-1/3}N_v \qquad \textbf{(Eq 14)}$$

which, when combined with Eq 12, yields the number of particles per unit area assuming a flexible boundary model, N_s^F:

$$N_s^F = \frac{3f_v^{2/3}}{4p\,r^2} \qquad \textbf{(Eq 15)}$$

The most realistic of these models was the one proposed by Hansen *et al.* (Ref 68). This model considered the effect of a precipitate distribution that could exist on austenite subgrain boundaries prior to the start of recrystallization (Ref 53, 69). Assuming that the average subgrain intercept is l, the surface area per unit volume for such subgrain boundaries would be $2/l$, and the number of particles per unit subgrain boundary area would be given by (Ref 68):

$$N_s = \frac{lN_v}{2} \qquad \textbf{(Eq 16)}$$

As before, combining Eq 12 and 16 gives the number of particles per unit area assuming a subgrain boundary model, N_s^S:

$$N_s^S = \frac{3 f_v l}{8 p r^3} \quad \textbf{(Eq 17)}$$

Substitution of the expressions for N_s^R, N_s^F, and N_s^S into Eq 10 gives the respective pinning force for each model:

$$F_{PIN}^{R} = \frac{6\sigma f_v}{\pi r} \quad \textbf{(Eq 18)}$$

$$F_{PIN}^{F} = \frac{3\sigma f_v^{2/3}}{\pi r} \quad \textbf{(Eq 19)}$$

$$F_{PIN}^{S} = \frac{3\sigma f_v l}{2\pi r^2} \quad \textbf{(Eq 20)}$$

where F_{PIN}^R, F_{PIN}^F, and F_{PIN}^S are pinning forces for rigid boundary model, flexible boundary model, and subgrain boundary model, respectively.

Microalloying, Solubility, and Precipitation in Austenite

The achievement of high levels of S_v depends on the ability to control the restoration processes that could otherwise occur during thermomechanical processing. Obviously, for a given deformation process, this means that the level of retarding force must be controlled during the process. In the ideal system, the partitioning of solutes between solid solution and precipitate could be controlled (that is, when low retarding forces are required), the solutes could be kept in solid solution and when high retarding forces are required, the solutes could form precipitates. The ability of a solute to be partitioned in this way is directly controlled by its solubility product. Elements such as niobium, titanium, and vanadium have been shown to have solubility products that vary with temperature in such a way as to make them particularly useful in generating retarding forces under controlled and predictable conditions during thermomechanical processing. These elements are known as the microalloying elements and are central to thermomechanical processing. The microalloying elements perform three major roles in thermomechanically processed steels:

- Help maximize S_v through their ability to generate retarding forces
- Contribute to hardenability when they are in solid solution at the transformation temperature
- Can cause precipitation hardening of the transformation product

Solubility Product. The extent to which elements can be maintained in solid solution in austenite is governed by the appropriate solubility product. If, for example, we are interested in the extent of solid solubility of niobium and carbon in austenite ($[NB]\gamma$ and $[C]\gamma$) that is in equilibrium with pure, stoichiometric niobium carbide, NbC, then we must consider the following reaction:

$$[Nb]\gamma + [C]\gamma = NbC \quad \textbf{(Eq 21)}$$

This reaction will have an associated equilibrium constant K_1 (that is, solubility product):

$$\log K_1 = \log[Nb][C] = A_1 - \frac{B_1}{T} \quad \textbf{(Eq 22)}$$

where A_1 and B_1 are constants normally specified such that [NB] and [C] can be expressed by their weight percent and T is the absolute temperature. If, however, we wanted to consider the extent of solubility of the austenite in equilibrium with $NbC_{0.85}$, then the appropriate solubility product would be:

$$\log K_2 = \log[Nb][C]^{0.85} = A_2 - \frac{B_2}{T} \qquad \textbf{(Eq 23)}$$

Similarly, the solubility product for austenite in equilibrium with NbC_xN_y would be:

$$\log K_3 = \log[Nb][C]^x[N]^y = A_3 - \frac{B_3}{T} \qquad \textbf{(Eq 24)}$$

The solubility of NbC in austenite has been studied in numerous investigations, and this work has been carefully Summarized and reviewed by Nordberg and Aronsson (Ref 73). The 13 independent investigations reviewed by Nordberg and Aronsson examined the solubility products associated with NbC, NbC_x, NbC_xN_y, and NbN. Several solubility products are illustrated in Fig. 12, and the equations for these products are listed in Table 3.

Table 3 Solubility product of niobium carbonitride precipitates in austenite at 1000 °C (1830 °F)

Precipitate	**Solubility product equation**	**Solubility product at *T* of 1000 °C (1830 °F) K × 10^6 × $(wt\%)^2$**
$NbC_{0.87}$	log $[Nb][C]^{0.87}$ = 3.43 - 7170/*T*	1510
NbC	log [Nb][C] = 2.96 - 7510/*T*	1070
$NbC_{0.83}N_{0.14}$	log $[Nb][C]^{0.83}[N]^{0.14}$ = 4.46 - 9800/*T*	525
$NbC_{0.24}N_{0.65}$	log $[Nb][C]^{0.24}[N]^{0.65}$ = 4.09 - 10400/*T*	77.6
NbN	log [Nb][N] = 2.80 - 8500/*T*	8.0

Source: Ref 74

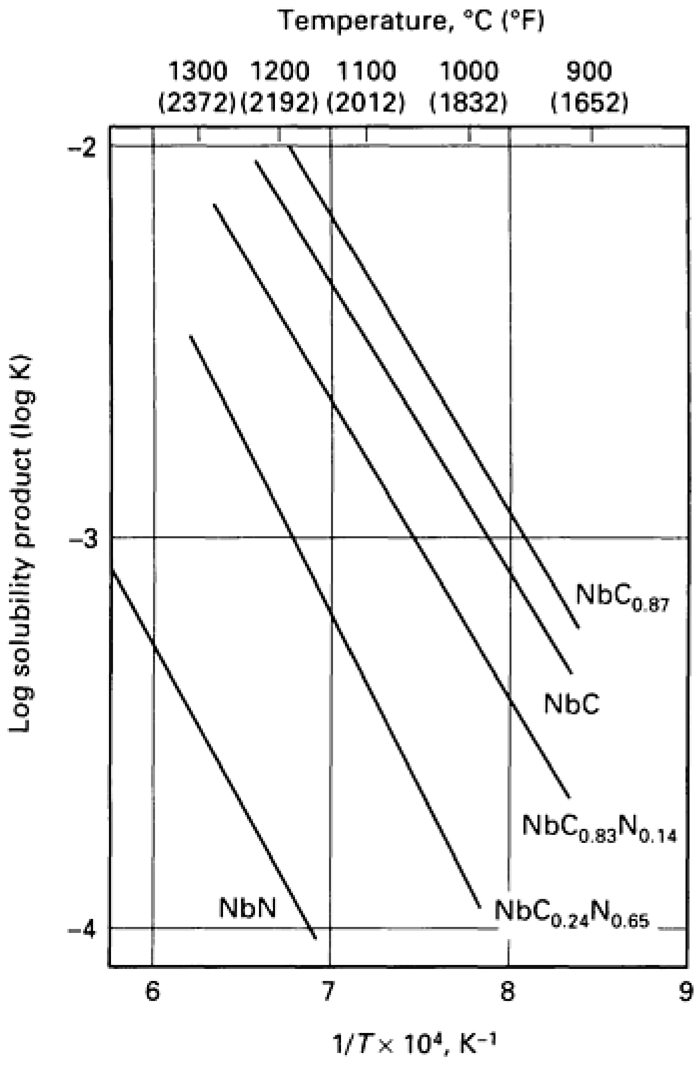

Fig. 12 Solubility products for various niobium precipitates in austenite. Source: Ref 74

Effect of Solubility Product on Niobium Precipitation. The relationship between the solubility product and the nature or composition of the niobium precipitate is evident in Fig. 12. If the solubility product line for pure stoichiometric NbC is used as a reference, two interesting trends are observed:

- There is a substantial lowering of the solubility product as the precipitate becomes more enriched with nitrogen
- There is an apparent increase in solubility product with a reduction in *x* (that is, with an increase in vacancy concentration)

These two trends are demonstrated in Table 3 with a comparison of selected solubility products for several precipitates in austenite at 1000 °C (1830 °F).

Solubility products play a vital role in understanding the physical metallurgy of microalloyed steel, especially those aspects that are concerned with precipitation-related phenomena. Solubility products can be plotted in either one of two ways. Consider the case for the solubility product of NbC in austenite at some given temperature. If the abscissa [C] and ordinate [NB] axes have a linear scale, then any given solubility isotherm will have the shape of a hyperbole. If, however, the axes have a logarithmic scale, then the solubility isotherm will be a straight line. Both approaches have been widely used in the literature.

A hypothetical solubility isotherm for NbC in equilibrium with austenite at 1000 °C (1830 °F) is shown in Fig. 13(a). The solubility isotherm gives the locus of niobium and carbon products that represent the limit of solid solubility of NbC in austenite at 1000 °C (1830 °F), that is, any combination of products located above the line will be in the (γ + NbC) phase field at 1000 °C (1830 °F). The straight line with a positive slope on the diagram represents the stoichiometric ratio. The precipitation of NbC can be followed by considering the slightly curved line that is nearly equidistant from the stoichiometric line and passes through the point with the niobium and carbon coordinates which describe the composition of the steel. A schematic illustration is presented in Fig. 13(b). Consider a steel of composition given by point B that is reheated to 1300 °C (2370 °F) and is very slowly cooled to 900 °C (1650 °F). Because 1300 °C (2370 °F) is the solution temperature for the NbC under consideration here, the NbC can be assumed to be completely dissolved after reheating. If it is further assumed that precipitation occurs during the cooling, then the composition of the austenite in equilibrium with NbC would move along the curve passing through point B that is equidistant from the stoichiometric line. The distance moved along the curved line through point B is proportional to the volume fraction of precipitate formed as a result of the cooling, assuming that equilibrium is established at all temperatures. In other words, the distance moved along the curved line through point B during cooling is proportional to the solute supersaturation and would also be proportional to the volume fraction of precipitate formed if equilibrium prevailed. Therefore, if steel B is reheated to 1300 °C (2370 °F) and then cooled to and rolled at 900 °C (1650 °F), the distance $\overline{BC}$ in Fig. 13(b) will be proportional to the volume fraction of NbC formed in austenite. This precipitation would be of two types: that formed during cooling and that formed during or after rolling. The first type is not likely to be significant because precipitation in recrystallized austenite is normally very sluggish, as will be discussed in the section "Effect of Microalloying Elements on the Critical Temperatures of Austenite" of this article. The second type is referred to as strain-induced precipitation (labelled ε -induced in Fig. 13b). A second interesting case would occur if steel of composition A in Fig. 13(b) is considered. If this steel is reheated at 1300 °C (2370 °F) and hot rolled at 900 °C (1650 °F), then two arrays of NbC particles would be expected. The first would be the precipitates that survived the reheating treatment (having a volume fraction proportional to $\overline{AB}$) and the second would be a strain-induced precipitate (having a volume fraction proportional to $\overline{BC}$).

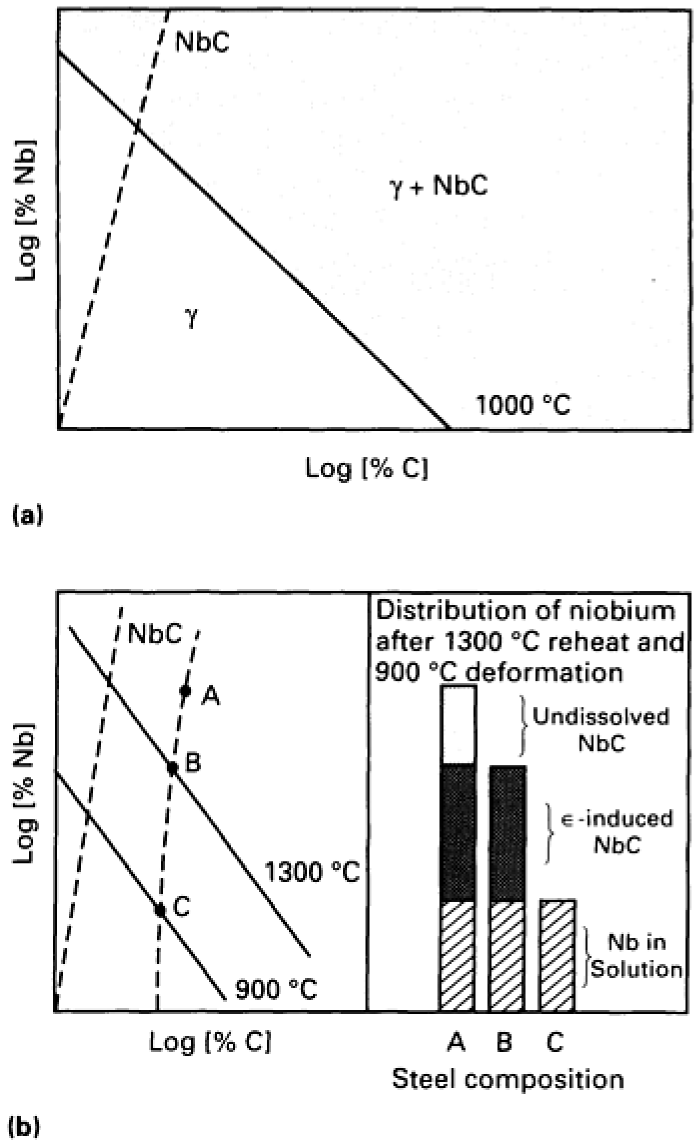

Fig. 13 Hypothetical solubility diagrams describing equilibrium between NbC and austenite. (a) Relationship at 1000 °C (1830 °F). (b) Interrelationships among isotherms, steel composition, processing, and potential amount of precipitation. Source: Ref 74

Finally, solubility products appear to be influenced by the presence of elements that do not directly precipitate in the precipitation sequence. Koyama *et al.* (Ref 75, 76, 77) have examined the influence of several elements on the solubility of NbC in austenite. These elements can affect the solubility of NbC in austenite by altering the activity coefficients of both niobium and carbon. By way of an example, the solubility product for NbC in otherwise unalloyed austenite at 1150 °C (2100 °F) is approximately 5×10^{-3}. An addition of manganese increased log K by about 5%/wt% Mn added while an addition of silicon reduced log K by about 45% per wt% Si added. The solubility product at 1150 °C (2100 °F) for a steel containing 1.5 wt% Mn and 0.4 wt% Si was $\approx 4 \times 10^{-3}$. Hence, the addition of both manganese and silicon acted to reduce the solubility product by approximately 20%.

Effect of Microalloying Elements on the Critical Temperatures of Austenite

The influence of microalloying elements on the response of austenite to thermomechanical processing can be understood by the way in which the microalloying elements influence the three critical temperatures of austenite:

- Grain coarsening temperature, T_{GC}
- Recrystallization stop temperature, T_{RXN}

- Transformation temperature, Ar_3 or B_s

Grain Coarsening Temperature. The grain coarsening temperature T_{GC} is defined to be that temperature above which grain coarsening by secondary recrystallization commences and refers to the temperature above which the undissolved precipitates can no longer suppress grain growth. The influence of various microalloying elements on grain growth during reheating is shown in Fig. 14. While it does not appear that the final average austenite grain size is very dependent on the reheated grain size prior to multipass deformation (Ref 78), it does appear likely that the distribution of grain sizes about the average is much smaller when the reheating temperature is kept below the grain coarsening temperature (Ref 79).

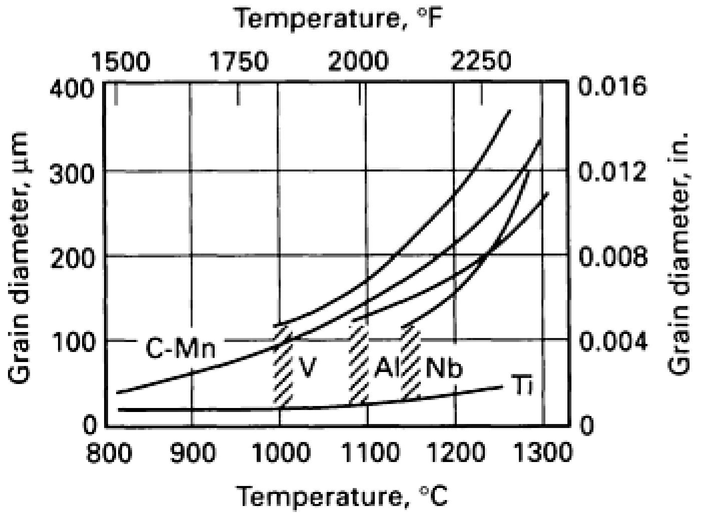

Fig. 14 Austenite grain coarsening characteristics in steels containing various microalloying additions. Source: Ref 43

During reheating, a slab is slowly heated from room temperature to the reheating temperature, where it is soaked for an appropriate period of time and after which it is available for hot rolling. During this heating and soaking period, events occur which ultimately control the grain size and composition of austenite prior to hot rolling. The ultimate response of a given steel to subsequent processing will, to a large extent, be strongly influenced by the reheating stage. The major events which may occur during reheating include:

- Nucleation, growth, and possible coarsening of austenite grains
- Elimination of inhomogeneities in solute distribution
- Dissolution of microalloy precipitates that were inherited from the original microstructure

Austenite first forms at ferrite-carbide (cementite) interfaces (Ref 80) and the increase in amount of austenite is accompanied by a decrease in the amount of cementite, at least in the early stages of austenite formation (Ref 80). Also, although the kinetics of austenite formation are very rapid at normal reheating temperatures, the elimination of heterogeneities in solute distribution is very sluggish (Ref 80).

Once the austenite grains have formed from the F-P starting structure, they will coarsen with time and temperature. This coarsening behavior has been reviewed in some detail (Ref 74).

Reheating controls not only the grain size, but also the initial composition of the austenite (Ref 74, 78). Cuddy has shown that niobium is not fully taken into solution until a steel is heated to approximately 100 °C (180 °F) above its grain coarsening temperature (Ref 78). Similar results have been found in a separate work (Ref 81). The factors that control the composition of the austenite at various stages of processing have recently been reviewed by Gray and DeArdo (Ref 82).

Recrystallization Stop Temperature. Perhaps the most important effect of microalloying elements is in controlling the recrystallization stop temperature of austenite (Ref 53, 81). The influence of several microalloying elements on the

recrystallization stop temperature is shown in Fig. 15 (Ref 53). As shown in Fig. 15, niobium has the most profound effect in increasing the T_{RXN} value and this accounts for its selection as the primary microalloying element in modern HSLA steels. Some early steels used vanadium in conjunction with nitrogen additions to produce a moderate effect in retarding austenite recrystallization but such practices are not compatible with current ideas for limiting free nitrogen concentrations, nor were they particularly effective. Consequently, the predominant use of vanadium is for precipitating vanadium carbide in the low-temperature transformation product. Similarly, titanium is not considered useful for retarding austenite recrystallization but is highly effective in preventing grain growth (Fig. 14). Titanium's grain refining benefits have another primary use in welding that are unrelated to their benefit during austenite processing, and this has led to widespread use of approximately 0.015 wt% Ti in plate and pipeline steels. This approach is not readily accessible when nitrogen concentrations are above 0.008 wt% N or when the ingot casting route is involved.

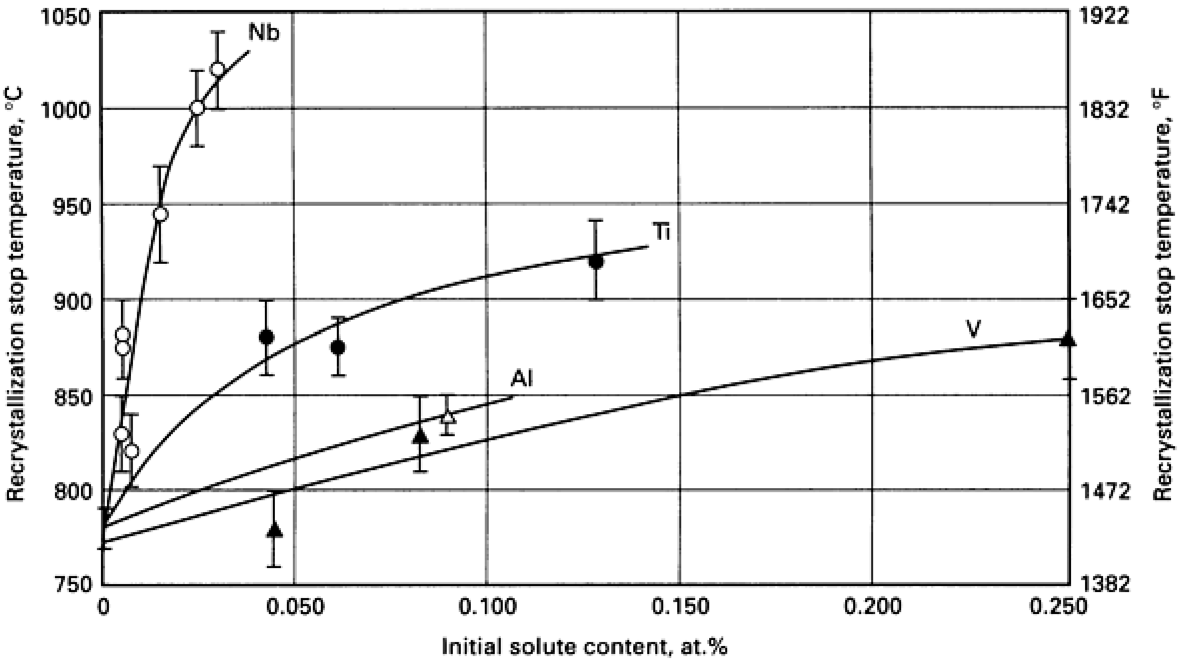

Fig. 15 Effect of microalloying additions on the recrystallization stop temperature of austenite. Source: Ref 53

The data shown in Fig. 14 and 15 reveal that the various microalloying elements all show the same general behavior. The differences between them are predominantly the temperature range over which they exert their influence and the level of intensity of that influence. This difference in behavior is chiefly due to differences in the solubility of the various precipitates in austenite. The difference in the temperature range of precipitation in austenite is clearly shown in Fig. 16 for vanadium and niobium carbonitrides (Ref 83, 84). In Fig. 16, the deformation temperature is plotted against the deformation time required to initiate dynamic recrystallization (that is, time-to-peak stress, t^p), which is one form of austenite restoration. When no strain-induced precipitation forms, the curves are only slightly offset from the base steel. This is indicative of the weak retarding effect of solute drag as a retarding force. However, when precipitation accompanies the early stages of deformation as it does in the vanadium plus nitrogen steel at low temperatures and the two niobium steels at higher temperatures, there is a drastic retardation of dynamic recrystallization, and the curves display a plateau. Notice that when precipitation occurs, the curves are virtually identical. They are only displaced on the temperature scale.

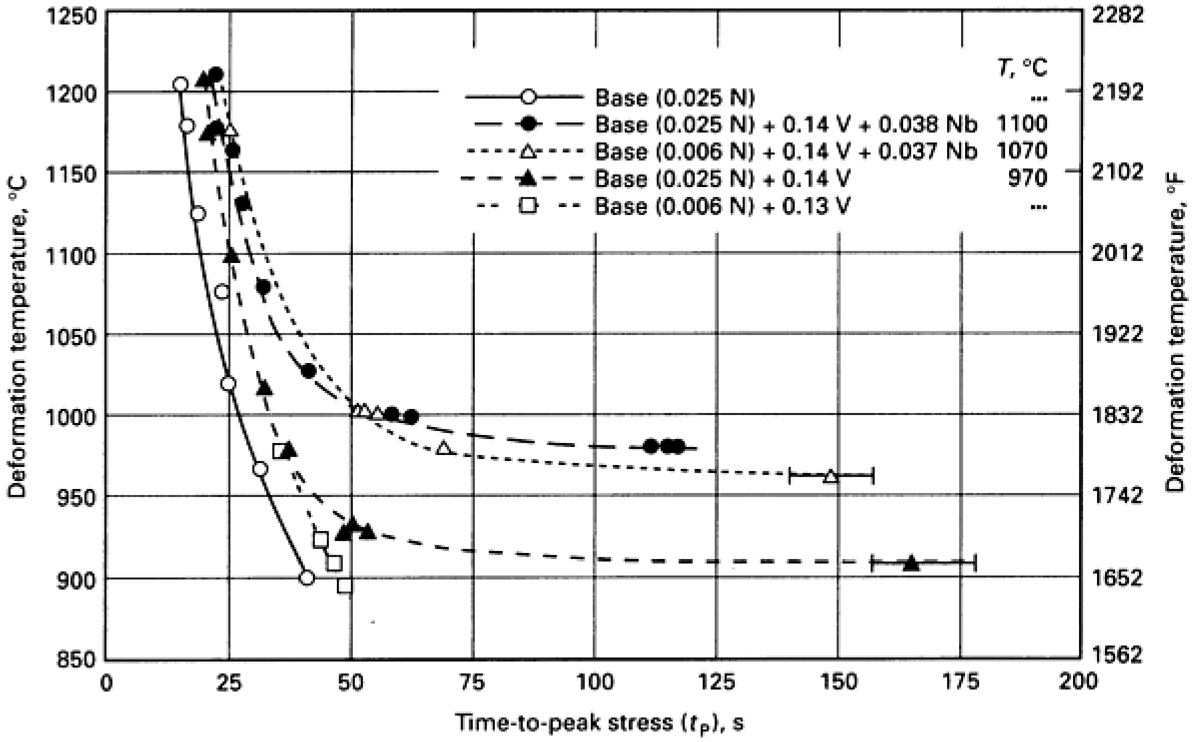

Fig. 16 Dependence of the time-to-peak stress (t_p) on deformation temperature at a low strain rate ($\dot{\epsilon}$ is 0.006 s^{-1}) for selected microalloyed steels containing two levels of nitrogen (0.006 and 0.025% N). The 0.025% N steel is a reference steel. Source: Ref 83

A good comparison of the various precipitation systems can be made through the use of the appropriate solubility relations. For example, the driving force for precipitation at a given temperature is directly related to the solute supersaturation at that temperature (Ref 81). A comparison of the variation of supersaturation with temperature is shown in Fig. 17 for several important systems. Figure 17 reveals that the titanium-base system shows a large supersaturation at temperatures well above those associated with hot rolling. The VC and VN systems, on the other hand, display a large supersaturation at the very lowest range of hot-rolling temperatures. Finally, the niobium-base system shows a large supersaturation at temperatures that are well situated within the hot-rolling range. Hence, titanium precipitates are very effective for high-temperature control (for example, during reheating), niobium precipitates are very effective for intermediate temperature exploitation (for example, control of recrystallization stop temperature) and the vanadium can easily be retained in solid solution in the austenite for the eventual precipitation hardening of the transformation product.

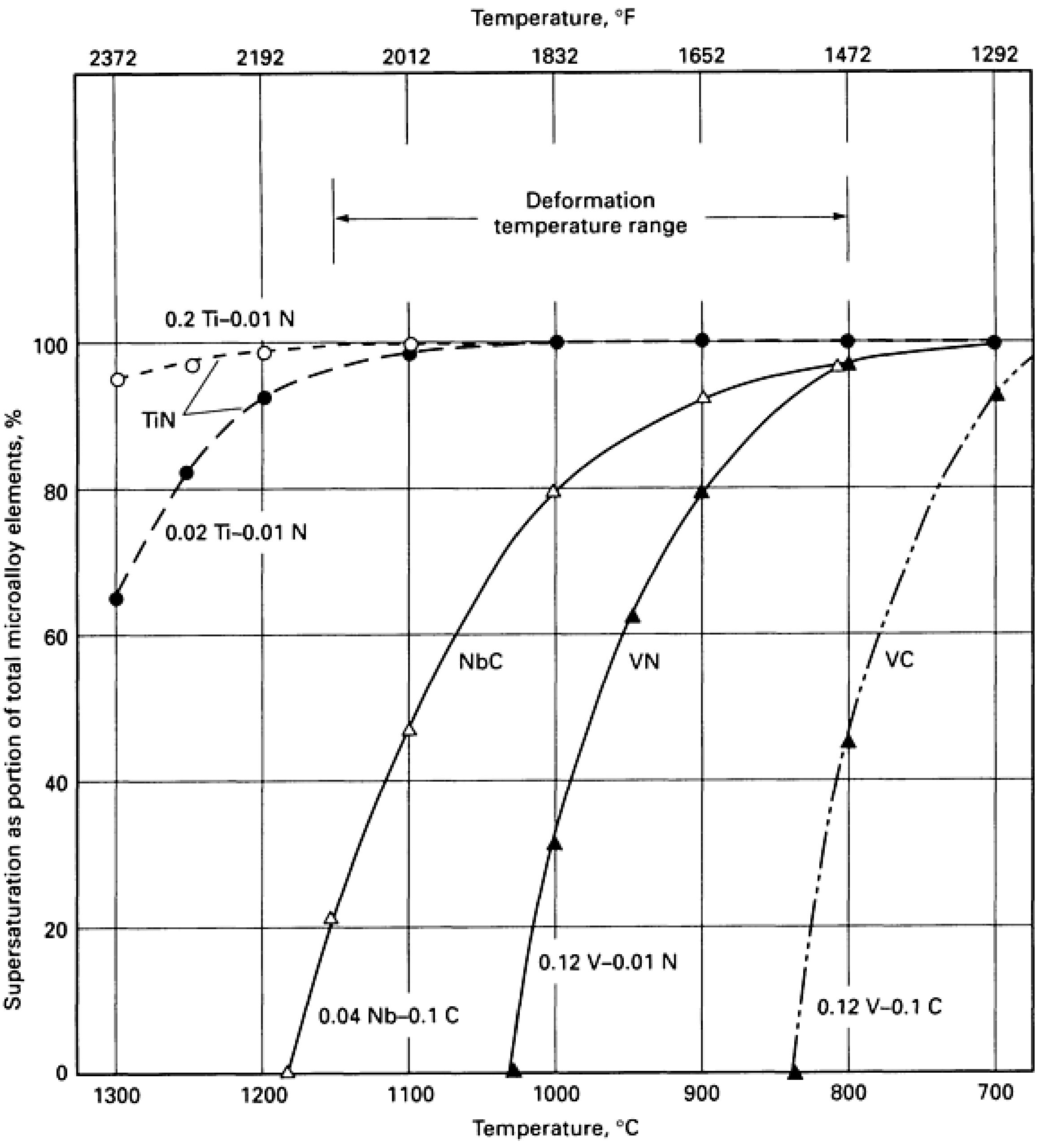

Fig. 17 Precipitation potential of various microalloying element systems. Source: Ref 85

Transformation Temperature. The third critical temperature that can be strongly influenced by microalloying elements is the transformation temperature, either the Ar_3 or B_s temperature. In either case, the effect of the microalloying elements is based on hardenability concepts. The transformation temperature is important because it has a direct influence on the scale of the resulting microstructure (for example, ferrite grain size or bainitic lath size). This effect occurs because the thermodynamic driving force for nucleation is inversely related to the square of the difference between the equilibrium transformation temperature, Ae_3, and the actual transformation temperature, Ar_3. Hence, lower Ar_3 temperatures result in lower transformation temperatures that result in higher nucleation rates and lower rates of growth and coarsening (Ref 86). There are, therefore, two major contributors to the ferrite grain size in F-P steels: S_v and Ar_3. The Ar_3 in F-P steels is defined as the temperature where the cooling rate intersects the start of the polygonal ferrite transformation. Hence, both the cooling rate and the hardenability of the steel will contribute to the Ar_3 temperature. An example of the influence of the composition of austenite on the transformation temperature is shown in Fig. 18 for the air cooling of niobium bearing steels (Ref 87). In Fig. 18, the cooling time for transformation is inversely related to the transformation temperature. When the steels were reheated at 900 °C (1650 °F), the addition of 0.04 wt% Nb had little effect on the transformation temperature. This is because virtually none of the niobium had been dissolved into the austenite during reheating at that low temperature. The transformation temperature in this case was about the same as for the niobium-free steels. The

behavior at 1100 °C (2190 °F) reheating in Fig. 18 was very different. Here, the addition 0.04 wt% Nb had a very large effect on depressing the transformation temperature. In this case, virtually all of the niobium had been taken into solution during reheating and had a large effect on the hardenability.

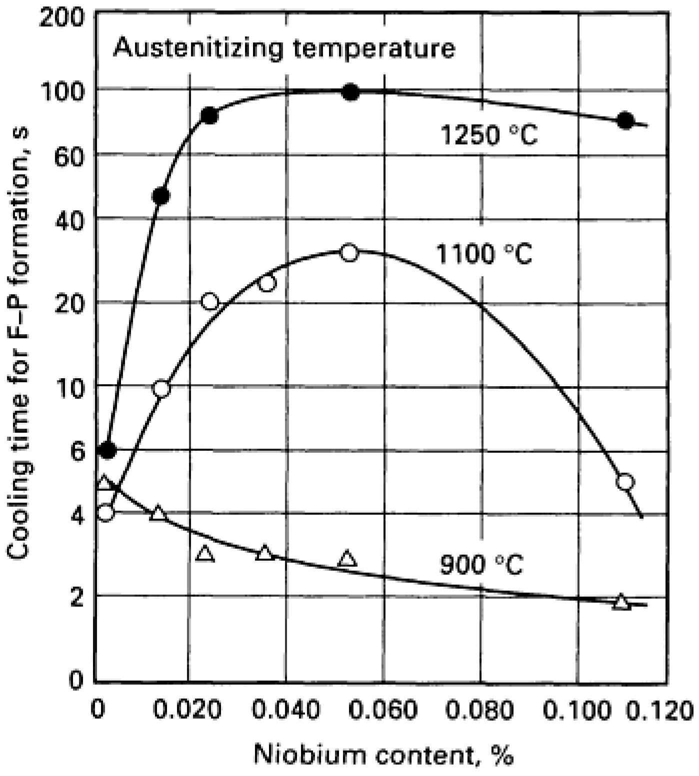

Fig. 18 Cooling time between 800 and 500 °C (1470 and 930 °F) for the start of F-P formation in niobium-alloy steels after austenitizing at different temperatures. The steel also contained 0.2% C and 1.2% Mn. Source: Ref 87

The effects of nickel in solution and of accelerated cooling on the Ar_3 temperature and the resulting ferrite grain size are shown in Fig. 19 (Ref 88). A comparison of Fig. 18 and 19 reveals the differences in effectiveness between niobium in solution and nickel in solution. The niobium in solution is a much stronger contributor to hardenability than is nickel. Accelerated cooling from the finish rolling temperature also has a dramatic effect on both the Ar_3 temperature and the resulting ferrite grain size (see Fig. 19). The beneficial effects of accelerated cooling have been so pronounced that two major international symposia have been dedicated to this technology (Ref 88, 89) and have been the subject of recent reviews (Ref 90, 91). The effects of alloying on the Ar_3 temperature (Ref 46) for proeutectoid ferrite and the B_s temperature (Ref 92) for bainite have been quantified and are shown below:

$$Ar_3(°C) = 910 - 310(C) - 80(Mn) - 20(Cu) - 15(Cr) - 55(Ni) + 0.35(t - 8) \quad \textbf{(Eq 25)}$$

$$B_s(°C) = 830 - 270(C) - 90(Mn) - 37(Ni) - 70(Cr) - 83(Mo) \quad \textbf{(Eq 26)}$$

In Eq 26 *t* refers to the plate thickness in millimeters and all elements are represented by their weight percent.

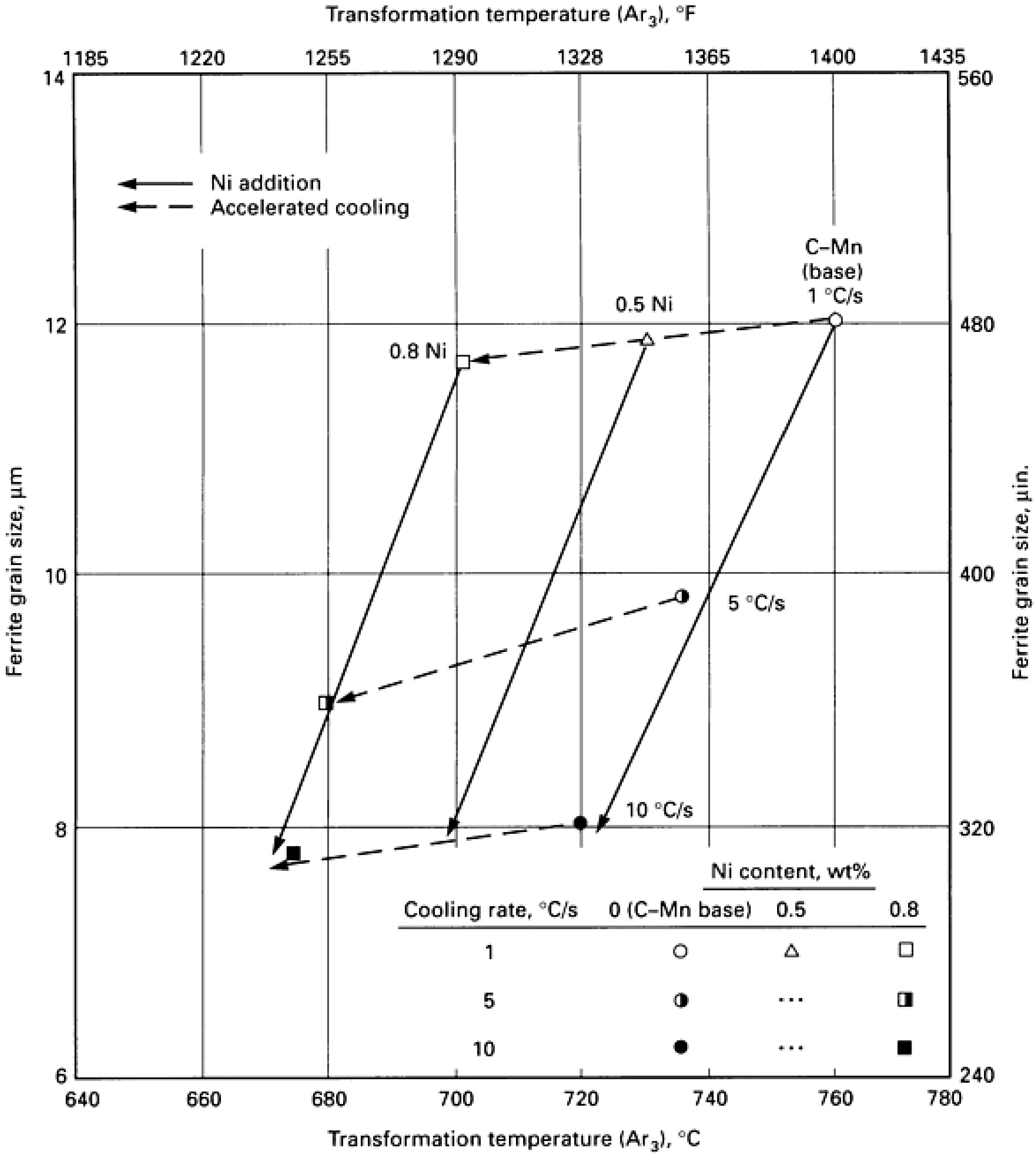

Fig. 19 Effect of accelerated cooling and nickel content on ferrite grain size transformed from deformed and unrecrystallized austenite. Source: Ref 88

When microalloyed austenite undergoes multipass hot rolling at temperatures where large supersaturations exist, various amounts of strain-induced precipitation may occur depending on factors such as the finishing temperature and the interpass holding time. The effect on the amount of precipitation caused by variations in deformation temperature, extent of recrystallization, and interpass holding time is shown in Fig. 20. Figure 20 shows that the amount of strain-induced precipitation, which attends hot rolling, is a variable and hence, the amount of niobium in solution can also vary. Because it is known that the Ar_3 temperature varies with the amount of niobium in solution, it should be expected that the Ar_3 temperature may also vary with the details of the rolling practice. This is, in fact, the case. Figure 21 shows the dependence of the Ar_3 temperature on the amount of deformation that takes place below the recrystallization stop temperature (Ref 46). In Fig. 21, the amount of strain-induced precipitation increases with the amount of deformation below the T_{RXN}. The resulting amount of niobium in solution becomes lower with increasing reduction, leading to an increase in the Ar_3 temperature. Hence, when most of the niobium is in solution in austenite (that is, with little or no deformation below the T_{RXN}), the Ar_3 temperature is relatively low. On the other hand, when most of the niobium is in the

form of precipitate (that is, at large strains below the T_{RXN}), the Ar_3 temperature is relatively high (Ref 46). The correspondence between the behavior of the Ar_3 value with niobium in solution in Fig. 18 and 21 is quite striking.

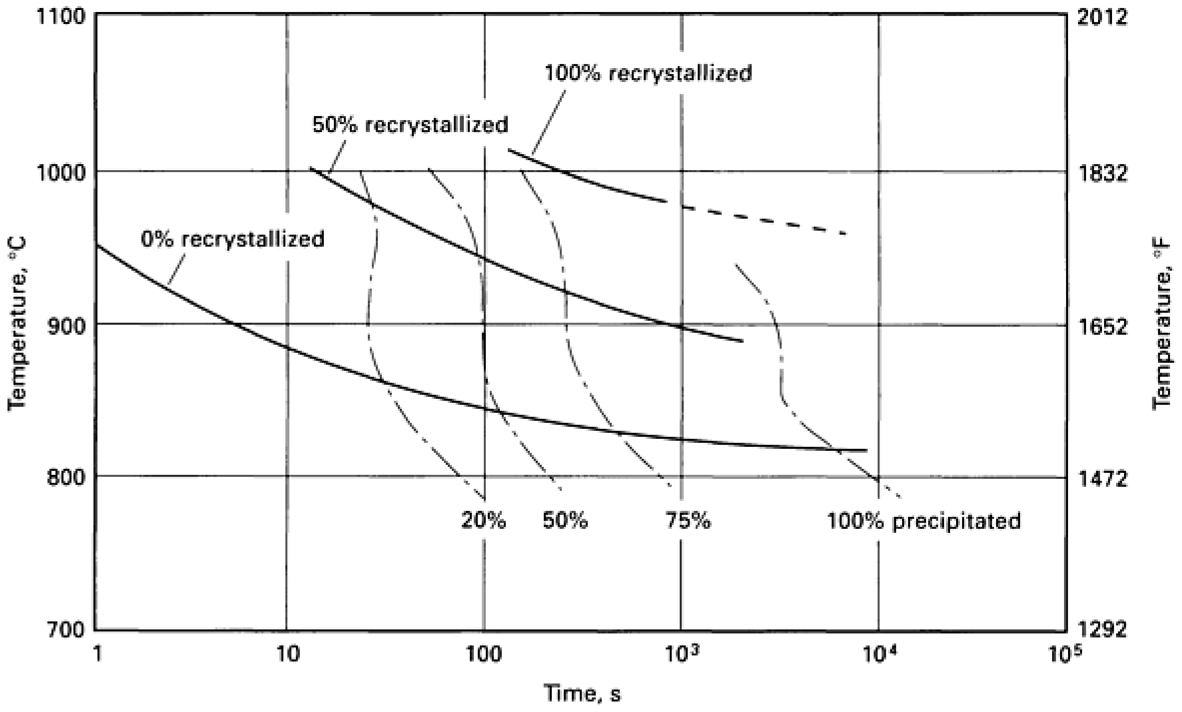

Fig. 20 Isothermal recrystallization and precipitation in a niobium steel after 50% deformation. The steel composition was 0.10C-0.99Mn-0.04Nb-0.008N. Source: Ref 92

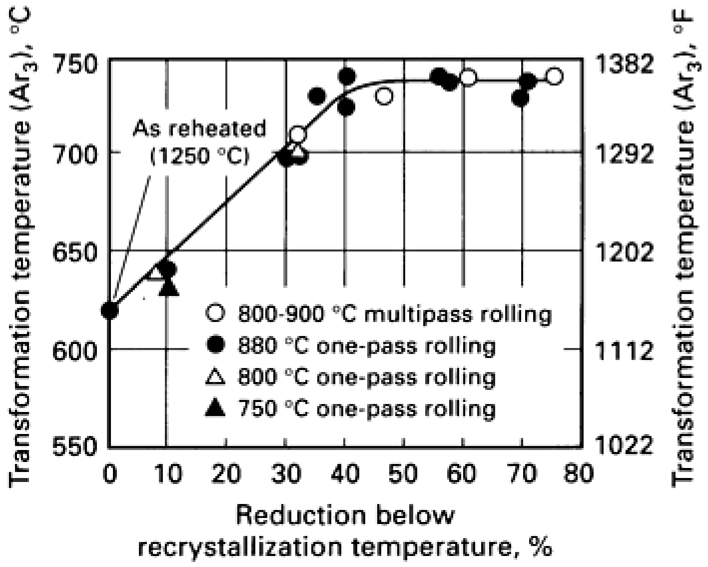

Fig. 21 Increase in Ar_3 temperature as a result of controlled rolling. Source: Ref 46

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Applications of Thermomechanical Processing to Heat Treat As-Rolled Microalloyed Steels

In the most general sense, thermomechanical processing is comprised of reheating, hot rolling, and cooling. The difference between thermomechanical processing and conventional hot rolling (CHR) and the differences among various forms of thermomechanical processing can perhaps most simply be described using Fig. 22. The first method presented in Fig. 22 is conventional hot rolling, which shows that the reheating, rough rolling, and finish rolling all occur at the highest possible temperatures. The goal of conventional hot rolling has traditionally been to optimize productivity while neglecting the as-rolled mechanical properties. The second method shown in Fig. 22 is conventional controlled rolling (CCR) (Ref 93). The goal of conventional cold rolling is to produce very fine ferrite grain sizes by conditioning the austenite through extensive rolling in the non-recrystallization region of austenite. Another rolling technique shown in Fig. 22 is recrystallization controlled rolling (RCR). This technique differs from the previous two methods in that both rough rolling and finish rolling take place above the recrystallization stop temperature (Ref 21, 93, 94, 95, 96). The goal of the RCR method is to produce a fine ferrite grain size by transforming a fine, fully recrystallized austenite.

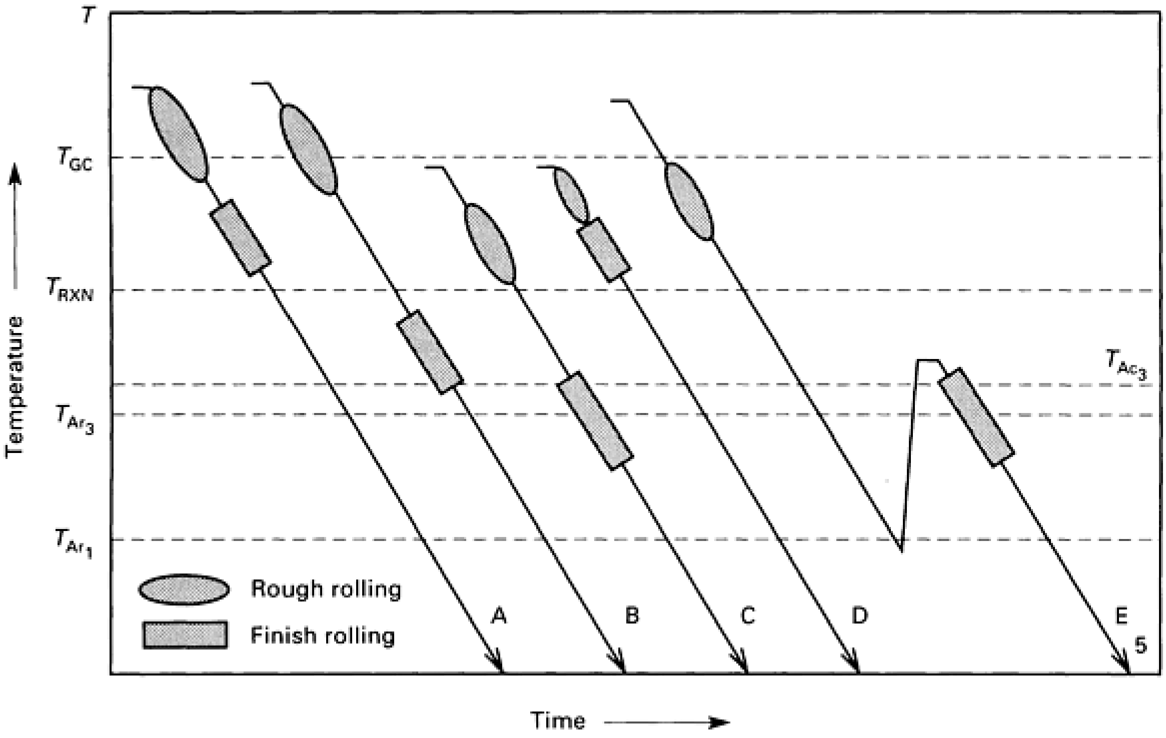

Fig. 22 Comparison of selected thermomechanical treatments based on critical austenite temperatures, transformation temperatures, and rough and finish rolling operations: A, conventional hot rolling; B, conventional controlled rolling; C, intensified controlled rolling; D, recrystallization controlled rolling; E, Sumitomo high toughness rolling

Conventional Controlled Rolling

As mentioned above, one of the principal goals of thermomechanical processing is to have well-conditioned austenite (that is, austenite having the proper composition, texture, and S_v) prior to transformation. Because S_v comprises near-planar crystalline defects such as grain boundaries, deformation bands, and twin boundaries, the control of recrystallization during thermomechanical processing is critical: it dictates the size and shape of grains as well as the presence or absence of the intragranular defects. We now turn to a discussion of multistage hot deformation with

particular emphasis on the principal factors that control the recrystallization stop temperature, or the suppression of recrystallization. The question arises, however, as to which form of recrystallization is, in fact, to be suppressed.

During multipass hot rolling, there are three possible forms of recrystallization that may take place (Ref 97, 98):

- Dynamic recrystallization that might occur during deformation in the roll gap
- Static recrystallization that might occur in the time period between deformations
- Metadynamic recrystallization that, if it occurred, would begin in the roll gap and go to completion in the time period between deformations

Hence, any discussion of recrystallization must begin with some understanding of the form(s) of recrystallization that is most likely to actually control the austenite microstructure.

Dynamic Recrystallization and Metadynamic Recrystallization. In the opinion of the authors, it is extremely unlikely that either dynamic recrystallization or metadynamic recrystallization could occur during industrial processing. This position can be summarized by stating that the time required for substantial amounts of dynamic recrystallization to occur is orders of magnitude longer than the times actually available in the roll gap (Ref 99, 100, 101, 102).

Static Recrystallization. The elimination of dynamic and metadynamic recrystallization leaves static recrystallization as the most likely candidate for the recrystallization process, which must be suppressed in defining the recrystallization stop temperature observed in multipass hot rolling. Fortunately, static recrystallization has been rather extensively studied over the last two decades; hence, our understanding of this phenomenon is fairly well advanced (Ref 97, 98, 103, 104, 105, 106, 107). Two major techniques have been used to study high-temperature static recrystallization. One, based on optical metallography, relies on changes in grain structure with holding time after deformation. The second is based on changes in flow strength with isothermal holding, the so-called double hit test (Ref 69). The overall static softening behavior of the austenite is monitored by a fractional softening parameter that is based on either yield or offset flow stresses.

Static Softening Behavior of Austenite. When the static softening behavior of single-phase austenite is studied, curves of the type shown in Fig. 23 are obtained (Ref 69, 101). The curves shown in Fig. 23 are for a plain carbon steel (K-0). Note that the softening begins with a short, but finite, incubation period that is followed by a monotonic increase in softening to saturation. The change in recrystallization with softening and holding time is also apparent. This behavior is, of course, exactly that which is expected: an initial period of static recovery, which causes no appreciable change in strength, followed by static recrystallization, which leads to appreciable softening.

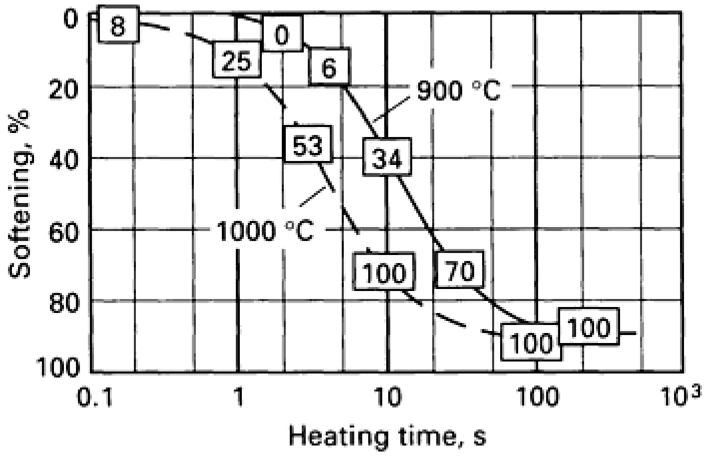

Fig. 23 Relationship between softening and fractional recrystallization in a plain carbon steel (K-0 with composition 0.1C-0.008N-Fe) deformed at 0.1 s^{-1} with an applied prestrain of 0.3. The peak strains were 0.48 at 900 °C (1650 °F) and 0.35 at 1000 °C (1830 °F) Numbers in boxes represent the percentage of recrystallization measured by the point-count method. Source: Ref 69

The static softening behavior becomes much more complicated if the experiment is performed on a supersaturated solid solution (for example, VCN or NbCN in austenite at temperatures where the appropriate solubility product has been exceeded). The static softening behavior of a niobium-bearing austenite that contains high and low levels of nitrogen is illustrated in Fig. 24 (Ref 69, 101). Superimposed on the softening curves are the amounts of static recrystallization determined by quantitative optical metallography. The curves shown in Fig. 24 can be divided into two classes: those with shapes resembling the shapes of single-phase austenite and those with shapes differing from single-phase austenite. It is fairly clear that the change in shape is related to both the suppression of static recrystallization and to precipitation hardening in certain cases. A comparison of the conditions that lead to suppressed versus unsuppressed static recrystallization kinetics reveals that the suppressed kinetics are associated with relatively large potentials for precipitation (that is, large supersaturations at the test temperature). The results of a study of precipitation revealed that precipitation-start times correlated closely with deviations in static softening curves (see Fig. 24). Curves of the type shown in Fig. 24 lead to two important questions:

- Is the precipitation observed capable of suppressing static recrystallization?
- How does niobium in solution compare to niobium in precipitate in terms of suppressing recrystallization?

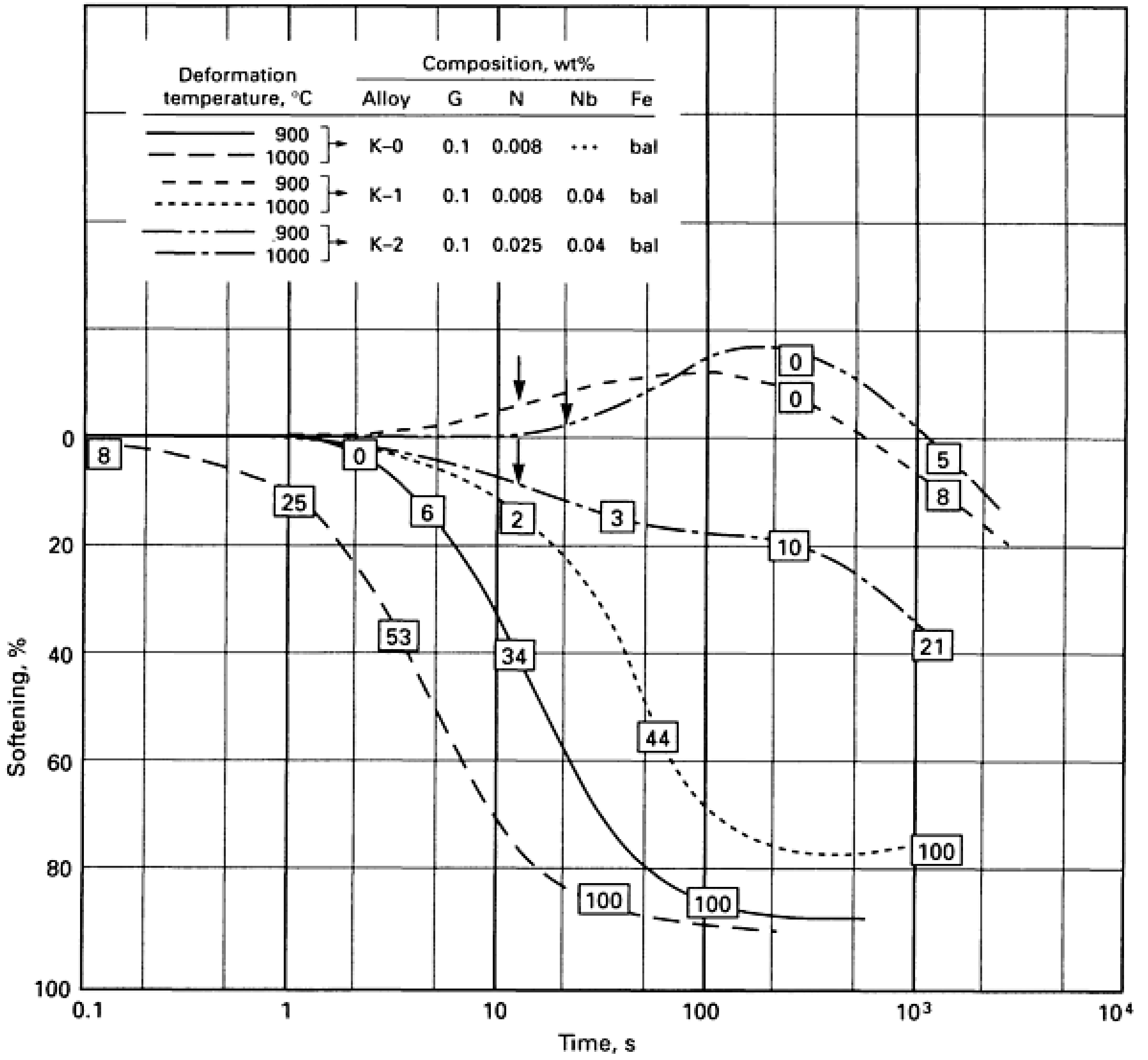

Fig. 24 Static restoration behavior of three steels (K-0, K-1, and K-2) isothermally deformed at 900 °C (1650 °F) and 1000 °C (1830 °F) and then held at temperature for various times. Arrows denote first observable precipitation. Strain rate is 0.1 s^{-1}; prestrain, 0.3. Numbers in boxes represent the fractional recrystallization. Source: Ref 69, 101

Local Pinning Force Generated by Precipitates. Recently, precipitation dispersion parameters were used to calculate the pinning force that the precipitates could exert on various boundaries (Ref 53, 68, 69, 81, 101, 107). For the experiments described in Fig. 24, this pinning force was found to be sufficiently large to suppress recrystallization. The driving force for static recrystallization was estimated to be approximately 9.0 MPa (1.3 ksi) whereas the local pinning forces for different conditions are shown in Table 4 (Ref 101). Clearly, there are conditions under which the pinning force can equal or exceed the driving force.

Table 4 Results of local pinning force calculations based on the rigid boundary model (RB), flexible boundary model (FB), and subgrain boundary model (SB). Specimens were deformed at 900 °C (1650 °F) using a strain rate of 10 s^{-1}

Time, s	Alloy	Precipitation distribution data		Number of particles per unit area (N_S), 10^{-14} m^{-2}	Local pinning force, MN · m^{-2}					
		Particle diameter (*d*), nm	Standard deviation, nm		RB		FB		SB	
					MPa	ksi	MPa	ksi	MPa	ksi
10	K-1	4.7	3.5	2.98	3.48	0.505	9.95	1.44	2.24	0.325
	K-2	4.1	2.7	1.02	0.96	0.14	4.41	0.639	0.67	0.097
100	K-1	6.3	3.7	4.32	5.86	0.850	12.76	1.85	4.35	0.631
	K-2	6.5	3.4	2.76	3.66	0.531	16.32	2.37	2.86	0.415
1000	K-1	9.2	3.5	2.08	3.50	0.508	7.99	1.16	3.06	0.444
	K-2	9.8	3.8	1.52	2.74	0.397	6.64	0.963	2.38	0.345

Additional information regarding the nature of the pinning force is evident from transmission electron microscopy (TEM) observations of the actual precipitation dispersions. Excellent evidence of these dispersions of strain-induced microalloy precipitates has been published (Ref 68, 69, 74, 81, 108, 109). A good example of this is shown in Fig. 25 for the precipitation of NbCN in austenite after low-temperature rolling and holding. The similarity between the precipitate dispersion shown in Fig. 25 and that shown for strain-induced precipitates of VCN formed in austenite in a vanadium-bearing steel after rolling at 870 °C (1600 °F) is striking (Ref 96). It has been suggested for some time that the strain-induced precipitation that forms in conjunction with hot rolling appears to decorate the subgrain boundaries of the statically (or dynamically) recovered austenite grains (Ref 96, 104). Recent work has revealed that the volume fraction of precipitates found on the subgrain boundaries is appreciably larger than that which would have been predicted by equilibrium solubility products (Ref 69, 81, 101). It appears that niobium has segregated to the subgrain boundaries causing an abnormally large volume fraction of NbCN to subsequently form. Because the pinning force varies with the volume fraction, this unexpectedly high localized volume fraction of NbCN would be expected to lead to larger than expected pinning forces. Alternatively, the niobium supersaturation eventually available to drive the precipitation reaction is larger than normally thought for a given bulk niobium concentration.

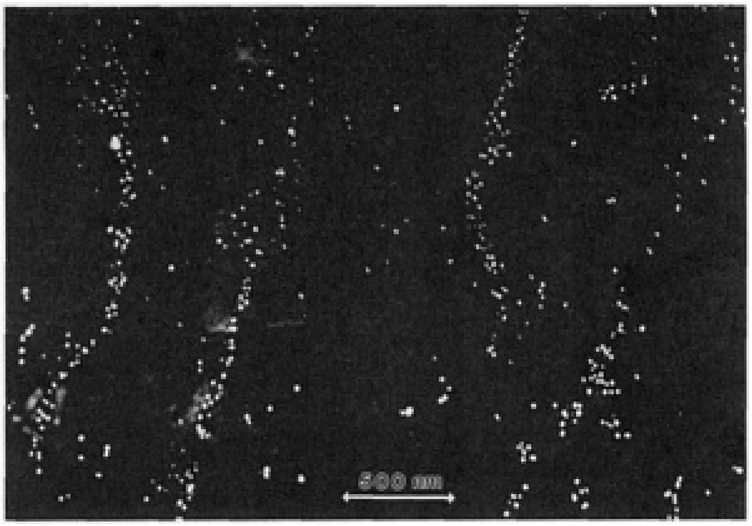

Fig. 25 Strain-induced precipitation of NbCN in austenite in a steel containing 0.9 wt% C and 0.07 wt% Nb. Specimen was reheated at 1250 °C (2280 °F), rolled 25%, and held at 950 °C (1740 °F), and then air cooled to room temperature. Centered dark field electron micrograph was obtained using a (111) NbC zone axis. Source: Ref 74

Effect of Niobium in Suppressing Recrystallization. The second question comparing the suppression of recrystallization by solute and precipitate is addressed in Table 5. In this case, the time to 20% static softening was measured for a variety of conditions, including those where niobium was largely in solution and those where niobium was present as a precipitate. The data for the strain rate of 10 s^{-1} are perhaps the more interesting because they have been generated under conditions approximating industrial plate rolling. When the niobium is in solution, the measured delay was less than 1.5 s at 1000 °C (1830 °F), whereas the delay caused by precipitates was on the order of several minutes. Furthermore, a comparison of the curves presented in Fig. 23 and 24 indicates that the precipitation-start time at 900 °C (1650 °F) corresponds to about 34% recrystallization in the niobium-free reference steel. A close examination of Fig. 24 reveals that this means the niobium in solution has retarded recrystallization for about 8 s at 900 °C (1650 °F) in the niobium steel.

Table 5 Times required for 20% softening in three selected steels at strain rates of 0.1 and 10 s^{-1}

Strain rate (ε), s^{-1}	Temperature		Time to 20% static softening ($t_{20\%}$), s		
	°C	°F	Alloy K-0	Alloy K-1	Alloy K-2
0.1	900	1650	5	2000[(a)]	3000[(a)]
	1000	1830	2	15	200[(a)]
	1100	2010	0.6	3	3.5
10	900	1650	0.2	300[(a)]	1000[(a)]
	1000	1830	0.1	1	1.5

Source: Ref 69

(a) Condition where extensive precipitation occurs.

Recrystallization Controlled Rolling

An alternate form of thermomechanical processing exists in addition to controlled rolling. This new process is called recrystallization controlled rolling. The metallurgical basis of the RCR process and how it is distinguished from the CCR or CHR processes and intensified controlled rolling (ICR) can be understood with the help of Fig. 22.

Whereas there is a clear distinction in processing (that is, finish rolling temperatures) between recrystallization controlled rolling and conventional controlled rolling, the difference between recrystallization controlled rolling and conventional hot rolling is not initially obvious because they both rely on high-temperature deformation. There are in fact two major differences between recrystallization controlled rolling and conventional hot rolling. First, all of the deformation in recrystallization controlled rolling is completed in the region of full recrystallization. This is in contrast to the CHR method, where a portion of the deformation takes place in the region of partial recrystallization. Second, only certain steels are amenable to the RCR method since a mechanism to inhibit grain coarsening must be present in the steel. Alloys not configured for recrystallization controlled rolling undergo static recrystallization following each high-temperature deformation. This is followed by rapid grain coarsening in the remaining interpass time. Hence, this leads to coarse, as-rolled austenite grain sizes. This austenite structure is characterized by a small S_v and is therefore indicative of poor thermomechanical processing. The central feature of steels exhibiting RCR behavior is the presence of a grain coarsening inhibition system. Recent research has indicated that this inhibition system can take one of two forms (Ref 44, 94, 96). The first relies on the presence of stable particles whose distribution provides an adequate pinning force to suppress coarsening following post-deformation static recrystallization. These particles must have sufficient stability to resist Ostwald ripening (solution-crystallizer phenomenon in which small crystals, more soluble than large ones, dissolve and reprecipitate onto larger particles) themselves and must be present in a sufficiently fine dispersion. As was shown above, the pinning force exerted by an array of particles on a boundary is given by Equation 18 assuming a rigid boundary model. As was shown by Ashby (Ref 65), the driving force for normal grain coarsening is nearly three orders of magnitude smaller than that for recrystallization. Hence, the particle pinning force required to suppress coarsening is much smaller than that required to suppress recrystallization. Because the particle pinning force varies with f_v/r, even particle distributions with rather small f_v and large r can still be effective barriers to grain coarsening. This, of course, would not be true in the suppression of recrystallization, where only large, local volume fractions of fine particles are effective. Particles such as titanium nitride have been shown to be particularly well suited for the suppression of grain coarsening (Ref 44, 96). In this regard, the titanium nitride particles are formed via solid state precipitation immediately following solidification and, hence, exist prior to deformation.

An alternate grain coarsening inhibition mechanism has recently been discovered (Ref 110). This mechanism involves intense solute drag as the critical element. It has been found that high levels of soluble molybdenum and niobium can be very effective in retarding boundary motion at high reheating temperatures (see Fig. 26). Hence, these solute effects act to retard grain coarsening both during reheating and after post-deformation static recrystallization. In summary, recrystallization controlled rolling offers an attractive alternative to conventional controlled rolling in several applications where low-temperature rolling is impractical (for example, older underpowered plate mills and hot forgings) (Ref 112, 113). That recrystallization controlled rolling can lead to excellent austenite conditioning is evidenced by values of S_v well in excess of 100 mm^{-1} which can be easily realized (Ref 11).

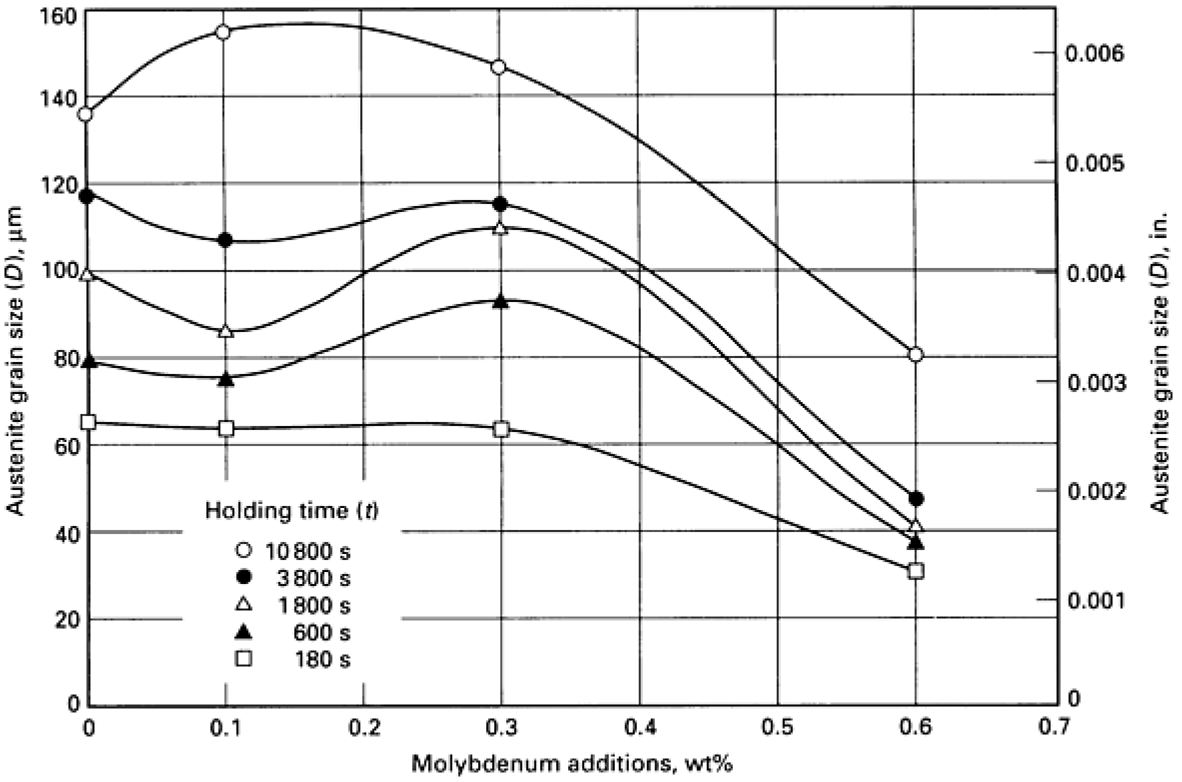

Fig. 26 Effect of molybdenum addition on austenite grain size after reheating at 1150 °C (2100 °F) and holding at this temperature for various times. Source: Ref 111

Intensified Controlled Rolling

A variation in conventional controlled rolling, known as intensified controlled rolling, is shown in Fig. 22. Note that intensified controlled rolling differs from conventional controlled rolling in that finish rolling not only occurs below the T_{RXN}, but also extends to temperatures below the Ar_3. The goal of intensified controlled rolling is to increase the strength and toughness of the as-rolled MA steel over what could be achieved through conventional controlled rolling. The combination of the lower reheat and lower rolling temperatures leads to finer as-rolled austenite. Furthermore, because a portion of the rolling occurs in the intercritical or two-phase ($\alpha + \gamma$) region, a certain amount of proeutectoid ferrite would be deformed during this rolling. This deformed ferrite is partially responsible for the higher strengths observed with intensified controlled rolling (Ref 93, 114).

High Toughness Rolling Processes

Heat treatment processes incorporating high toughness rolling have been developed by Sumitomo and Broken Hill Proprietary.

Sumitomo High Toughness Rolling. An additional rolling practice shown in Fig. 22 is known as the Sumitomo high toughness (SHT) process (Ref 93, 115, 116). The goal of the SHT process is to produce steels with very high resistance to brittle fracture at the expense of strength when compared to a steel processed by the CCR process. In the SHT process, extra grain refinement of the austenite is achieved by the introduction of a cooling and low-temperature reheating cycle positioned between rough and finish rolling. The finish rolling is performed in the intercritical region as with intensified controlled rolling.

Broken Hill Proprietary High Toughness Rolling. There are some conditions where neither the CCR process nor the ICR process will achieve a resistance to brittle fracture in plate steels. Such conditions exist when the plate thickness exceeds $\approx$ 18 mm ($\approx \frac{23}{32}$ in.) or when the plate width causes the mill loads to exceed acceptable levels. These shortcomings have been overcome by Broken Hill Proprietary (BHP) through a variation of both the alloy design and controlled rolling practice of their plate steels intended for line pipe and offshore applications (Ref 117, 118, 119). During conventional

controlled rolling, the total reduction is fairly evenly distributed between the roughing and finishing passes. In the BHP process, a larger portion of the deformation takes place in the roughing passes and, consequently, a smaller portion in the finishing passes. Hence, while the low-temperature deformation in conventional controlled rolling and intensified controlled rolling is used to generate high values of S_v through extensive pancaking, the high-temperature passes and the associated recrystallization and grain refinement are responsible for the high S_v found in the BHP process. This emphasis on high-temperature rolling is beneficial for the rolling of both heavy sections and large widths. Because the BHP process involves high-temperature rolling, the phenomenon of grain coarsening must be avoided. This is accomplished by a microtitanium addition to a niobium MA steel. The titanium nitride that forms is effective in suppressing grain coarseing.

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Applications of Thermomechanical Processing to Heat Treat Low-Alloy Steels

Up until this point, the benefits of thermomechanical processing have been examined for as-hot rolled strip and plate microalloyed steels. By definition, these steels contain less than about 2 wt% in total alloying and usually exhibit F-P microstructures. Recently, the benefits of thermomechanical processing have been extended to the low-alloy steels, including the HY steels, the HSLA steels, the ultralow carbon bainitic steels, and the multiphase steels. These steels differ from the as-rolled microalloyed steels in two ways:

- Steels contain >3 wt% in total alloying
- Steels may be heat treated after rolling

These steels are often bainitic, martensitic, or multiphase in microstructure.

HSLA Steels. Thermomechanical processing has been shown to greatly improve the resistance to brittle fracture in the new HSLA-80 and HSLA-100 steels (Ref 120). Figure 27 compares the notch toughness of quenched and aged steels that had been either hot rolled or controlled rolled prior to heat treatment. The benefit of the controlled rolling is obvious. Note that the benefits derived from the controlled rolling existed even after the post-rolling reheating treatment.

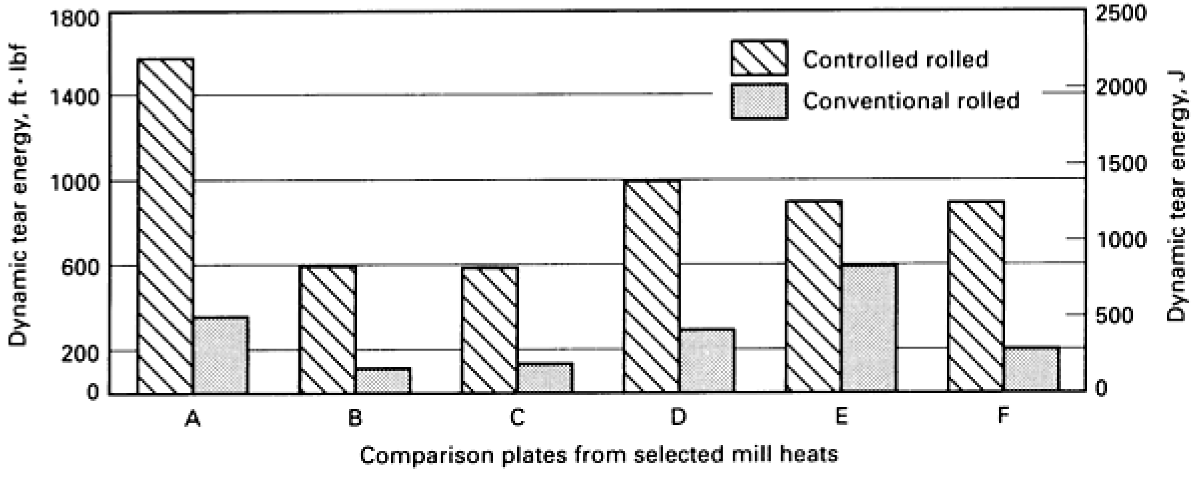

Fig. 27 Comparison of dynamic tear toughness at -40 °C (-40 °F) of 25 mm (1 in.) thick HSLA-80 plates produced either by controlled rolling or conventional rolling prior to reheating, water quenching, and aging. Source: Ref 120

ULCB Steels. Austenite conditioning has also been shown to be critical in achieving low-temperature toughness in as-hot rolled ULCB steels (Ref 11, 121). A study of the factors that control the resistance to brittle fracture in these steels indicated the importance of the prior austenite grain size (see Fig. 4). In a similar study (Ref 121), an important relationship was found between low-temperature toughness and the S_v of the controlled rolled austenite that existed prior to transformation. While S_v improves the toughness of F-P steels through the refinement of the ferrite grain size, the role of S_v in ULCB steels is somewhat different. As was shown in a later study (Ref 11), the only significant barrier to a growing cleavage crack in a high-strength bainitic matrix is the prior austenite grain boundary. Hence, the higher the S_v, the smaller the growth phase of the cleavage cracking event. It was shown that when these cleavage cracks could be kept relatively small, their existence did not preclude an otherwise high-toughness value at low temperatures.

Multiphase steels intended for long product applications have also benefitted from thermomechanical processing. Low-carbon steels based on the manganese-molybdenum-niobium system have been shown to exhibit ferrite-lower bainite microstructures after controlled rolling. These steels display excellent ductility and work hardening characteristics and, hence, are ideal steels for cold forging applications. In this case, the controlled rolling not only leads to grain refinement but also to establishing the proper balance between the phases in the final microstructure (Ref 11, 122, 123). This same steel exhibits austenite conditioning via recrystallization controlled rolling during high-temperature forging processing. In the as-direct quenched condition, these forgings display unusually high levels of strength, toughness, and fatigue resistance (Ref 124).

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Future Outlook

The thermomechanical processing of austenite is often associated with significant improvements in final properties and offers a degree of flexibility in achieving various packages of properties that are quite impressive. While the elements of thermomechanical processing (reheating, hot rolling, and cooling) are easily distinguishable and individually amenable to thorough investigation, the response of a given MA steel to a given processing step will, to a large measure, depend on what had occurred in previous stages. It is this interdependence that makes the rationalization of commercial hot rolling so very complex and challenging. This is specially true in the MA steels, where the dissipation or retention of microalloy solute supersaturation in a given process step might have drastically different effects on microstructural evolution in subsequent steps. There is little doubt that thermomechanical processing offers a very cost-effective route to good properties in steel. It is interesting to consider where the concepts of thermomechanical processing and microalloying technology may lead us in the future.

Introduction to Surface Hardening of Steels

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Introduction

SURFACE HARDENING, a process which includes a wide variety of techniques (Table 1), is used to improve the wear resistance of parts without affecting the more soft, tough interior of the part. This combination of hard surface and resistance to breakage upon impact is useful in parts such as a cam or ring gear that must have a very hard surface to resist wear, along with a tough interior to resist the impact that occurs during operation. Further, the surface hardening of steel has an advantage over through hardening because less expensive low-carbon and medium-carbon steels can be surface hardened without the problems of distortion and cracking associated with the through hardening of thick sections.

Table 1 Engineering methods for surface hardening of steels

Layer Additions
Hardfacing
Fusion hardfacing (welded overlay)
Thermal spray (nonfusion bonded overlay)
Coatings:
Electrochemical plating
Chemical vapor deposition (electroless plating)
Thin films (physical vapor deposition, sputtering, ion plating)
Ion mixing
Substrate treatment
Diffusion methods:
Carburizing
Nitriding
Carbonitriding
Nitrocarburizing
Boriding
Titanium-carbon diffusion
Toyota diffusion process
Selective hardening methods:
Flame hardening
Induction hardening
Laser hardening
Electron beam hardening
Ion implantation
Selective carburizing and nitriding
Use of arc lamps

There are two distinctly different approaches to the various methods for surface hardening (Table 1):

- Methods that involve an intentional buildup or addition of a new layer
- Methods that involve surface and subsurface modification without any intentional buildup or increase in part dimensions

The first group of surface hardening methods includes the use of thin films, coatings, or weld overlays (hardfacings). Films, coatings, and overlays generally become less cost effective as production quantities increase, especially when the entire surface of workpieces must be hardened. The fatigue performance of films, coatings, and overlays may also be a limiting factor, depending on the bond strength between the substrate and the added layer. Fusion-welded overlays have strong bonds, but the primary surface-hardened steels used in wear applications with fatigue loads include heavy case-hardened steels and flame- or induction-hardened steels. Nonetheless, coatings and overlays can be effective in some applications. With tool steels, for example, TiN and Al_2O_3 coatings are effective not only because of their hardness but also because their chemical inertness reduces crater wear and the welding of chips to the tool. Overlays can be effective when the selective hardening of large areas is required.

This introductory article on surface hardening focuses exclusively on the second group of methods, which is further divided into diffusion methods and selective hardening methods (Table 1). Diffusion methods modify the chemical composition of the surface with hardening species such as carbon, nitrogen, or boron. Diffusion methods allow effective hardening of the entire surface of a part and are generally used when a large number of parts are to be surface hardened. In contrast, selective surface hardening methods allow localized hardening. Selective hardening generally involves transformation hardening (from heating and quenching), but some selective hardening methods (selective nitriding, ion implantation and ion beam mixing) are based solely on compositional modification. Factors affecting the choice of these surface hardening methods are discussed in the section "Process Selection" in this article.

Diffusion Methods of Surface Hardening

As previously mentioned, surface hardening by diffusion involves the chemical modification of a surface. The basic process used is thermochemical because some heat is needed to enhance the diffusion of hardening species into the surface and subsurface regions of a part. The depth of diffusion exhibits a time-temperature dependence such that:

$$\text{Case depth} \propto K\sqrt{time} \qquad \textbf{(Eq 1)}$$

where the diffusivity constant, *K*, depends on temperature, the chemical composition of the steel, and the concentration gradient of a given hardening species. In terms of temperature, the diffusivity constant increases exponentially as a function of absolute temperature. Concentration gradients depend on the surface kinetics and reactions of a particular process.

Methods of hardening by diffusion include several variations of hardening species (such as carbon, nitrogen, or boron) and of the process method used to handle and transport the hardening species to the surface of the part. Process methods for exposure involve the handling of hardening species in forms such as gas, liquid, or ions. These process variations naturally produce differences in typical case depth and hardness (Table 2). Factors influencing the suitability of a particular diffusion method include the type of steel (Fig. 1), the desired case hardness (Fig. 2), and the case depth (Fig. 3).

Table 2 Typical characteristics of diffusion treatments

Process	Nature of case	Process temperature,	Typical case	Case hardness,	Typical base	Process characteristics

		°C (°F)	depth	HRC	metals	
Carburizing						
Pack	Diffused carbon	815-1090 (1500-2000)	125 µm-1.5 mm (5-60 mils)	50-63[(a)]	Low-carbon steels, low-carbon alloy steel	Low equipment costs, difficult to control case depth accurately
Gas	Diffused carbon	815-980 (1500-1800)	75 µm-1.5 mm (3-60 mils)	50-63[(a)]	Low-carbon steels, low-carbon alloy steels	Good control of case depth, suitable for continuous operation, good gas controls required, can be dangerous
Liquid	Diffused carbon and possibly nitrogen	815-980 (1500-1800)	50 µm-1.5 mm (2-60 mils)	50-65[(a)]	Low-carbon steels, low-carbon alloy steels	Faster than pack and gas processes, can pose salt disposal problem, salt baths require frequent maintenance
Vacuum	Diffused carbon	815-1090 (1500-2000)	75 µm-1.5 mm (3-60 mils)	50-63[(a)]	Low-carbon steels, low-carbon alloy steels	Excellent process control, bright parts, faster than gas carburizing, high equipment costs
Nitriding						
Gas	Diffused nitrogen, nitrogen compounds	480-590 (900-1100)	125 µm-0.75 mm (5-30 mils)	50-70	Alloy steels, nitriding steels, stainless steels	Hardest cases from nitriding steels, quenching not required, low distortion, process is slow, is usually a batch process
Salt	Diffused nitrogen, nitrogen compounds	510-565 (950-1050)	2.5 µm-0.75 mm (0.1-30 mils)	50-70	Most ferrous metals including cast irons	Usually used for thin hard cases <25 µm (1 mil), no white layer, most are proprietary processes
Ion	Diffused nitrogen, nitrogen compounds	340-565 (650-1050)	75 µm-0.75 mm (3-30 mils)	50-70	Alloy steels, nitriding, stainless steels	Faster than gas nitriding no white layer, high equipment costs, close case control
Carbonitriding						
Gas	Diffused carbon and nitrogen	760-870 (1400-1600)	75 µm-0.75 mm (3-30 mils)	50-65[(a)]	Low-carbon steels, low-carbon alloy steels, stainless steel	Lower temperature than carburizing (less distortion), slightly harder case than carburizing gas control critical

Liquid (cyaniding)	Diffused carbon and nitrogen	760-870 (1400-1600)	2.5-125 µm (0.1-5 mils)	50-65[(a)]	Low-carbon steels	Good for thin cases on noncritical parts, batch process, salt disposal problems
Ferritic nitrocarburizing	Diffused carbon and nitrogen	565-675 (1050-1250)	2.5-25 µm (0.1-1 mil)	40-60[(a)]	Low-carbon steels	Low-distortion process for thin case on low-carbon steel, most processes are proprietary
Other						
Aluminizing (pack)	Diffused aluminum	870-980 (1600-1800)	25 µm-1 mm (1-40 mils)	<20	Low-carbon steels	Diffused coating used for oxidation resistance at elevated temperatures
Siliconizing by chemical vapor deposition	Diffused silicon	925-1040 (1700-1900)	25 µm-1 mm (1-40 mils)	30-50	Low-carbon steels	For corrosion and wear resistance, atmosphere control is critical
Chromizing by chemical vapor deposition	Diffused chromium	980-1090 (1800-2000)	25-50 µm (1-2 mils)	Low-carbon steel, <30; high-carbon steel, 50-60	High- and low-carbon steels	Chromized low-carbon steels yield a low-cost stainless steel, high-carbon steels develop a hard corrosion-resistant case
Titanium carbide	Diffused carbon and titanium, TiC compound	900-1010 (1650-1850)	2.5-12.5 µm (0.1-0.5 mil)	>70[(a)]	Alloy steels, tool steels	Produces a thin carbide (TiC) case for resistance to wear, high temperature may cause distortion
Boriding	Diffused boron, boron, compound	400-1150 (750-2100)	12.5-50 µm (0.5-2 mils)	40->70	Alloy steels, tool steels, cobalt and nickel alloys	Produces a hard compound layer, mostly applied over hardened tool steels, high process temperature can cause distortion

Source: Ref 1

(a) Requires quench from austenitizing temperature.

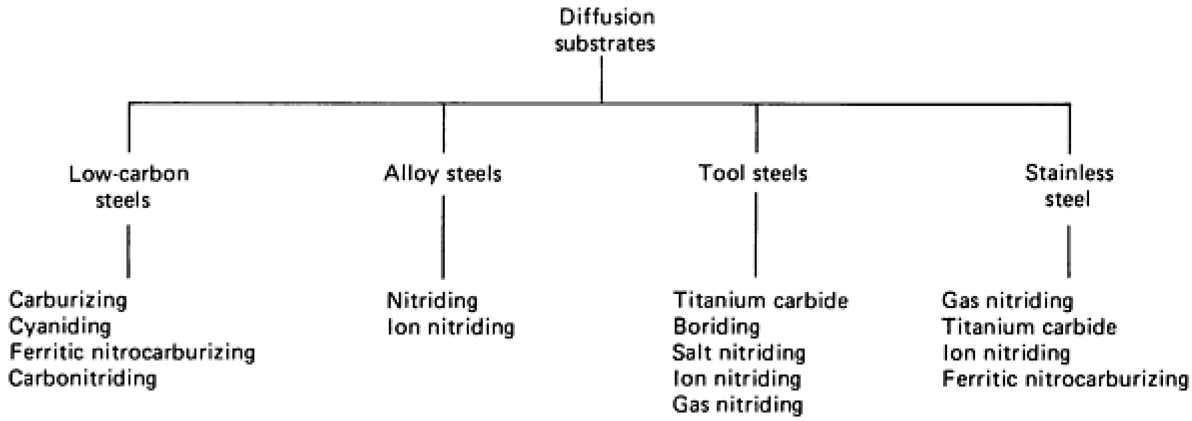

Fig. 1 Types of steels used for various diffusion processes

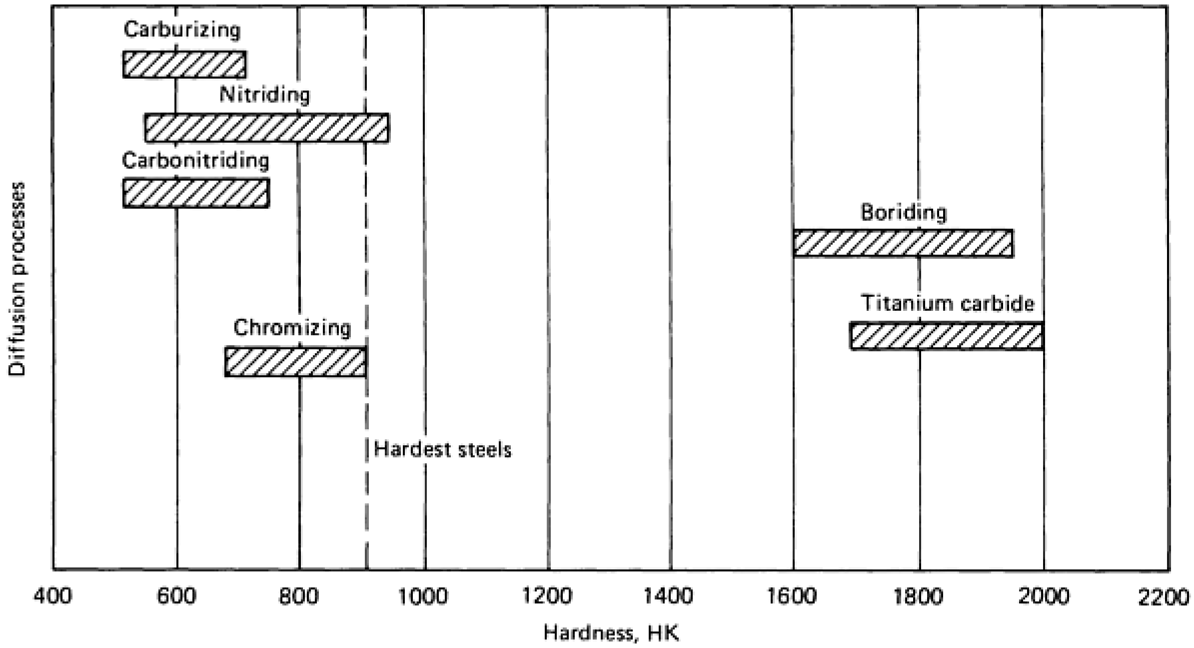

Fig. 2 Spectrum of hardness obtainable with selected diffusion processes of steel

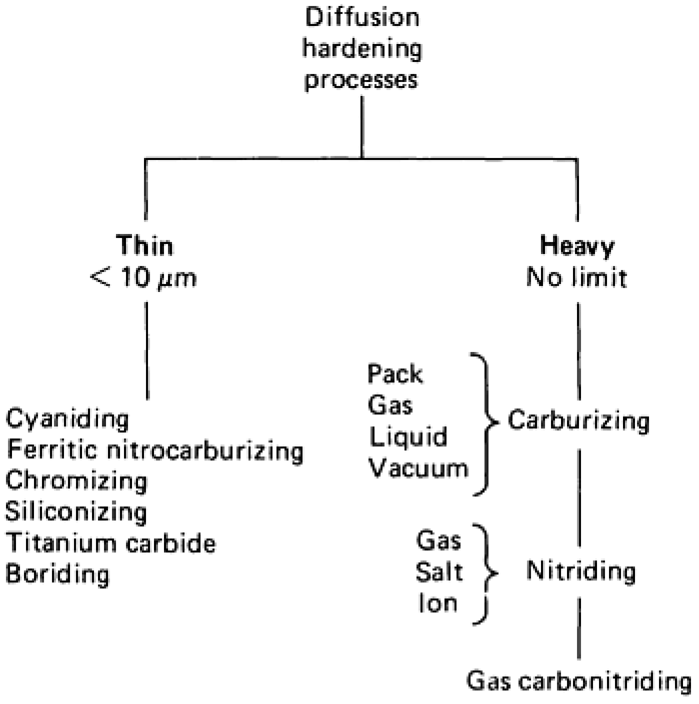

Fig. 3 Categorization of diffusion processes by typical case depth

It is also important to distinguish between total case depth and effective case depth. The effective case depth is typically about two-thirds to three-fourths the total case depth. The required effective depth must be specified so that the heat treater can process the parts for the correct time at the proper temperature.

Carburizing

Carburizing is the addition of carbon to the surface of low-carbon steels at temperatures (generally between 850 and 950 °C, or 1560 and 1740 °F) at which austenite, with its high solubility for carbon, is the stable crystal structure. Hardening is accomplished when the high-carbon surface layer is quenched to form martensite so that a high-carbon martensitic case with good wear and fatigue resistance is superimposed on a tough, low-carbon steel core. Of the various diffusion methods (Table 2), gas carburization is the most widely used, followed by gas nitriding and carbonitriding.

Case hardness of carburized steels is primarily a function of carbon content. When the carbon content of the steel exceeds about 0.50%, additional carbon has no effect on hardness but does enhance hardenability. Carbon in excess of 0.50% may not be dissolved, which would thus require temperatures high enough to ensure carbon-austenite solid solution.

Case depth of carburized steel is a function of carburizing time and the available carbon (carbon potential) at the surface. When prolonged carburizing times are used for deep case depths, a high carbon potential produces a high surface-carbon content, which may thus result in excessive retained austenite or free carbides. These two microstructural elements both have adverse effects on the distribution of residual stress in the case-hardened part. Consequently, a high carbon potential may be suitable for short carburizing times but not for prolonged carburizing. Selection of carbon potential also depends on the carburizing response of a particular steel. Further information on the characteristics of carburized steels is covered in the article "Microstructures and Properties of Carburized Steels" in this Volume.

Carburizing steels for case hardening usually have base-carbon contents of about 0.2%, with the carbon content of the carburized layer generally being controlled at between 0.8 and 1% C (Ref 2). However, surface carbon is often limited to 0.9% (Ref 3) because too high a carbon content can result in retained austenite and brittle martensite (due to the formation of proeutectoid carbides on the grain boundaries).

Most steels that are carburized are killed steels (deoxidized by the addition of aluminum), which maintain fine grain sizes to temperatures of about 1040 °C (1900 °F). Steels made to coarse grain practices can be carburized if a double quench

provides grain refinement. Double quenching usually consists of a direct quench and then a requench from a lower temperature. In most instances, however, carbonitriding of coarse-grained steels is more appropriate because of the lower temperatures and shorter cycle times.

Many alloy steels for case hardening are now specified on the basis of core hardenability. Although the same considerations generally apply as apply to the selection of uncarburized grades, there are some peculiarities in carburizing applications.

First, in a case-hardened steel, the hardenability of both case and core must be considered. Because of the difference in carbon content, case and core have quite different hardenabilities, and this difference is much greater for some steels than for others. Moreover, the two regions have different in-service functions to perform. Until the introduction of lean alloy steels such as the 86*xx* series, with and without boron, there was little need to be concerned about case hardenability because the alloy content combined with the high carbon content always provided adequate hardenability. This is still generally true when the steels are direct quenched from carburizing, so that the carbon and alloying elements are in solution in the case austenite. In parts that are reheated for hardening and in heavy-sectioned parts, however, both case and core hardenability requirements should be carefully evaluated.

The hardenability of the steels as purchased is the core hardenability. Because these low-carbon steels, as a class, are shallow hardening and because of the wide variation in the section sizes of case-hardened parts, the hardenability of the steel must be related to some critical section of the part, for example, the pitch line or the root of a gear tooth. This is best accomplished by making a part of a steel of known hardenability, heat treating it, and then, by means of equivalence of hardness, relating the hardenability in the critical section or sections to the proper positions on the endquench hardenability specimens, both base carbon and carburized.

Finally, the relationship between the thermal gradient and the carbon (hardenability) gradient during quenching of a carburized part can make a measurable difference in the case depth as measured by hardness. That is, an increase in base hardenability can produce a higher proportion of martensite for a given carbon level, yielding an increased measured case depth. Therefore, a shallower carbon profile and shorter carburizing time could be used to attain the desired result in a properly chosen steel.

Core Hardness. A common mistake is to specify too narrow a range of core hardness. When the final quench is from a temperature high enough to allow the development of full core hardness, the hardness variation at any location will be that of the hardenability band of the steel at the corresponding position on the end-quenched hardenability specimen. One way to alter this state of affairs is to use higher-alloy steels. In the commonly used alloy steels having a maximum of 2% total alloy content, the range for the core hardness of sections such as gear teeth is 12 to 15 points HRC. Higher-alloy steels exhibit a narrower range; for example, in 4815 the range is 10 points, while in 3310 it is 8 points. Such steels are justified only for severe service or special applications.

In standard steels purchased to chemical composition requirements rather than to hardenability, the range can be 20 or more HRC points; for example, 8620 may vary from 20 to 45 HRC at the $\frac{4}{16}$ in. position. The 25 point range emphasizes the advantage of purchasing to hardenability specifications to avoid the intolerable variation possible within the ranges for standard-chemistry steels. Another way to control core hardness within narrow limits without resorting to the use of high-alloy steels is to use a final quench from a lower temperature so that full hardness in the case will be developed without the disadvantage of excessive core hardness.

Gears and Low-Distortion Applications. Gears are almost always oil quenched because distortion must be held to the lowest possible level. Therefore, alloy steels are usually selected, with much debate about which particular alloy. The lower-alloy steels such as 4023, 5120, 4118, 8620, and 4620, with a carbon range between 0.15 and 0.25%, are widely used and generally satisfactory. Usually, the first choice is one of the last two steels mentioned, either of which should be safe for all ordinary applications. The final choice, based on service experience or dynamometer testing, should be the least expensive steel that will do the job. To this list should be added 1524, which, although not classified commercially as an alloy steel, has sufficient manganese to make it oil hardening up to an end-quench correlation point of $\frac{3}{16}$.

For heavy-duty applications, higher-alloy grades such as 4320, 4817, and 9310 are justifiable if based on actual performance tests. The life testing of gears in the same mountings used in service to prove both the design and the steel selection is particularly important.

The carbonitriding process extends the use of carbon steels such as 1016, 1018, 1019, and 1022 into the field of light-duty gearing by permitting the use of oil quenching in teeth of eight diametral pitch and finer. Steels selected for such applications should be specified silicon killed fine grained in order to ensure uniform case hardness and dimensional control. The core of such gears will, of course, have the properties of low-carbon steel, oil quenched. In the thin sections of fine-pitch teeth, this may be up to 25 HRC. The carbonitriding process is usually limited, for economic reasons, to maximum case depths of approximately 0.6 mm (0.025 in.).

Nongear Applications. In other applications, when distortion is not a major factor, the carbon steels described above, water quenched, can be used up to a 50 mm (2 in.) diameter. In larger sizes, low-alloy steels, water quenched, such as 5120, 4023, and 6120, can be used, but possible distortion and quench cracking must be avoided.

Carburizing Methods. While the basic principle of carburizing has remained unchanged since carburizing was first employed, the method used to introduce the carbon into the steel has been a matter of continuous evolution. In its earliest application, parts were simply placed in a suitable container and covered with a thick layer of carbon powder (pack carburizing). Although effective in introducing carbon, this method was exceedingly slow, and as the demand for greater production grew, a new process using a gaseous atmosphere was developed. In gas carburizing, the parts are surrounded by a carbon-bearing atmosphere that can be continuously replenished so that a high carbon potential can be maintained. While the rate of carburizing is substantially increased in the gaseous atmosphere, the method requires the use of a multicomponent atmosphere whose composition must be very closely controlled to avoid deleterious side effects, for example, surface and grain-boundary oxides. In addition, a separate piece of equipment is required to generate the atmosphere and control its composition. Despite this increased complexity, gas carburizing has become the most effective and widely used method for carburizing steel parts in large quantities.

In efforts required to simplify the atmosphere, carburizing in an oxygen-free environment at very low pressure (vacuum carburizing) has been explored and developed into a viable and important alternative. Although the furnace enclosure in some respects becomes more complex, the atmosphere is greatly simplified. A single-component atmosphere consisting solely of a simple gaseous hydrocarbon, for example, methane, may be used. Furthermore, because the parts are heated in an oxygen-free environment, the carburizing temperature may be increased substantially without the risk of surface or grain-boundary oxidation. The higher temperature permitted increases not only the solid solubility of carbon in the austenite but also its rate of diffusion, so that the time required to achieve the case depth desired is reduced.

Although vacuum carburizing overcomes some of the complexities of gas carburizing, it introduces a serious new problem that must be addressed. Because vacuum carburizing is conducted at very low pressures, and the rate of flow of the carburizing gas into the furnace is very low, the carbon potential of the gas in deep recesses and blind holes is quickly depleted. Unless this gas is replenished, a great nonuniformity in case depth over the surface of the part is likely to occur. If, in an effort to overcome this problem, the gas pressure is increased significantly, another problem arises, that of free-carbon formation, or sooting. Thus, in order to obtain cases of reasonably uniform depth over a part of complex shape, the gas pressure must be increased periodically to replenish the depleted atmosphere in recesses and then reduced again to the operating pressure. Clearly, a delicate balance exists in vacuum carburizing: The process conditions must be adjusted to obtain the best compromise between case uniformity, risk of sooting, and carburizing rate. A method that overcomes both of these major problems, yet retains the desirable features of a simple atmosphere and a higher permissible operating temperature is plasma or ion carburizing.

To summarize, carburizing methods include:

- Gas carburizing
- Vacuum carburizing
- Plasma carburizing
- Salt bath carburizing
- Pack carburizing

These methods introduce carbon by the use of gas (atmospheric-gas, plasma, and vacuum carburizing), liquids (salt bath carburizing), or solid compounds (pack carburizing). All of these methods have limitations and advantages, but gas carburizing is used most often for large-scale production because it can be accurately controlled and involves a minimum of special handling.

Vacuum carburizing and plasma carburizing have found applications because of the absence of oxygen in the furnace atmosphere. Salt bath and pack carburizing are still done occasionally, but have little commercial importance today.

In a survey of 800 commercial shops in the United States and Canada (Ref 4), 70% offered carburizing services, of which:

- 48% offered gas atmosphere carburizing
- 19% offered pack carburizing
- 12% offered salt carburizing
- 5% offered carburizing in fluid beds
- 2% offered vacuum carburizing
- 1% offered ion carburizing

Each of these methods is described in separate articles in this Volume.

Process characteristics of the above-mentioned carburizing methods fall into two general groups:

- Conventional methods, which introduce carbon by gas atmospheres, salt baths, or charcoal packs
- Plasma methods, which impinge positive carbon ions on the surface of a steel part (the cathode)

The main difference between conventional and glow-discharge (or plasma) methods is the reduced carburizing times achieved in plasma-assisted methods. The quickly attained surface saturation also results in faster diffusion kinetics. Furthermore, plasma carburizing produces very uniform case depths, even in parts with irregular surfaces (Ref 5, 6). This uniformity is caused by the glow-discharge plasma, which closely envelops the specimen surface, provided that recesses or holes are not too small (Ref 6).

With the conventional methods, carburization always takes place by means of a gaseous phase of carbon monoxide; however, each method also involves different reaction and surface kinetics, producing different case-hardening results. In general, with conventional methods, carbon monoxide breaks down at the steel surface:

$$2CO \rightleftharpoons CO_2 + C \qquad \textbf{(Eq 2)}$$

The liberated carbon is readily dissolved by the austenite phase and diffuses into the body of the steel. For some process methods (gas and pack carburizing), the carbon dioxide produced may react with the carbon atmosphere or pack charcoal to produce new carbon monoxide by the reverse reaction of Eq 2. Because the reaction can proceed in both directions, an equilibrium relationship exists between the constituents (Fig. 4). If the temperature is increased at constant pressure, more carbon monoxide is produced (Fig. 4). In turn, the equilibrium percentages of carbon monoxide and carbon dioxide influence the carbon concentrations in steel (Fig. 5). Carburizing is most frequently performed between 850 and 950 °C (1550 and 1750 °F), but sometimes higher temperatures are used to reduce cycle times and/or produce deeper depths of the high-carbon surface layer.

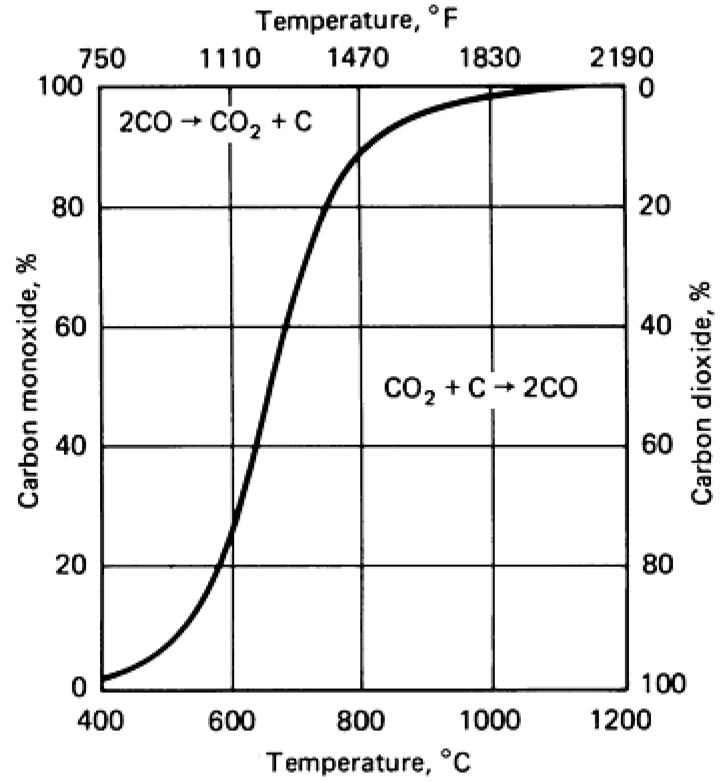

Fig. 4 Equilibrium diagram for reaction 2CO € C + CO_2 at pressure of one atmosphere. Source: Ref 7

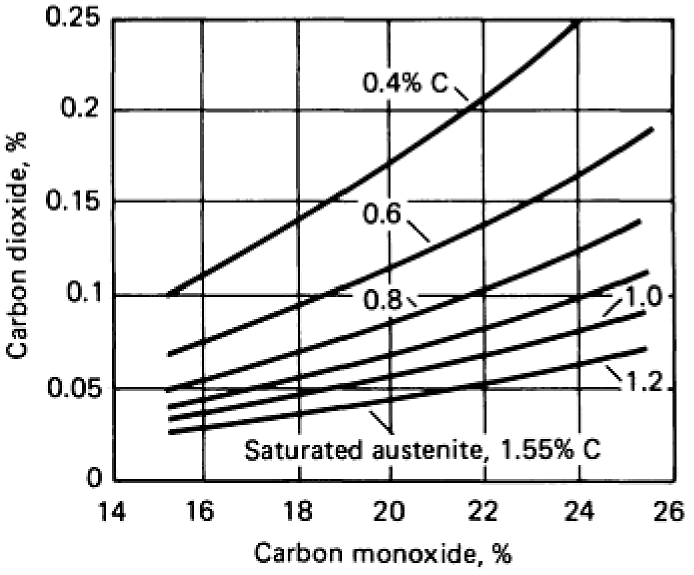

Fig. 5 Equilibrium percentages of carbon monoxide and carbon dioxide required to maintain various carbon concentrations at 975 °C (1790 °F) in plain carbon and certain low-alloy steels. *K* = 89.67. Source: Ref 8

Quantitative algorithms for estimating case depth from carburization often focus on making the proportional relation of Eq 1 explicit (Case depth = $K\sqrt{time}$) for gas carburization only (Ref 2, 3). Even with gas carburization, however, heat treaters have long recognized that considering only the kinetics of carbon diffusion gives an incomplete picture of carburizing. A comprehensive model of gas carburization must include algorithms that describe:

- Carbon diffusion
- Kinetics of the surface reaction
- Kinetics of the reaction between endogas and enriching gas
- Purging (for batch processes)
- The atmosphere control system

Reference 9 discusses possible modeling of each of these factors for gas carburization. The effects of process variables are also covered in the article "Gas Carburizing" in this Volume.

Nitriding

Nitriding is a surface-hardening heat treatment that introduces nitrogen into the surface of steel at a temperature range (500 to 550 °C, or 930 to 1020 °F), while it is in the ferritic condition. Thus, nitriding is similar to carburizing in that surface composition is altered but different in that nitrogen is added into ferrite instead of austenite. Because nitriding does not involve heating into the austenite phase field and a subsequent quench to form martensite, nitriding can be accomplished with a minimum of distortion and with excellent dimensional control.

The mechanism of nitriding is generally known, but the specific reactions that occur in different steels and with different nitriding media are not always known. Nitrogen has partial solubility in iron. It can form a solid solution with ferrite at nitrogen contents up to about 6%. At about 6% N, a compound called gamma prime (γ'), with a composition of Fe_4N, is formed. At nitrogen contents greater than 8%, the equilibrium reaction product is ε compound, Fe_3N. Nitrided cases are stratified. The outermost surface can be all γ' and, if this is the case, it is referred to as the white layer (it etches white in metallographic preparation). Such a surface layer is undesirable: It is very hard but is so brittle that it may spall in use. Usually it is removed; special nitriding processes are used to reduce this layer or make it less brittle. The ϵ zone of the case is hardened by the formation of the Fe_3N compound, and below this layer there is some solid solution strengthening from the nitrogen in solid solution (Fig. 6).

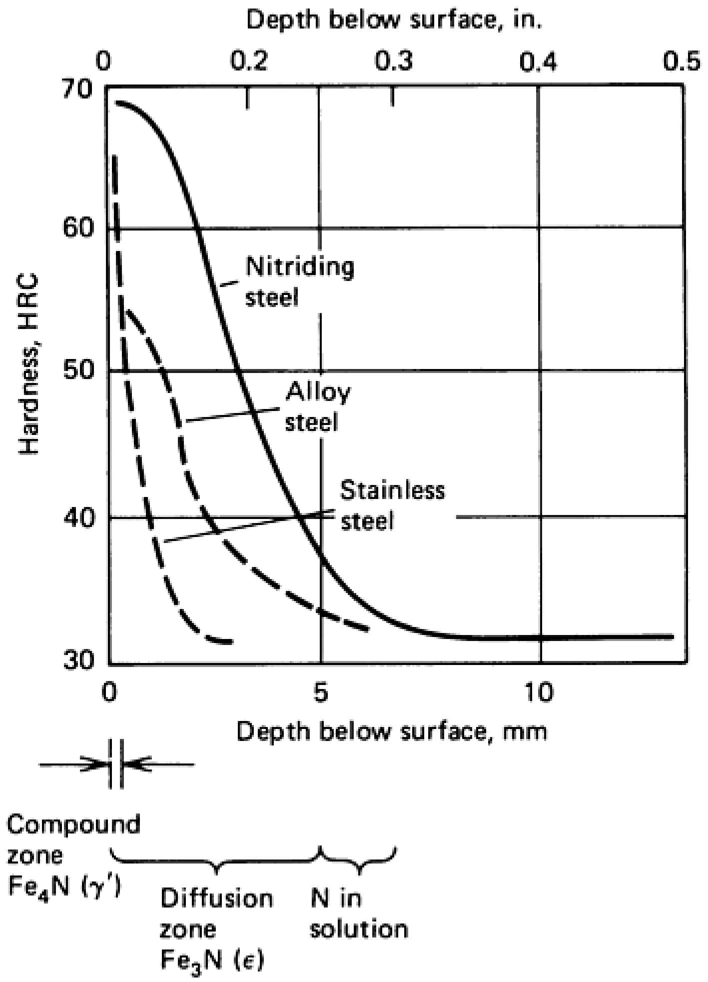

Fig. 6 Nitride case profiles for various steels. Source: Ref 1

Nitrided steels are generally medium-carbon (quenched and tempered) steels that contain strong nitride-forming elements such as aluminum, chromium, vanadium, and molybdenum. The most significant hardening is achieved with a class of alloy steels (nitralloy type) that contain about 1% Al (Fig. 6). When these steels are nitrided, the aluminum forms AIN particles, which strain the ferrite lattice and create strengthening dislocations. Titanium and chromium are also used to enhance case hardness (Fig. 7a), although case depth decreases as alloy content increases (Fig. 7b). The microstructure also influences nitridability because ferrite favors the diffusion of nitrogen and because a low carbide content favors both diffusion and case hardness. Usually alloy steels in the heat-treated (quenched and tempered) state are used for nitriding (Ref 7).

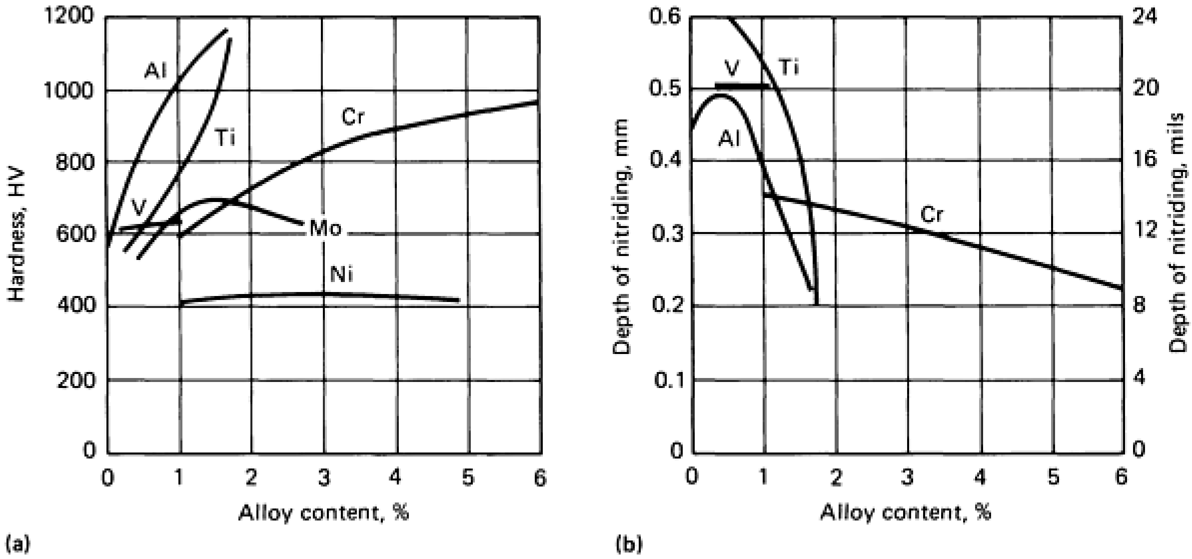

Fig. 7 Influence of alloying elements on (a) hardness after nitriding (base alloy, 0.35% C, 0.30% Si, 0.70% Mn) and (b) depth of nitriding measured at 400 HV (nitriding for 8 h at 520 °C, or 970 °F). Source: Ref 7

Process methods for nitriding include gas (box furnace or fluidized bed), liquid (salt bath), and plasma (ion) nitriding. In a survey of 800 commercial shops in the United States and Canada, 30% offered nitriding services, of which (Ref 4):

- 21% offered gas nitriding
- 7% offered salt bath nitriding
- 6% offered fluidized-bed nitriding
- 5% offered plasma nitriding

The advantages and disadvantages of these techniques are similar to those of carburizing. However, times for gas nitriding can be quite long, that is, from 10 to 130 h depending on the application, and the case depths are relatively shallow, usually less than 0.5 mm (0.020 in.). Plasma nitriding allows faster nitriding times, and the quickly attained surface saturation of the plasma process results in faster diffusion. Plasma nitriding can also clean the surface by sputtering.

Other Diffusion Methods

Surface hardening with carbon and nitrogen offers processing temperatures between those of carburizing and nitriding. In general, there are three techniques that use carbon and nitrogen for surface hardening:

- Carbonitriding
- Austenitic nitrocarburizing
- Ferritic nitrocarburizing

The latter two methods rely on the formation of a thin white layer of ε carbonitride while the first method, carbonitriding, uses nitrogen as a hardening agent in carburized austenite. Although all three methods have higher processing temperatures than does nitriding (Table 2), they have the advantage of being suitable for plain carbon steels.

Carbonitriding is a surface-hardening heat treatment that introduces carbon and nitrogen in the austenite of steel. This treatment is similar to carburizing in that the austenite composition is changed and high surface hardness is produced by quenching to form martensite. However, because nitrogen enhances hardenability, carbonitriding makes possible the use of low-carbon steel to achieve surface hardness equivalent to that of high-alloy carburized steel without the need for

drastic quenching, resulting in less distortion and reducing the danger of cracking the work. To some extent, hardening is also dependent on nitride formation.

Although the process of carbonitriding can be performed with gas atmospheres or salt baths, the term carbonitriding often refers solely to treatment in a gas atmosphere (see the article "Carbonitriding" in this Volume). Basically, carbonitriding in a salt bath is the same as cyanide bath hardening. In both processes, nitrogen enhances hardenability and case hardness but inhibits the diffusion of carbon.

Like carbon, nitrogen is an austenite stabilizer. Therefore, considerable austenite may be retained after quenching a carburized part. If the retained austenite content is so high that it reduces hardness and wear resistance, it may be controlled by reducing the ammonia content of the carbonitriding gas either throughout the cycle or during the latter portion of the cycle. Another consequence of excessive nitrogen content in the carbonitrided case is porosity (Ref 10).

Austenitic Nitrocarburizing. Although the lower carbonitriding temperatures (700 to 760 °C, or 1300 to 1400 °F) are not used because of the explosion hazard and the brittle structures formed, a lower-temperature variant of carbonitriding has been developed. This technique, which is sometimes referred to as austenitic nitrocarburizing, is optimally applied in the temperature range of 675 to 775 °C (1250 to 1425 °F). Unlike carbonitriding, the hardening effect in nitrocarburizing relies primarily on the formation of ε carbonitrides. This may eliminate the need for quenching.

Ferritic nitrocarburizing involves the diffusion of carbon and nitrogen into the ferrite phase and the formation of a thin white layer of ε carbonitrides. The diffusion of nitrogen into the substrate is necessary for fatigue resistance. The case depths are thin (Table 2), but the ε carbonitrides formed in nitrocarburizing have a reduced tendency to spall, compared to the white layer formed during conventional nitriding. Further information on this process is given in the article "Gaseous and Plasma Nitrocarburizing" in this Volume.

Specialized Diffusion Methods. In addition to carburizing, nitriding, and carbonitriding, there are a number of specialized diffusion methods that induce chemical modification with elements such as aluminum, boron, chromium, silicon, titanium, and vanadium. Of these, boron and titanium treatments offer high levels of hardness (Fig. 2), while aluminum, chromium, and silicon treatments are primarily used for corrosion resistance. Another specialized diffusion method is the Toyota diffusion process (see the article "Thermoreactive Deposition/Diffusion Process" in this Volume). Specialized methods such as chromizing and vanadizing are discussed in the Selected References section at the end of this article.

Boriding involves the diffusion of boron into metal surfaces for the enhancement of hardness and wear resistance. Boriding is most often applied to tool steels that have already been hardened by heat treatment. Boriding techniques include metallizing, chemical vapor deposition, and pack cementation. For additional information, see the article "Boriding (Boronizing)" in this Volume.

Titanium Carbide. With process temperatures in the range of 900 to 1010 °C (1650 to 1850 °F), titanium and carbon will diffuse to form a diffused case of titanium carbide during chemical vapor deposition. This treatment is most commonly applied to tool steels and hardenable stainless steels. Because the treatment is performed above the austenitizing temperatures of these steels, the core must be hardened by quenching.

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Selective Surface Hardening

The selective hardening of steel surfaces is typically achieved by localized heating and quenching, without any chemical modification of the surface. However, selective surface hardening can also include chemical modification by such techniques as ion implantation and selective carburization.

The more common methods currently used to harden the surface of steels include flame and induction hardening. However, each of these methods has shortcomings that can prevent its use in some applications. For example, the disadvantages of flame hardening include the possibility of part distortion, while induction hardening requires very small part-to-coil distances (especially when using high frequencies), which must be precisely maintained.

Flame hardening consists of austenitizing the surface of a steel by heating with an oxyacetylene or oxyhydrogen torch and immediately quenching with water. The result is a hard surface layer of martensite over a softer interior core with a ferrite-pearlite structure. There is no change in composition, and therefore the flame-hardened steel must have adequate carbon content for the desired surface hardness. The rate of heating and the conduction of heat into the interior appear to be more important in establishing case depth than the use of a steel of high hardenability.

Flame-heating equipment may be a single torch with a specially designed head or an elaborate apparatus that automatically indexes, heats, and quenches parts. Large parts such as gears and machine tool ways, with sizes or shapes that would make furnace heat treatment impractical, are easily flame hardened. With improvements in gas-mixing equipment, infrared temperature measurement and control, and burner design, flame hardening has been accepted as a reliable heat-treating process that is adaptable to general or localized surface hardening for small and medium-to-high production requirements. Further information on this process is given in the article "Flame Hardening" in this Volume.

Induction heating is an extremely versatile heating method that can perform uniform surface hardening, localized surface hardening, through hardening, and tempering of hardened pieces. Heating is accomplished by placing a steel part in the magnetic field generated by high-frequency alternating current passing through an inductor, usually a water-cooled copper coil. The depth of heating produced by induction is related to the frequency of the alternating current: The higher the frequency, the thinner or more shallow the heating. Therefore, deeper case depths and even through hardening are produced by using lower frequencies. The electrical considerations involve the phenomena of hysteresis and eddy currents. Because secondary and radiant heat are eliminated, the process is suited for production line areas. Further information on this technique is given in the article "Induction Heat Treating of Steel" in this Volume.

Laser surface heat treatment is widely used to harden localized areas of steel and cast iron machine components. The heat generated by the absorption of the laser light is controlled to prevent melting and is therefore used in the selective austenitization of local surface regions, which transform to martensite as a result of rapid cooling (self-quenching) by the conduction of heat into the bulk of the workpiece. This process is sometimes referred to as laser transformation hardening to differentiate it from laser surface melting phenomena (Fig. 8). There is no chemistry change produced by laser transformation hardening, and the process, like induction and flame hardening, provides an effective technique to harden ferrous materials selectively. Other methods of laser surface treatments include surface melting and surface alloying. Laser surface melting results in a refinement of the structure due to the rapid quenching from the melt. In surface alloying, alloying elements are added to the melt pool to change the composition of the surface. The novel structures produced by laser surface melting and alloying can exhibit improved electrochemical behavior.

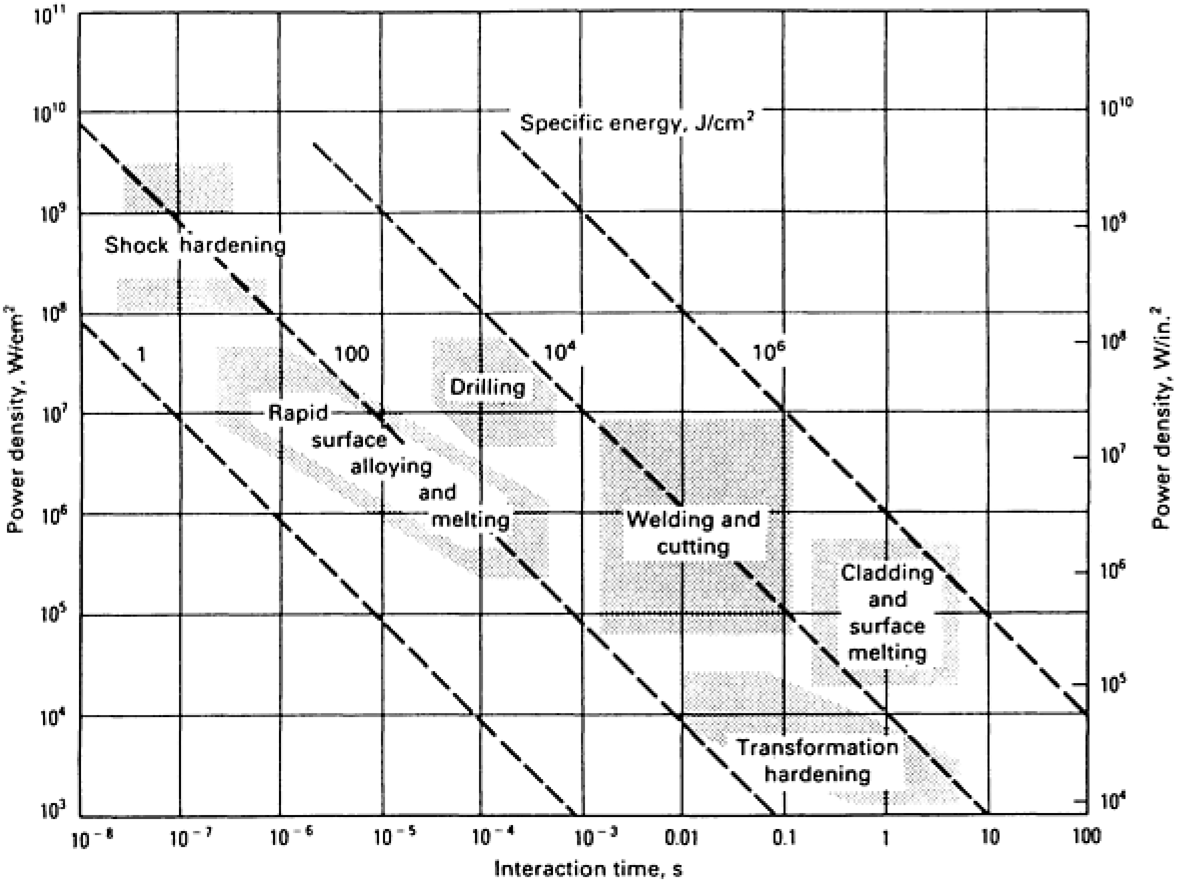

Fig. 8 Interaction times and power densities necessary for various laser surface modification processes

Laser transformation hardening produces thin surface zones that are heated and cooled very rapidly, resulting in very fine martensitic microstructures, even in steels with relatively low hardenability. High hardness and good wear resistance with less distortion result from this process. The laser method differs from induction and flame heating in that the laser can be located at some distance from the workpieces. Also, the laser light is reflected by mirrors to the focusing lens, which control the width of the heated spot or track.

Molian (Reference 11) has tabulated the characteristics of 50 applications of laser transformation hardening. The materials hardened include plain carbon steels (1040, 1050, 1070), alloy steels (4340, 52100), tool steels, and cast irons (gray, malleable, ductile). Because the absorption of laser radiation in cold metals is low, laser surface hardening often requires energy-absorbing coatings on surfaces. Reference 11 lists some energy-absorbing coatings.

Typical case depths for steels are 250 to 750 μm (0.01 to 0.03 in.) and for cast irons are about 1000 μm (0.04 in.). The flexibility of laser delivery systems and the low distortion and high surface hardness obtained have made lasers very effective in the selective hardening of wear and fatigue-prone areas on irregularly shaped machine components such as camshafts and crankshafts. Further information is contained in the article "Laser Surface Hardening" in this Volume.

Electron beam (EB) hardening, like laser treatment, is used to harden the surfaces of steels. The EB heat-treating process uses a concentrated beam of high-velocity electrons as an energy source to heat selected surface areas of ferrous parts. Electrons are accelerated and are formed into a directed beam by an electron beam gun. After exiting the gun, the beam passes through a focus coil, which precisely controls beam density levels (spot size) at the workpiece surface and then passes through a deflection coil. To produce an electron beam, a high vacuum of 10^{-5} torr (1.3×10^{-3} Pa) is needed in the region where the electrons are emitted and accelerated. This vacuum environment protects the emitter from oxidizing and avoids scattering of the electrons while they are still traveling at a relatively low velocity.

Like laser beam hardening, the EB process eliminates the need for quenchants but requires a sufficient workpiece mass to permit self-quenching. A mass of up to eight times that of the volume to be EB hardened is required around and beneath

the heated surfaces. Electron beam hardening does not require energy-absorbing coatings, as does laser beam hardening. Processing considerations and property changes associated with EB hardening are covered in Ref 12 and in the article "Electron Beam Surface Hardening" in this Volume.

Ion implantation is a surface modification process in which ions with very high energy are driven into a substrate. Ions of almost any atom species can be implanted, but nitrogen is widely used to improve corrosion resistance and the tribological properties of steels and other alloys. Although the nitrogen content of alloy surfaces is increased by both nitrogen ion implantation and plasma nitriding, major differences exist between the two processes and the surface modifications they create. The major difference is that ion implantation can be performed at room temperature.

Ion implantation machines accelerate ions, generated by specially designed sources, at very high energies (from 10 to 500 keV). In contrast, the energy of ions and atoms in plasma nitriding is much lower (<1 keV). Ion implantation is carried out with the substrate at about room temperature, thereby minimizing the diffusion-controlled formation of precipitates and coarsening of the subsurface microstructure. Because the temperature of application is low and the process is carried out in accelerators with very good vacuums ($\geq 10^{-5}$ torr, or 1.3×10^{-3} Pa), clean surfaces are ensured and undesirable surface chemical reactions such as oxidation are lessened. Ion implantation is a line-of-sight process; that is, only relatively small areas directly exposed to the ion beam are implanted. For the coverage of areas larger than the beam, either the specimen must be translated or the ion beam must be rastered over the specimen surface.

Because of the virtual absence of diffusion-controlled case formation during ion implantation, case depths are shallow (generally <0.25 μm). Very high strengths or hardnesses of the nitrogen-implanted surface layers compensate for the shallow case depths of ion implantation. Ion implantation is a complex, nonequilibrium process that creates significant lattice damage in the form of vacancies and interstitial point defects. Concentrations of implanted species much higher than equilibrium solubility limits may be introduced. In fact, the incorporation of high densities of atoms of significantly different size than those of the substrate lattice may produce amorphous structures or metastable phases (Ref 13).

The properties of ion-implanted surfaces and shallow case depths make ion implantation suitable for very special applications. Because the surface of the part itself is modified, the adhesion problems sometimes encountered with coated layers of high hardness do not arise. Also, because ion implantation is usually accomplished with very little heating, dimensional stability is excellent. Examples of applications of ion implantation include the surface hardening of razor blades (Ref 5) and knives (Ref 13), a variety of tool steel applications (Ref 14), and the implantation of 52100 and 440C bearings with titanium and/or nitrogen to improve rolling-contact fatigue resistance (Ref 15, 16, 17). In the latter applications, titanium was found to reduce the coefficient of friction, and nitrogen was found to raise hardness by intermetallic compound formation. Additional information on ion implantation is given in Ref 18 and Volume 13 of *ASM Handbook*, formerly 9th Edition *Metals Handbook.*

Selective Carburizing. If it is necessary to prevent carburization on certain areas of a part, stopoff compounds or copper plating may be used. Preventing carburization requires attention to cleanliness and handling to achieve the desired stopoff. Copper plate thicknesses of a minimum of 0.03 mm (0.001 in.) are required. Stopoff compounds are proprietary, and instructions should be closely followed because it is difficult to achieve 100% stopoff. Carburization prevention may be necessary on areas to be machined further after heat treating or to prevent a thin area from being carburized all the way through its section, thereby becoming brittle (Ref 3).

Surface hardening with arc lamps is used in applications that involve surface remelting or surface hardening by solid-phase recrystallization. Examples include the surface remelting of cast iron and the large-area remelting of titanium in the presence of nitrogen or methane to produce titanium carbides in the surface layer. In the surface remelting of cast irons, lasers are also used (see the article "Heat Treating of Ductile Irons" in this Volume). Another area in which arc lamps are finding application is in the selective hardening of the edges on agricultural sweeps and tilling equipment blades.

Surface treating using white light from a high-power arc lamp offers several advantages over traditional methods and the beam techniques. For example, arc lamp treatment can achieve higher surface radiation intensities than can flame heating, making the procedure faster and less likely to cause distortion. Compared with induction hardening, arc lamp treatment allows much larger distances between the part and heat source, providing more flexibility in treating irregularly shaped surfaces. Unlike the EB treatment, this method does not require the use of a vacuum chamber, and an arc lamp can deliver greater power to the part surface than can a laser beam.

However, with the arc lamp method, significant power loss is encountered if arc radiation is concentrated onto surface areas smaller than the arc itself. Therefore, the illuminated spot on the sample surface should always be larger than the arc. This necessitates extremely high arc power to achieve the surface intensities needed for thermal treatment. Such high power is achieved in a very small space with specially designed arc lamps.

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Process Selection

The benefits of the most common methods of surface hardening are compared in Table 3. Flame and induction hardening are generally limited to certain families of steels such as medium-carbon steels, medium-carbon alloy steels, some cast irons, and the lower-alloy tool steels. There is no size limit to parts that can be flame hardened because only the portion of the part to be hardened need be heated. With induction hardening, the part or area to be hardened usually must fit within an inductor coil. Flame hardening is generally used for very heavy cases (in the range of about ~1.2 to 6 mm, or 0.6 to 0.25 in.); thin case depths are difficult to control because of the nature of the heating process. Diffusion methods are compared in Table 2.

Table 3 Relative benefits of five common surface-hardening processes

Process	Benefits
Carburizing	Hard, highly wear-resistant surface (medium case depths); excellent capacity for contact load; good bending fatigue strength; good resistance to seizure; excellent freedom from quench cracking; low-to-medium-cost steels required; high capital investment required
Carbonitriding	Hard, highly wear-resistant surface (shallow case depths); fair capacity for contact load; good bending fatigue strength; good resistance to seizure; good dimensional control possible; excellent freedom from quench cracking; low-

	cost steels usually satisfactory; medium capital investment required
Nitriding	Hard, highly wear-resistant surface (shallow case depths); fair capacity for contact load; good bending fatigue strength; excellent resistance to seizure; excellent dimensional control possible; good freedom from quench cracking (during pretreatment); medium-to-high-cost steels required; medium capital investment required
Induction hardening	Hard, highly wear-resistant surface (deep case depths); good capacity for contact load; good bending fatigue strength; fair resistance to seizure; fair dimensional control possible; fair freedom from quench cracking; low-cost steels usually satisfactory; medium capital investment required
Flame hardening	Hard, highly wear-resistant surface (deep case depths); good capacity for contact load; good bending fatigue strength; fair resistance to seizure; fair dimensional control possible; fair freedom from quench cracking; low-cost steels usually satisfactory; low capital investment required

Transformation hardening introduces compressive residual stresses, which are beneficial for fatigue strength. In selective hardening, however, some residual tensile stress will exist in the region where the hardened zone meets the unhardened zone. Consequently, selective hardening by methods such as flame or induction heating should be applied away from geometric stress concentrations. Both nitriding and carburizing provide good resistance to surface fatigue and are widely used for gears and cams. In terms of bending fatigue resistance, the ideal case depth appears to be reached where the failure initiation point is transferred from the core to the surface (Ref 19). However, specification of required case depth is a complex subject, which is briefly discussed in Ref 19 for carburized steels.

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Flame Hardening of Steels

Revised by Thomas Ruglic, Hinderliter Heat Treating, Inc.

Introduction

FLAME HARDENING is a heat-treating process in which a thin surface shell of a steel part is heated rapidly to a temperature above the critical point of the steel. After the grain structure of the shell has become austenitic (austenitized), the part is quickly quenched, transforming the austenite to martensite while leaving the core of the part in its original state. In contrast, slow cooling causes transformation, as the temperature passes through the corresponding ranges, to pearlite, bainite, and martensite, with the final structure being a combination of the three. The result is a relatively soft and ductile steel. To achieve hardness, therefore, the steel must be cooled rapidly so that it bypasses the first two transformation phases and transforms directly from austenite to martensite.

Flame hardening employs direct impingement of a high-temperature flame or high-velocity combustion product gases. The part is then cooled at a rate that will produce the desired levels of hardness and other properties. The high-temperature flame is obtained by combustion of a mixture of fuel gas with oxygen or air; flame heads are used for burning the mixture. Depths of hardening from about 0.8 to 6.4 mm ($\frac{1}{32}$ to $\frac{1}{4}$ in.) or more can be obtained, depending on the fuels used, the design of the flame head, the duration of heating, the hardenability of the work material, and the quenching medium and method of quenching used. The process can be used for the through hardening of work 75 mm (3 in.) or less in cross section, depending on the hardenability of the steel.

Hardening by flame differs from true case hardening because the hardenability necessary to attain high levels of hardness is already contained in the steel, and hardening is obtained by localized heating. Although flame hardening is mainly used to develop high levels of hardness for wear resistance, the process also improves bending and torsional strength and fatigue life. One of the major advantages of flame hardening is the ability to satisfy stringent engineering requirements with carbon steels.

Scope and Application

Flame hardening is applied to a wide diversity of workpieces and ferrous materials for one or more reasons. This process is used because:

- Parts are so large that conventional furnace heating and quenching are impracticable or uneconomical. Typical examples include large gears, machineways, dies, and rolls
- Only a small segment, section, or area of a part requires heat treatment, or because heat treating all over would be detrimental to the function of the part. Typical examples include the ends of valve stems and pushrods and the wearing surfaces of cams and levers
- The dimensional accuracy of a part is impracticable or difficult to attain or control by furnace heating and quenching. A typical example is a large gear of complex design for which flame hardening of the teeth would not disturb the dimensions of the gear
- The use of flame hardening permits a part to be made from a less costly material, thereby effecting an overall cost saving in comparison with other technically acceptable methods. The process gives inexpensive steels the wear properties of alloyed steels, and parts can be hardened without scaling or decarburization, thereby eliminating costly cleaning operations. For example, a large steel part might be made at a lower cost if produced from a flame-hardened plain carbon steel rather than from a carburized low-carbon alloy steel

For a detailed discussion of materials suitable for flame hardening and for a comparison of flame hardening with other methods used to attain similar results, see the sections "Selection of Process" and "Selection of Material" near the end of this article.

Methods of Flame Hardening

The versatility of flame-hardening equipment and the wide range of heating conditions obtainable with gas burners often permit flame hardening to be done by a variety of methods, of which the principal ones are:

- Spot, or stationary
- Progressive
- Spinning
- Combination progressive-spinning

The selection of the appropriate method depends on the shape, size, and composition of the workpiece; the area to be hardened; the depth of case required; and the number of pieces to be hardened. In many instances, more than one method will provide the desired result; the choice will then depend on comparative costs.

The spot (stationary) method, shown in Fig. 1(a), consists of locally heating selected areas with a suitable flame head and subsequently quenching. The heating head may be of either single-orifice or multiple-orifice design, depending on the extent of the area to be hardened. The heat input must be balanced to obtain a uniform temperature over the entire selected area. After being heated, the parts are usually immersion quenched; however, in some mechanized operations, a spray quench may be used.

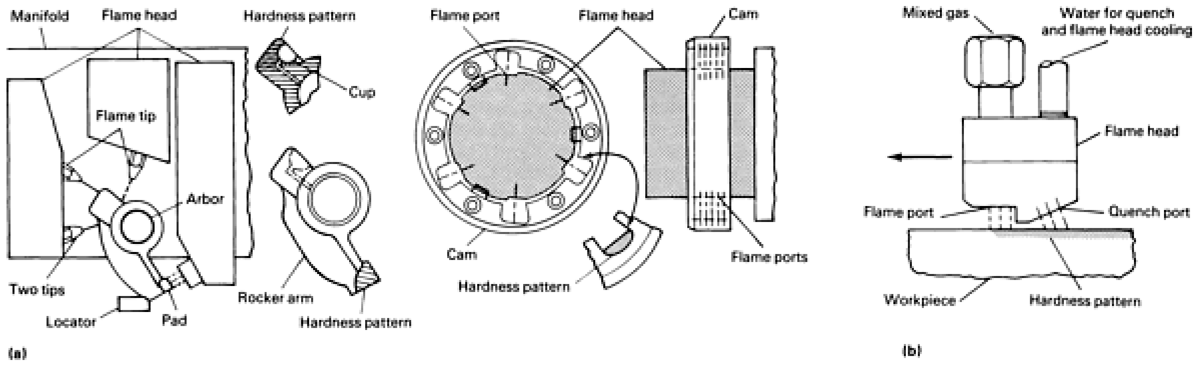

Fig. 1 Spot (stationary) and progressive methods of flame hardening. (a) Spot (stationary) method of flame hardening a rocker arm and the internal lobes of a cam; quench not shown. (b) Progressive hardening method

Basically, the spot method requires no elaborate equipment, except, perhaps, fixtures and timing devices to ensure the uniform processing of each piece. However, the operation may be automated by indexing the heated parts into either a spray quench or a suitable quench bath.

The progressive method, shown in Fig. 1(b), is used to harden large areas that are beyond the scope of the spot method. The size and shape of the workpiece, as well as the volume of oxygen and fuel gas required to heat the specified area, are factors in the selection of this method. In progressive hardening, the flame head is usually of the multiple-orifice type, and quenching facilities may be either integrated with the flame head or separate from it. The flame head progressively heats a narrow band that is subsequently quenched as the head and quench traverse the workpiece.

The equipment needed for flame hardening by the progressive method consists of one or more flame heads and a quenching means mounted on a movable carriage that runs on a track at a regulated speed (flame-cutting machines are adaptable to this type of flame hardening). Workpieces mounted on a turntable or in a lathe can be hardened readily by the progressive method; either the flame head or the workpiece may move. There is no practical limit on the length of parts that can be hardened by this method, because it is easy to lengthen the track over which the flame head travels. Single passes as wide as 1.5 m (60 in.) can be made; wider areas must be hardened in more than one pass.

When more than one pass is required to cover a flat surface, or when cylindrical surfaces are hardened progressively, such surfaces will exhibit soft bands because of overlapping or underlapping of the heated zones. These soft bands can be minimized, however, by closely controlling the extent of the overlapping. Wherever overlapping occurs, the possibility of severe thermal upset and cracking should be anticipated. Tests should be conducted to determine whether overlapping will cause cracking or other harmful effects. Simple curved surfaces may be hardened progressively by means of contoured flame heads, and some irregular surfaces may be traversed by the use of tracer template methods.

The rate of travel of the flame head over the surface is mainly governed by the heating capacity of the head, the depth of case required, the composition and shape of the work, and the type of quench used. Speeds ranging from 0.8 to 5 mm/s (2 to 12 in./min) are typical with oxyacetylene heating heads. Ordinarily, water at ambient temperatures is used as a quenchant, although air is sometimes used when a less-severe quench is indicated; under special conditions (particularly for quenching alloy steels), warm or hot water or a polymer-base synthetic quenchant may be employed.

The spinning method (Fig. 2) is applied to round or semiround parts such as wheels, cams, or gears. In its simplest form, the method uses a mechanism for rotating or spinning the workpiece, in either a horizontal or a vertical plane, while the surface is being heated by the flame head. One or more water-cooled heating heads equal in width to the surface to be heated are employed. The speed of rotation is relatively unimportant, provided uniform heating is obtained. After the surface has been heated to the desired temperature, the flame is extinguished or withdrawn and the work is quenched by immersion or spray or a combination of both.

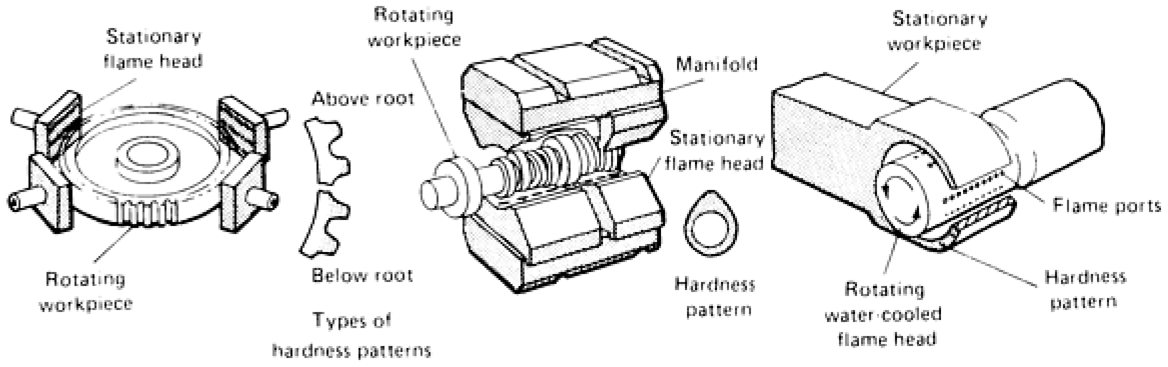

Fig. 2 Spinning methods of flame hardening. In methods shown at left and at center, the part rotates. In method at right, the flame head rotates. Quench not shown

The spinning method is particularly adaptable to extensive mechanization and automation. This makes it possible, for example, for all the cams on a camshaft to be hardened at the same time.

Today, fully automatic flame-heating equipment is available that can treat round components up to 1.5 m (60 in.) in diameter and up to 2 Mg (2.2 tons) in weight. Much of it has been designed to treat gear wheels of all types.

Commercial machines have been built that can provide automatic control of timing, temperature, and quenching, as well as accurate control of gas flow, so that close metallurgical specifications can be met consistently. Frequently, when production is sufficient, the spinning method can be set up so that either parts are loaded manually and unloaded automatically or they are loaded and unloaded automatically.

This method has been extended to components of irregular cross section and mass distribution. Typical are large drive wheels for tracked vehicles, cams and camshafts for marine diesel engines, and crane traveling wheels. Speed, deep hardness penetration, localized hardness zone, and uniformity of hardness pattern are the main advantages.

In one technique, a rotating flame head is used for internal spin hardening of odd-shape parts that would present handling problems if the parts themselves were rotated. Each part is positioned by a simple handling device, and the flame head rotates inside the part.

In contrast to the progressive method, in which acetylene is usually used (because of its high flame temperature and rapid heating rates), satisfactory results can be obtained in spin hardening with natural gas, propane, or manufactured gas. The choice of gas depends on the shape, size, and composition of the workpiece and on the depth of case required, as well as on the relative cost and availability of each gas.

A wide choice of quenchants also is possible in the spin hardening method. Because the flame is extinguished or withdrawn before the part is quenched, any appropriate quenchant may be used for immersion quenching. In spray quenching, the quenchant is usually water, a water-based liquid such as soluble oil, or a simulated oil in the form of a polymer-base quenchant; air also has been used.

The combination progressive-spinning method (Fig. 3), as the name implies, combines the progressive and spinning methods for hardening long parts such as shafts and rolls. The workpiece is rotated as in the spinning method; but, in addition, the heating heads traverse the roll or shaft from one end to the other. Only a narrow circumferential band is heated progressively as the flame head moves from one end of the work to the other. The quench follows immediately behind the heating head, either as an integral part of the head or as a separate quench ring.

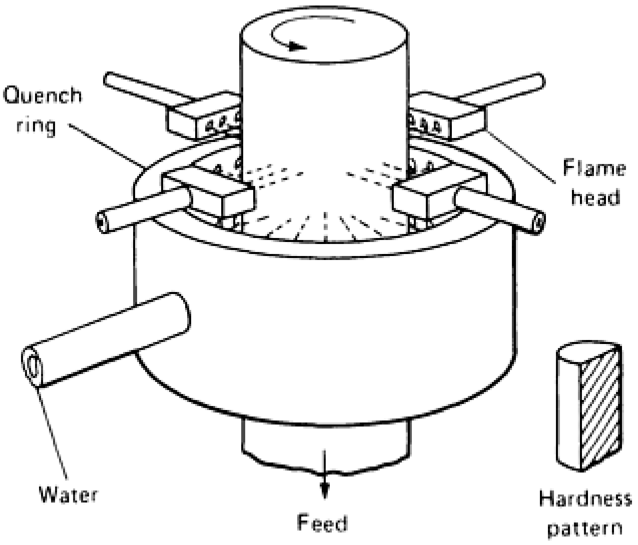

Fig. 3 Combination progressive-spinning flame hardening

This method provides a means of hardening large surface areas with relatively low gas flows. Progressive-spinning units designed to handle a broad range of diameters and lengths are available commercially.

Fuel Gases

Several different fuel gases are used in flame hardening. In selecting a fuel gas for a given application, the required rate of heating and the cost of the gas must be considered, along with the initial cost of equipment and maintenance costs.

Flame hardening does not alter the composition of the base metal if done properly. Carburizing, neutral, and oxidizing flames can be used. Oxidizing flames have high oxygen ratios and can be detrimental because they produce extremely hot temperatures that can cause decarburization and overheating. A carburizing flame can prevent some decarburization but can also introduce unwanted carbon into the surface. For best results, neutral or slightly carburizing flames should be used (Ref 1).

A comparison of the heating rates of fuel gases can be made when certain fundamental properties of usable mixtures with oxygen are known. A parameter that correlates well with actual heating speed is combustion intensity, or specific flame output. This is the product of the normal velocity of burning multiplied by the net heating value of the mixture of oxygen and fuel gas. A knowledge of these two properties often permits the selection of the most suitable fuel gas for a specific hardening speed and depth of case. The fuels of greatest commercial interest are ranked by combustion intensity (at metallurgically suitable ratios of mixture with oxygen) in the following order: acetylene, MAPP (methylacetylene propadiene), propane, methane. Values of normal burning velocity and the heating values of metallurgically suitable mixtures are listed in Table 1.

Table 1 Fuel gases used for flame hardening

Gas	Heating value		Flame temperature				Usual ratio of oxygen to fuel gas	Heating value of oxy-fuel gas mixture		Normal velocity of burning		Combustion intensity[a]		Usual ratio of air to fuel gas
			With oxygen		With air									
	MJ/m^3	Btu/ft^3	°C	°F	°C	°F		MJ/m^3	Btu/ft^3	mm/s	in./s	mm/s × MJ/m^3	in./s × Btu/ft^3	

Acetylene	53.4	1433	3105	5620	2325	4215	1.0	26.7	716	535	21	14,284	15,036	12
City gas	11.2-33.5	300-900	2540	4600	1985	3605	(b)	(b)	(b)	(b)	(b)	(b)	(b)	(b)
Natural gas (methane)	37.3	1000	2705	4900	1875	3405	1.75	13.6	364	280	11	3,808	4,004	9.0
Propane	93.9	2520	2635	4775	1925	3495	4.0	18.8	504	305	12	5,734	6,048	25.0
MAPP	90	2406	2927	5301	1760	3200	3.5	20.0	535	381	15	7,620	8,025	22

(a) Product of normal velocity of burning multiplied by heating value of oxy-fuel gas mixture.

(b) Varies with heating value and composition

The time required for heat penetration is another good criterion for judging the heating qualities of a fuel provided that all other variables remain constant. Figure 4 shows comparative heating times for stabilized MAPP, acetylene, and propane, using an efficient coupling distance for each fuel. These curves show that a greater depth of hardness can be obtained with MAPP in a shorter length of time (Ref 2).

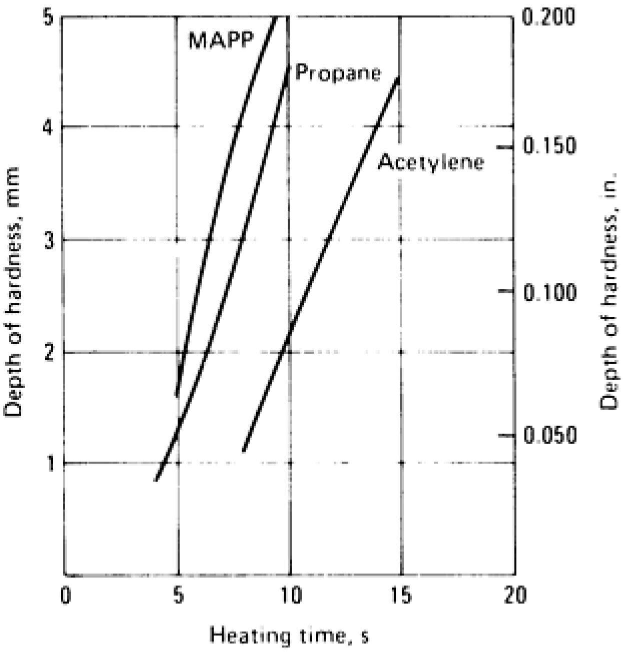

Fig. 4 Comparison of heating times for MAPP, acetylene, and propane. Flame velocity, 170 m/s (550 ft/s); port size, No. 69 drill (0.74 mm, or 0.0292 in.); coupling distance, 9.5 mm ($\frac{3}{8}$ in.); material, 1036 steel. Oxygen-to-fuel ratios: MAPP, 5.0; acetylene, 1.33; propane, 4.5

The ratio of oxygen to fuel is very important in obtaining maximum heating efficiency from the fuel. However, oxygen-to-fuel ratios should not be confused with oxygen and fuel consumption rates, which vary with flame velocity, port size, and heating time. Stoichiometrically, acetylene requires $2\frac{1}{2}$ mols of oxygen per mol of gas for complete combustion, MAPP requires 4 mols, and propane requires 5 mols. With acetylene, however, a range of only 1 to 1.5 volumes of oxygen is provided directly, with the remainder being drawn from the surrounding atmosphere. Neither MAPP nor propane has sufficient heat for flame hardening unless more oxygen is supplied, normally at a rate of four parts of oxygen per part of fuel. MAPP burns over a rather wide range of oxygen-to-fuel ratios, however, and thus permits a wider range of heat output while still providing high heat generation when necessary. The use of MAPP increases oxygen consumption, and fuel is more expensive than oxygen.

Bulk systems of supply for oxygen and fuel gases greatly reduce their cost, but of greater importance is the elimination of cylinder handling and of the residual losses usually attendant upon the use of gases in cylinders. Bulk systems also provide a more nearly constant supply of gas at uniform pressure. A disadvantage of acetylene is that it cannot be stored in bulk, thereby requiring manifolds of cylinders.

Depth of Heating. Shallow hardness patterns (less than 3.2 mm, or 0.125 in., deep) can be attained only with oxy-gas fuels. The high-temperature flames obtained with oxy-gas fuels provide the fast heat transfer necessary for effective localization of the heat pattern. Deeper hardness patterns permit the use of either oxy-gas fuels or air-gas fuels. Oxy-gas fuels will localize the heat, but care is required in their application to avoid overheating the surface during the development of the deeper-seated heat. Air-gas fuels, with their slower rates of heat transfer (lower flame temperatures), minimize or eliminate surface overheating but generally extend the heat pattern beyond the desired hardness pattern. For this reason, air-gas flame hardening is generally limited to steels of shallow hardenability. In this manner, the hardness pattern is controlled by the quench rather than by the heating. The deeper-seated heat produced by air-gas flames may preclude the use of air-gas mixtures because excessive distortion may occur. In consideration of these factors, the use of air-gas heating will depend primarily on the shape of the part insofar as the configuration favors heat localization and a lower rate of heat transfer.

Gas Consumption, Time, and Speeds. Gas consumption in flame hardening varies with the thickness of the case to be obtained; increasing or decreasing the depth of hardening increases or decreases the amount of gas used. Massive parts increase gas consumption because of their greater internal cooling effect. In order to take advantage of the maximum flame temperature from the oxy-fuel gas flame, the distance from the end of the inner cone of the flame to the work should be 1.6 mm ($\frac{1}{16}$ in.).

The speed of travel of the flame head over the work in the progressive method, as well as the time of heating in the spot and spinning methods, will vary with the thickness of the case desired and the capacity of the flame head. The proximity of the quench spray to the last row of flames will affect the speed somewhat in the progressive method. Progressive and progressive-spinning speeds usually vary between 0.8 and 5 mm/s (2 and 12 in./min) for most applications, although very thin parts may require speeds of 42 mm/s (100 in./min) or more to avoid overheating or burning. Because of the intense heat involved, the necessity for accurate control of the rate of travel in the progressive and progressive-spinning methods cannot be overemphasized.

Time-temperature-depth relationships for various fuel gases used in the spot (stationary), spinning, and progressive methods of flame hardening are shown in Fig. 5. The family of curves for the spot method (Fig. 5a) was obtained analytically by considering the flow of heat in three dimensions away from a heated spot on the surface of a rocker arm pad. The calculations were based on heat sources of different strengths, which were varied on the basis of the combustion intensity of the gases considered (acetylene, propane, and natural gas). It is understood that the strength of the heat source will also be affected by such factors as size of tip, distance from tip to work, total gas flow, and ratio of oxygen to fuel gas; hence, these curves are intended to indicate trends in time-temperature-depth relationships rather than to provide operational values for particular applications.

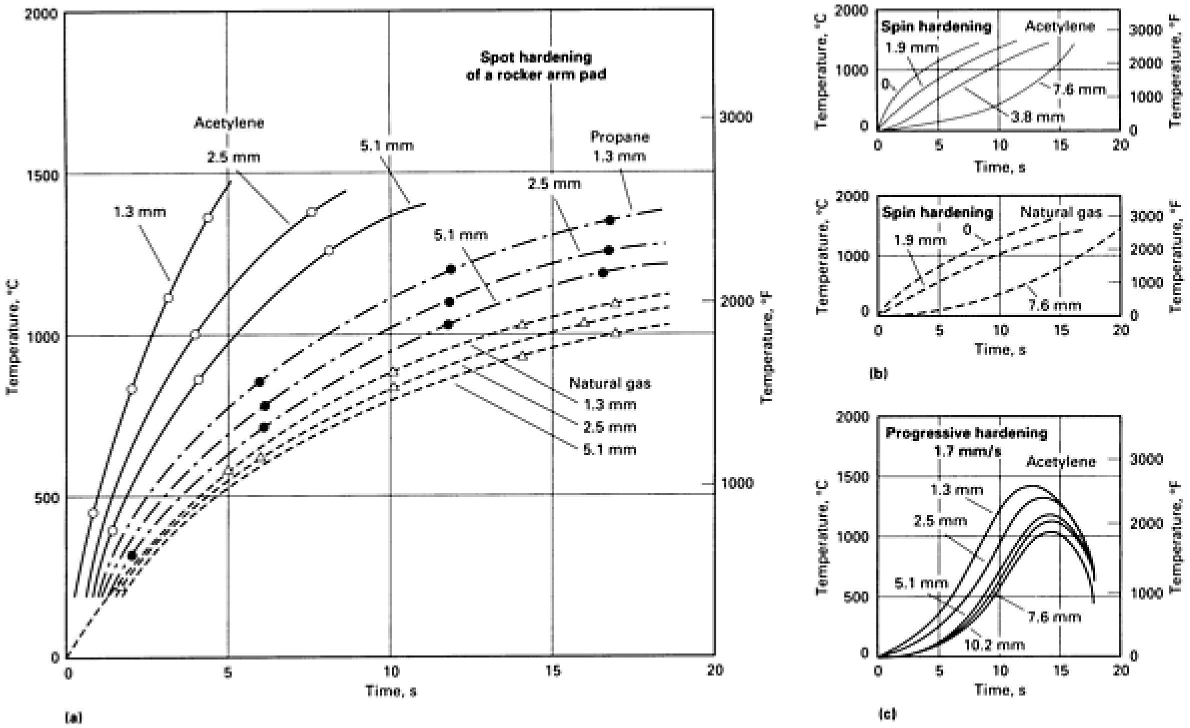

Fig. 5 Calculated time-temperature-depth relationships for spot (stationary), spinning, and progressive flame hardening. Depth of hardness given in millimeters

The curves for the time-temperature-depth relationships of fuel gases used in the spinning method, shown in Fig. 5(b), were obtained analytically by considering the flow of heat into a cylindrical body from a heat source supplying heat uniformly over the outer cylindrical surface. It was assumed that the temperature at the axis would not be raised appreciably during surface heating and that, in spin hardening, the cylinder would be rotated rapidly enough to give the effect of substantially uniform surface heating. No temperature decrease at high values of time is indicated, because in this type of process the body is quenched immediately when the surface temperature reaches a predetermined value.

The curves for the progressive method (Fig. 5c) were also obtained analytically by considering heat flow into a body from a line source moving along a flat side of the body. The heat source strength and body configuration were chosen to be representative of progressive flame hardening. In this instance, the time variable can be correlated with travel speed if the width of the flame zone is known. For example, a flame zone 25 mm (1 in.) wide will pass over a point on the work surface in 15 s when the travel speed of the tip is 1.7 mm/s (4 in./min). This width of flame zone indicates the probability of a multirow tip, and if the heat source is as strong as assumed for computing the curves, will undoubtedly damage the work surface. Consequently, a higher travel speed would be used, for example, 2.5 mm/s (6 in./min), which would heat a point on the work for 10 s and result in hardening to a depth of about 2.5 mm (0.100 in.). The rapid decrease in temperature at large values of time is due to the mass quenching effect, which, in practice, would be augmented by the use of water spraying or other quenching means.

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Burners and Related Equipment

Burners are basic components of equipment for all methods of flame hardening. Burners vary in design, depending on whether they are fired by an oxy-fuel or an air-fuel gas mixture. Flame temperatures obtained by oxy-fuel gas combustion are 2540 °C (4600 °F) and higher. Heat transfer is by direct impingement of the flame on the surface of the workpiece. This is the reason oxy-gas burners are more commonly referred to as flame heads. Flame temperatures obtained by air-

fuel gas combustion are considerably lower (Table 1), and heat transfer is by impingement of high-velocity combustion product gases (no direct flame) or by radiation from an incandescent refractory surface.

There is no universal flame head, and no flame head is designed specifically for one particular gas. A well-designed flame head can be used with MAPP, acetylene, or propane, for example. Better flame head design usually results in an improved operation and lower gas consumption. Both acetylene and MAPP gas are somewhat reactive with copper-base alloys having more than 67% Cu. This concern is only a problem with piping systems, not torches or tips.

In general, a large number of small ports will produce a more efficient heat pattern than a few larger ports. Port spacing of 2.3 to 3.2 mm (0.090 to 0.125 in.) on centers is, in most cases, advisable. Counterboring permits higher flame velocities and is frequently advantageous or necessary when propane or MAPP is used. Because acetylene has a higher flame propagation rate, counterboring is usually unnecessary and is frequently undesirable. Counterboring reduces coupling distance and permits a stabilized flame at higher flame velocities. For effective operation, the ratio of counterbore area to throat area should be on the order of 2 to 1. Ratios as high as 4 to 1 may be used in some cases, however (Ref 2).

Oxy-Fuel Gas Flame Heads. Oxy-fuel gas combustion develops flame temperatures above those at which useful metals and refractory materials can survive. Accordingly, the flame head is designed to provide a flame pattern that avoids any direct heating of its parts.

Generally, the flame head consists of a tube or a shell with one or more orifices drilled into it. The number and arrangement of orifices depend on the required area of heat coverage. Flame heads for use with oxy-fuel gas are shown in Fig. 6.

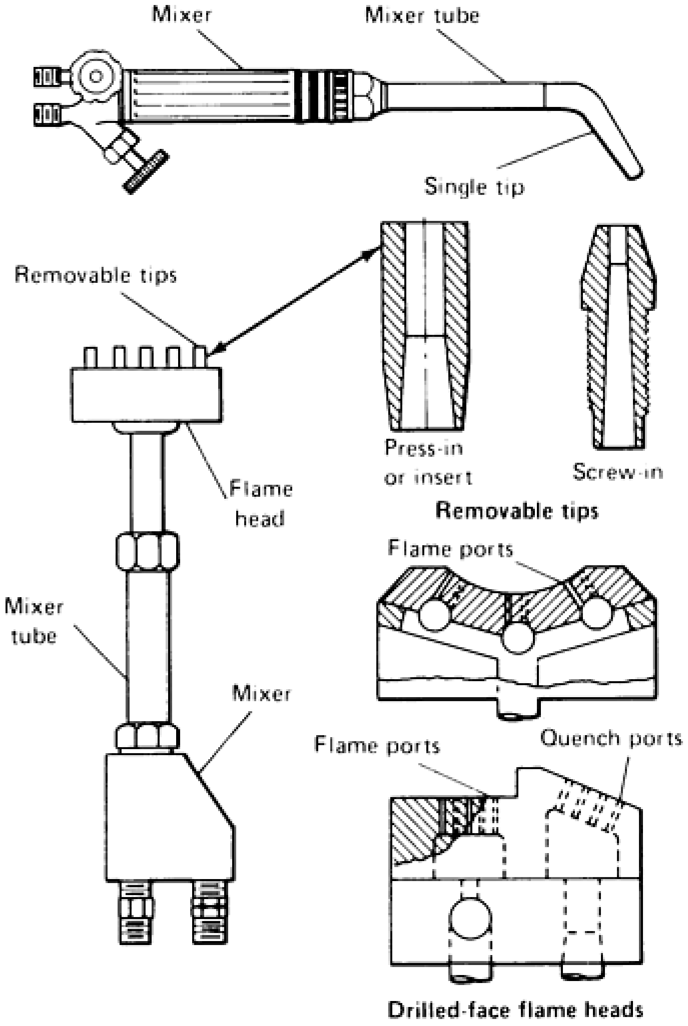

Fig. 6 Flame heads for use with oxy-fuel gas

The drilled-face flame head has a limited range of application and is usually designed to meet the requirements of one specific part to be flame hardened in appreciable quantity. For other applications, the flame head may be fitted with removable tips of the screw-in or insert type.

The screw-in type of removable tip shown in Fig. 6 is used widely enough that it is available in off-the-shelf commercial flame heads or is supplied as a standard item by manufacturers of flame-hardening equipment; it is also simple enough that it can be made to specification by plants applying the flame-hardening treatment.

The insert, or press-in, type of tip shown in Fig. 6 is smaller than the screw-in type and permits closer spacing of orifices, approaching that of a drilled flame head. Flame heads with removable and replaceable tips can be used over a wider range of applications by removing one or more tips and replacing them with plugs.

The heat output of the flame head is governed by the number and size of the orifices, other factors being equal. The individual orifices range from No. 73 to No. 51 drill size (0.6 to 1.7 mm, or 0.024 to 0.067 in., in diameter). Such small holes can readily become plugged, and when this occurs, the flame head will not function properly. Flame heads with removable tips have an advantage over fixed-tip heads in that oversize or out-of-round holes caused by mechanical or flame damage can be corrected without replacing the head.

Integral parts of the flame system are the mixer block and the mixer tube, which mix the component fuel gases and convey them through the orifices (Fig. 6). The capacities of mixer block and mixer tube must match the number and size of the orifices; if the mixer is too small, the flame will flash back, and if the mixer is too large, the flame head will not function efficiently.

To ensure identical velocity of mixed gases at all flame orifices, it is common practice to design a flame head with baffle orifices through which the gases must pass before they are burned at the flame orifices. Two rules apply to the design of baffle orifices: First, their total area must be 1.25 to 1.50 times the area of the flame orifices, and second, the number of baffle orifices within a single baffle should be one-fourth the total number of flame orifices.

Multiple-orifice flame heads are water cooled because otherwise the high temperatures developed at and around the flame head would cause early deterioration. On flame heads used for progressive hardening, the quench water cools the head. On multiple-orifice flame heads used in the spinning and progressive-spinning methods, the cooling water is circulated through chambers integrated into the head. Single-orifice flame heads (welding torches, for example) are generally not water cooled.

Typical flame-hardening installations that use oxy-fuel gas mixtures are shown in Fig. 7. The equipment in Fig. 7(a) was designed to handle the high production of similar parts. The equipment in Fig. 7(b) was designed to harden a variety of parts by changing the flame heads and work spindle.

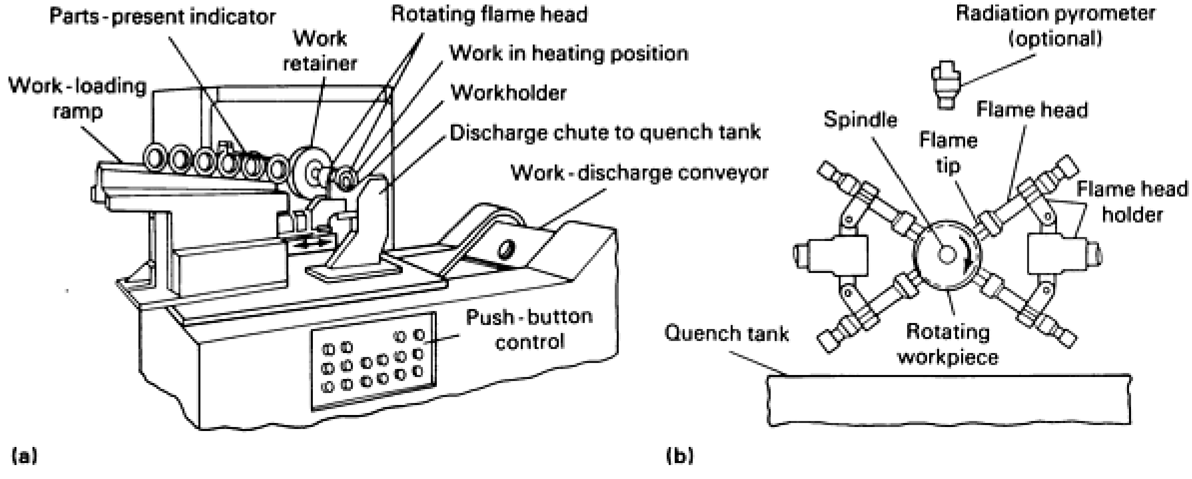

Fig. 7 Typical flame-hardening installations using oxy-fuel gas mixtures. (a) Installation for high production of similar parts: hardening the 54 mm ($2\frac{1}{8}$ in.) bores of hubs to a depth of about 3.2 mm ($\frac{1}{8}$ in.). Machine has a

standard, retractable spindle adapted with a rotary flame head. Spindle is driven by a variable-speed motor. Temperature of agitated quench is maintained by a water-cooled heat exchanger. (b) Installation for selective oxy-fuel gas heating of small production lots of gears, sprockets, and flanges within size limits of the equipment. A radiation pyrometer is used here to control heating cycle, but many operations use an electric timer instead. By changing work heads and spindles, equipment can be adapted to various parts.

New equipment configurations are being designed to handle specific problems. With conventional flame-hardening equipment, for example, it is difficult to obtain a zone of uniform temperature across the surface of the tooth gap in gears. The problem of obtaining uniform depth of hardness, not only from tooth to tooth but also across the entire face width, has been solved by the development of a two-chamber burner with individual control of energy input to each chamber. The system ensures uniform heating; particularly in the tooth root, and incorporates the separate control of nozzles for tooth-root and tooth-flank hardening (Ref 3).

With this system, complex components, too, can be processed by spin hardening. For example, both the straight and bevel gears of a double-pinion shaft can be hardened simultaneously if the quenching-bath immersion depth is adequate. By distributing heating power between spur wheel and bevel wheel, the austenitizing temperature can be reached under the tooth roots of both gears at the same time. This requires the selection of different heat-up times for the two gears and different rates of oxygen flow to the two sets of burners (Ref 3).

Air-Fuel Gas Burners. Air-fuel gas combustion develops lower flame temperatures that are compatible with available refractory materials. Thus, burners are designed with the aim of completely utilizing the heat generated. The burners, incorporating heat-resistant refractory liners, are of two types, generally designated as the radiant type and the high-velocity convection type (Fig. 8).

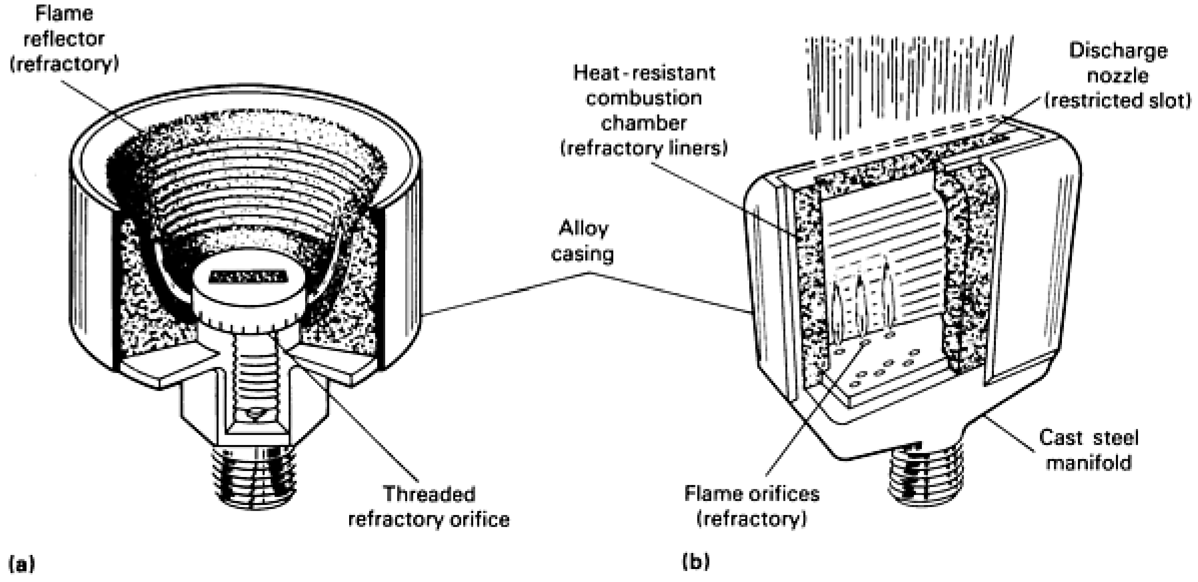

Fig. 8 Typical burners for use with air-fuel gas. (a) Radiant type. (b) High-velocity convection type (not water cooled)

The radiant-type burner (Fig. 8a) is essentially a refractory cup in a protective metal casing. Air-gas premixing is supplied through the pipe at the back and passed through an accurately molded ceramic tip that is screwed into the pipe and located at the bottom of the cup. With numerous narrow slots molded into its periphery, the tip essentially functions as the distributing head of a multiport burner. The many small flames wash the inner surface of the cup, making it highly incandescent for rapid heat transfer by radiation. Because combustion is completed within the cup, the burner may be positioned close to the work with no flame impingement.

The standard radiant burner used in flame hardening is approximately 75 mm (3 in.) in cup diameter. It is particularly effective for spin hardening the teeth of large gears. A single row of burners may be arranged in a ring surrounding a gear, as shown in Fig. 9(a), or multiple rows of burners may be arranged to cover completely the surface to be hardened.

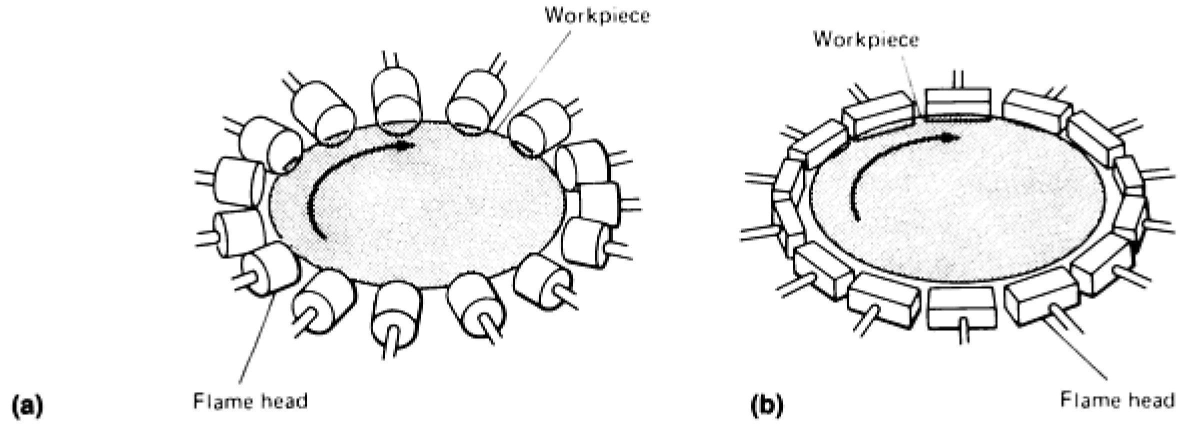

Fig. 9 Setups for flame-hardening gears, idler wheels, and sprockets. (a) Radiant burners. (b) High-velocity convection burners. Wide-face parts can be heated with double or staggered rings of burners.

The high-velocity convection burner is basically a miniature refractory-lined furnace in which heat is released at rates as high as 415 $MJ/m^3 \cdot s$ (4×10^7 $Btu/ft^3 \cdot h$). The air-gas premixture, supplied through a pipe connection, flows through the orifices of the ceramic port plate. The burner design is such that the burning gases heat the chamber lining to a temperature approaching the theoretical flame temperature. This permits preheating of the reacting gases and accelerates combustion. In this manner, gases at approximately 1650 °C (3000 °F) are discharged through a restricted slot opening to impinge on the workpiece at velocities up to 760 m/s (2500 ft/s). High-velocity convection burners are well adapted to the localized heating of parts in spin-hardening operations. Figure 9(b) shows their application for hardening the teeth of a thin gear.

Related Equipment. Burners for both the oxy-fuel gas and the air-fuel gas methods of flame hardening are implemented by pressure regulators, valves, flowmeters, and protection devices. For the air-fuel gas method, a separate mixer and compressor are used because the mixing function is not incorporated within the burners (Fig. 10).

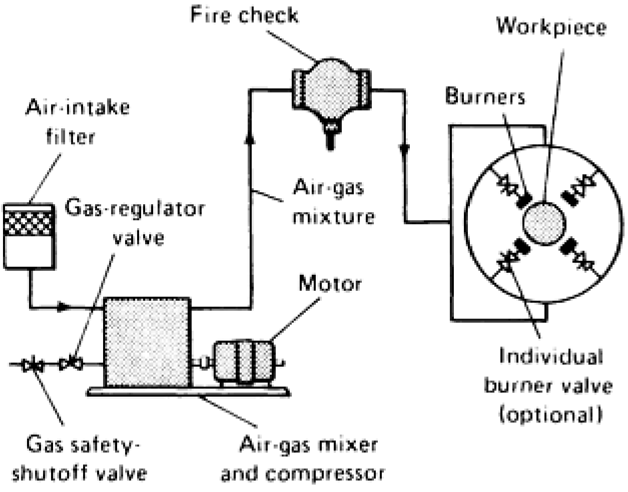

Fig. 10 Mixer-burner system for use with air-fuel gas

Materials of Construction for Burners. The metallic components of burners may be of a variety of materials, depending on the type of burner and the service to which it is subjected. The flame heads for oxy-fuel gas flame heating are in nearly all instances made of copper or a dense grade of lead-free brass (Ref 2). These metals are relatively inexpensive, have excellent thermal conductivity, and are readily machined. Because flame velocity is relatively low, there is little likelihood that the metal flame head will overheat and deteriorate as a result of the backwash of hot gases. Normally, the flow of gases within the head provides sufficient cooling to maintain a safe temperature. If additional cooling is required, the head may be water cooled. Under no circumstances should the flame head be permitted to overheat to the extent that the burner metal, brazed burner joints, or drilled flame ports are damaged.

The service life of oxy-fuel gas flame heads depends largely on the conditions of a particular application, such as containment of the heat resulting from the configuration of the piece being heated, and the degree of backwash of flame or hot gases impinging on the burner. Therefore, it is difficult to predict the exact service life that can be expected for a new application. Brass heads used for the progressive hardening of machineways have shown an average life of 1000 to 2000 h in continuous service.

The melting points and ranges of heat resistance of available materials are not greatly different (compared with the large differences between flame temperatures and metal melting points). Life expectancy, therefore, is a relatively unimportant basis for the selection of a particular metal. Availability, cost, and ease of fabrication are likely to be more important factors in material selection. A metal frequently used for flame heads is Muntz metal (60-40 lead-free brass); when cooling is a problem, however, copper is preferable.

Screw-in tips are usually made of copper, but when higher heat resistance is required, because of secondary flame, Monel K-500 can be used. Insert or press-in tips are usually made of copper, but when high wear resistance of the tip bore is desired, tips made of sintered carbide are employed.

Cast iron, stainless steel, and heat-resisting alloys are used for the casings that surround the refractory cups of radiation-type air-fuel gas burners. Heat-resisting alloys may provide reasonable life at temperatures up to 1150 °C (2100 °F). Casings of high-velocity convection burners are generally constructed of stainless steel, but may be of Inconel for more severe service. For the spin hardening of gears, either type of burner may have a useful life of 10 to 15 40-h weeks of continuous operation. In many applications, longer life for casings has resulted when the operator has exercised care in setting up and operating burners. Also, water cooling the burner casing can markedly extend its life and may be used if the added cost is justifiable and if space for the cooling arrangement is available in the heating setup.

The refractory parts of all types of air-gas burners are formed in steel dies and prefired in kilns and are capable of withstanding the most extreme temperatures generated in the burners. These parts generally fail from thermal or mechanical shock; hence, service life is unpredictable.

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Operating Procedures and Control

The success of many flame-hardening applications depends largely on the skill of the operator. This is especially true when the volume of work is so small or varied that the cost of automatic-control equipment is not justified.

The principal operating variables are:

- Distance from inner cone of oxy-fuel gas flames or from air-fuel gas burner to work surface
- Flame velocities and oxygen-to-fuel ratios
- Rate of travel of flame head or work
- Type, volume, and angle of quench

These variables must be closely controlled to ensure the duplication of desired surface hardness and depth of hardness. It is highly desirable to develop a specific procedure for each item to be flame hardened. The procedure is developed by preliminary tests on the production piece itself, if warranted, or on mock-up sections of approximately the same cross section as the production piece. After the desired contour and depth of hardened zone have been developed, the procedure is applied to production pieces and, when established, is made a part of the heat-treating specification. The critical importance of developing strict procedures is demonstrated in the following case study conducted by a flame-hardening firm (Ref 4).

Example 1: Test on Flame-Hardening Procedure of 1045 Steel Bar.

Each of five experienced flame hardeners was asked to flame harden a 1045 steel bar 25 × 50 × 450 mm (1 × 2 × 18 in.) using only experience and visual examination to guide the process. Only the traditionally and normally controlled variables were preset: coupling distance, 11 mm ($\frac{7}{16}$ in.); water pressure, 620 kPa (90 psi); quench, water; and angle of quench, 30°. Flowmeter readings were taken, speeds of travel recorded, and flame velocities determined. After treatment, each bar was ground to determine the hardness level and depth of hardness. Results are given in Table 2. Surface hardness and depth of hardness showed little consistency: Surface hardness ranged from 50 to 61 HRC and at 3.18 mm ($\frac{1}{8}$ in.) from 30 to 52 HRC.

Table 2 Results of operator skill test

Operator	Flame velocity		Oxygen-to-fuel ratio	Travel speed		Surface hardness, HRC	Hardness at 3.18 mm (0.125 in.), HRC
	m/s	ft/s		mm/s	in./min		
1	95	313	3.6:1	3.4	8.0	61	30
2	99	324	3.1:1	2.5	6.0	50	41
3	137	451	3.1:1	1.7	4.0	57	50
4	124	407	4.2:1	1.9	4.5	55	38

Speed of travel of the flame head, or the duration of heating, should be held constant for uniform results. In the progressive method, the flames gradually heat the work-piece in front of the flame head, and sometimes this effect must be compensated for by gradually increasing the speed of travel or by precooling. At the beginning of a pass when the progressive or progressive-spinning method is being used, the flame head or heads should be manipulated or otherwise adjusted to ensure that the beginning of the area to be hardened attains the proper temperature and depth of heating as progression begins.

Gas Pressures. Oxy-fuel gas and air-fuel gas pressures should be controlled closely for uniform input of heat. Flat oxy-fuel flame heads are somewhat less efficient when used on circular or curved surfaces because each cone of flame is at a different distance from the work. Overheating causes cracking.

Oxygen-to-fuel ratio is a key factor in determining flame temperature. For example, propane produces flame temperatures of 2700 °C (4900 °F) at a 5-to-1 ratio, 2540 °C (4600 °F) at a 4-to-1 ratio, and 2370 °C (4300 °F) at a 3-to-1 ratio.

Flame velocity is one of the most important variables because when balanced with other variables, it is the main determinant of case depth. In Example 1 for flame hardening 1045 steel (Ref 4), the basic flame velocity required for establishing a case depth of 3.2 to 4.8 mm ($\frac{1}{8}$ to $\frac{3}{16}$ in.) is 152 m/s (500 ft/s).

In flame hardening cast irons, where high surface temperatures are undesirable, the use of lower flame velocities is a distinct advantage. In this regard, both MAPP and propane are easy to control and are effective over a wide range of velocities. The ability to control the flame over a wide velocity range not only provides flexibility but also makes the operation much safer and results in better heat pattern control.

Coupling distance is another key parameter in flame hardening. The relations between coupling distance and depth of hardening for three fuel gases are shown in Fig. 11. In general, the coupling distance for MAPP is equal to or very slightly greater than that for acetylene. The effect of counterboring is a shortening of the coupling distance. By the same token, coupling distance increases as flame velocity increases. Efficient coupling distances for MAPP generally range from 6.4 to 9.5 mm ($\frac{1}{4}$ to $\frac{3}{8}$ in.) depending on gas velocity and port size. A counterbored port of No. 69 drill size (0.74 mm, or 0.0292 in.) will operate efficiently at a coupling distance of 4.8 mm ($\frac{3}{16}$ in.).

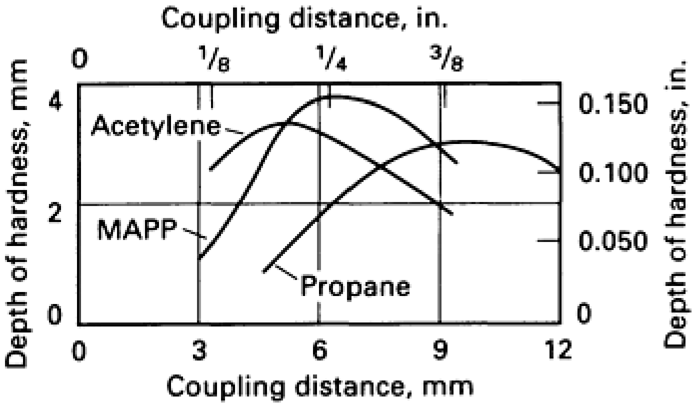


Fig. 11 Effect of coupling distance for MAPP, acetylene and propane. Flame velocity, 170 m/s (550 ft/s); port size, No. 69 drill (0.74 mm, or 0.0292 in.); material, 1052 steel. Oxygen-to-fuel ratios: MAPP, 4.5; acetylene, 1.33; propane, 4.5. Heating times: MAPP, 6 s; acetylene and propane, 8 s

Hardening temperatures can be judged by competent operators, but to the inexperienced the heated metal will appear colder than it actually is because of the light from the burning gases; the consequent tendency is to overheat unless the operator is equipped with didymium-tinted glasses. Radiation or optical pyrometers are often used to judge more accurately the temperatures being developed. Radiation-pyrometer systems of fast response are used extensively to control work temperatures and heating times. Metallurgical examination is the best method for establishing operating conditions. Overheated spots may appear under individual flames, but with properly designed flame heads and good scanning technique, this effect is minimized and not readily detectable by microscopic examination.

Examples of Flame-Hardening Procedures. The interrelationship of variables can best be illustrated by specific examples of procedures used for the production hardening of actual parts. The following six examples involve the hardening of gears, cams, shafts, and flat surfaces.

A small gear hub made of 1052 steel was flame hardened by the spinning method at a spindle speed of 140 rpm (Table 3). The aim was to harden to 52 HRC minimum to a depth of 0.9 mm (0.035 in.) maximum above the root of the gear teeth.

Table 3 Procedure for spin flame hardening the small converter gear hub (shown in Fig. 15a)

Preliminary operation
Turn on water, air, oxygen, power, and propane. Line pressures: water, 220 kPa (32 psi); air, 550 kPa (80 psi); oxygen, 825 kPa (120 psi); propane, 205 kPa (30 psi). Ignite pilots.
Loading and positioning
Mount hub on spindle. Hub is held in position by magnets. Flame head previously centered in hub within 0.4 mm ($\frac{1}{64}$ in.). Distance from flame head to inside diameter of gear teeth, approximately 7.9 mm ($\frac{5}{16}$ in.)
Cycle start
Spindle with hub advances over flame head and starts to rotate. Spindle speed, 140 rpm
Heating cycle
Propane and oxygen solenoid valves open (oxygen flow delayed slightly). Mixture of propane and oxygen ignited at flame head by pilots. Check propane and oxygen gages for proper pressure. Adjust flame by regulating propane. Heating cycle controlled by timer. Time predetermined to obtain specified hardening depth.
Propane and oxygen solenoid valves close (propane flow delayed slightly). Spindle stops rotating and retracts. Hub stripped from spindle by ejector plate. Machine ready for recycling
Propane regulated pressure, 125 kPa (18 psi); oxygen regulated pressure, 550 kPa (80 psi); oxygen upstream pressure, 400 kPa (58 psi); oxygen downstream pressure, 140 kPa (20 psi). Flame velocity (approximate), 135 m/s (450 ft/s). Gas consumptions (approximate): propane, 0.02 m^3 (0.6 ft^3) per piece; oxygen, 0.05 m^3 (1.9 ft^3) per piece. Total heating time, 9.5 s
Flame port design: 12 ports per segment; 10 segments; port size, No. 69 (0.74 mm, or 0.0292 in.), with No. 56 (1.2 mm, or 0.0465 in.) counterbore
Quench cycle
Hub drops into quench oil, is removed from tank by conveyor. Oil temperature, 54 ± 5.6 °C (130 ± 10 °F); time in oil (approximate), 30 s
Hardness and pattern aim
Hardness, 52 HRC minimum to a depth of 0.9 mm (0.035 in.) maximum above root of gear teeth

A large bevel ring gear of 8742 steel was flame hardened by the progressive method (Table 4). The hardness aim was 53 to 55 HRC.

Table 4 Progressive flame hardening of ring gear teeth

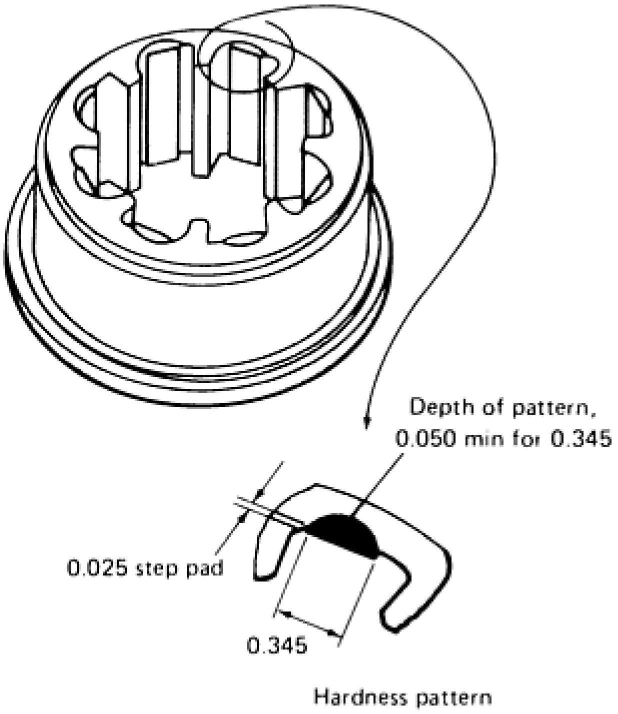
Workpiece
Bevel ring gear made of 8742 steel with 90 teeth. Diametral pitch, 1.5; face width, 200 mm (8 in.); outside diameter, 1.53 m (60.412 in.)
Mounting
Gear mounted on holding fixture to within 0.25 mm (0.010 in.) total indicator runout
Flame heads
Two 10 hole, double-row, air-cooled flame heads, one on each side of tooth. Flame heads set 3.2 mm ($\frac{1}{8}$ in.) from tooth
Operating conditions
Gas pressures. Acetylene, 69 kPa (10 psi); oxygen, 97 kPa (14 psi)
Speed. 1.9 mm/s (4.5 in./min). Complete cycle (hardening pass, overtravel at each end, index time, preheat return stroke on next tooth), 2.75 min
Indexing. Index every other tooth. Index four times before immersing in coolant.
Coolant. Mixture of soluble oil and water, at 13 °C (55 °F)
Hardness aim. 53 to 55 HRC

A free-wheel cam made of 1062 steel was flame hardened by the spot method (Table 5). The aim was 60 HRC minimum at the surface and 59 HRC at a depth of 1.3 mm (0.050 in.), for a width of 8.8 mm (0.345 in.) on the roller surface of the cam.

Table 5 Spot flame hardening of a 1062 steel free-wheel cam

Preliminary operation
Turn on water, air, oxygen, power, and propane. Line pressures: water, 205 kPa (30 psi); air, 550 kPa (80 psi); oxygen, 825 kPa (120 psi); propane, 205 kPa (30 psi). Ignite pilots.
Loading and positioning
Mount cam on flame head. Cam positioned on locating plate and two wear pads, and against three locating pins that are integral parts of flame head. Distance from flame head to cam surface, approximately 7.9 mm ($\frac{5}{16}$ in.)

Cycle start and heating cycle
Propane and oxygen solenoid valves open (oxygen flow delayed slightly). Mixture of propane and oxygen ignited at flame heads by pilots. Check propane and oxygen pressures. Adjust flame by regulating propane. Heating cycle controlled by timer. Time predetermined to obtain specified hardening depth. Propane and oxygen solenoid valves close (propane flow delayed slightly). Ejector plate (air operated) advances and strips cam from flame head.
Propane regulated pressure, 125 kPa (18 psi); oxygen regulated pressure, 585 kPa (85 psi); oxygen upstream pressure, 425 kPa (62 psi); oxygen downstream pressure, 110 kPa (16 psi). Flame velocity (approximate), 135 m/s (450 ft/s). Gas consumption (approximate): propane, 0.01 m^3 (0.4 ft^3) per piece; oxygen, 0.04 m^3 (1.3 ft^3) per piece. Total heating time, 11 s
Flame port design: nine ports per row; eight rows; port size, No. 69 (0.74 mm, or 0.0292 in.), with No. 56 (1.2 mm, or 0.0465 in.) counterbore
Quench cycle
Cam drops into quench oil, is removed from tank by conveyor. Oil temperature, 54 ± 5.6 °C (130 ± 10 °F). Time in oil (approximate), 30 s
Hardness and pattern aim
Hardness, 60 HRC minimum at surface and 59 HRC minimum at a depth of 1.3 mm (0.050 in.) below surface, for width of 8.8 mm (0.345 in.) on cam roller surface. Dimensions below given in inches



A 52100 steel shaft was flame hardened by the progressive method to 61 to 63 HRC (Table 6).

Table 6 Progressive flame hardening of a 52100 steel shaft

Setup

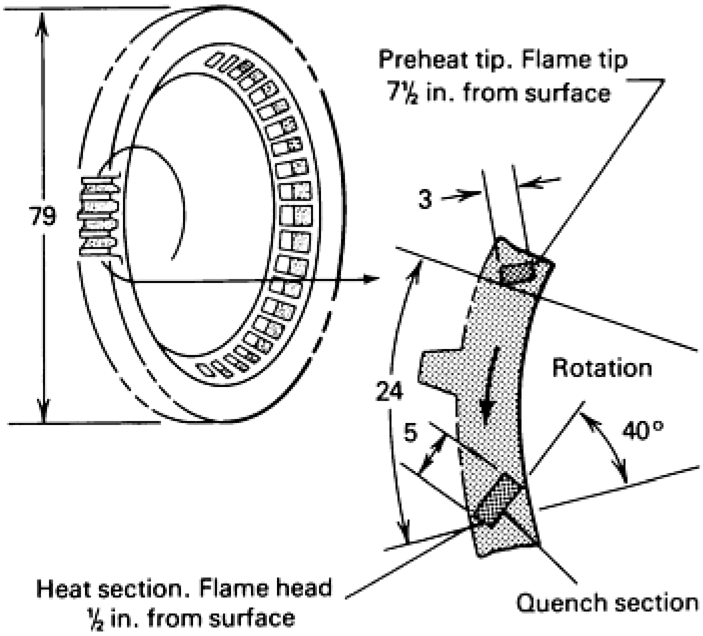
Shaft held vertically between centers to within 0.1 mm (0.005 in.) total indicator runout
Flame heads
Three water-cooled flame heads, each with eight holes 1.3 mm (0.052 in.) in diameter. One torch for each flame head. Flame heads set 6.4 mm ($\frac{1}{4}$ in.) from shaft
Operating conditions
Gas pressures. Acetylene, 55 kPa (8 psi); oxygen, 76 kPa (11 psi)
Speeds. Flame head travel, 1.3 mm/s (3 in/min); speed of shaft revolution, 20 rpm
Quench. Water nozzles directly below flame heads
Hardness aim. 61 to 63 HRC

The roller path of a large cast alloy steel ring gear was hardened according to the procedure outlined in Table 7. The hardness aim was 515 to 600 by portable Brinell, as specified in the last item above the schematic in Table 7.

Table 7 Flame hardening of roller path on side of large ring gear

Mounting on positioner
Gear should be centered on positioner in a vertical position, to approximately 1.7 mm (0.065 in.) total indicator runout on tooth outside diameter (see sketch).
Preheating
Flame head gap. Set 75 mm (3 in.) maximum flame head at 190 mm ($7\frac{1}{2}$ in.) gap from flame-hardened surface and approximately 610 mm (24 in.) ahead of hardening tip.
Gas pressures. Acetylene, 89 kPa (13 psi); oxygen, 185 kPa (27 psi)
Flowmeter. 2.1 divisions for acetylene; 2.65 divisions for oxygen
Tube readings (neutral flame). Flutter, approximately $\frac{1}{8}$ division, plus or minus
Speed setting. No. 9 notch on positioner; equivalent to 2.7 mm/s (6.42 in./min) on 5.79 m (228 in.) circumference of 1.84 m ($72\frac{1}{2}$ in.)

flame-hardened pitch circle (~35 $\frac{1}{2}$ min/rev)
Heat cutoff. Kill preheat when spread of flame toward oncoming hardened surface produces blue-purple temper color at flame-hardening starting point. (Air-block flame head may be set up for the same purpose.)
Flame hardening
Heating-head gap. (*Caution: Must be kept parallel with flame-hardened surface.*) Set and hold 125 mm (5 in.) flame head at 13 mm ($\frac{1}{2}$ in.) gap from flame-hardened surface and at an angle of about 35 to 40° to radius; adjust during flame hardening to follow in line with roller-path warp.
Gas pressures. Acetylene, 89 kPa (13 psi); oxygen, 185 kPa (27 psi)
Flowmeter. 2.7 divisions for acetylene; 3.2 divisions for oxygen
Tube readings (neutral flame). Normal flutter, approximately $\frac{1}{8}$ division; watch frequently for signs of gas failure.
Water pressure (flame-hardening quench). Set pressure-reducing valve for 205 kPa (30 psi).
Speed setting. Same as for preheating. (Note: Double-check setting just before flame hardening.)
Heat cutoff. (No overlap permissible; aim at 13 mm, or $\frac{1}{2}$ in.), maximum soft gap; use extreme caution.) As flame head approaches finish junction, gradually back off tip 1.6 mm ($\frac{1}{16}$ in.) during final 13 mm ($\frac{1}{2}$ in.) of gear travel and kill flame *abruptly* when nearest row of flames *just reaches* 6.4 mm ($\frac{1}{4}$ in.) clearance from starting point of flame hardening; immediately speed up table to fastest-speed notch.
Hardness aim (except at flame-hardening junction), 515 to 600 on portable Brinell at points 50 mm (2 in.) from inside diameter of flame-hardened roller path (50 HRC at a depth of approximately 5.1 mm, or 0.2 in.); total depth of contour, 7.9 mm ($\frac{5}{16}$ in.) Schematic shows ring gear (in vertical position) and position of flame heads for hardening roller path (located on side face of ring) by procedure summarized in table. Gas cost was approximately 25% of total processing cost. Hardening extended to a depth of 4.8 mm ($\frac{3}{16}$ in.). Hardness at surface, 530 HB. For hardness gradients, see Fig. 12.

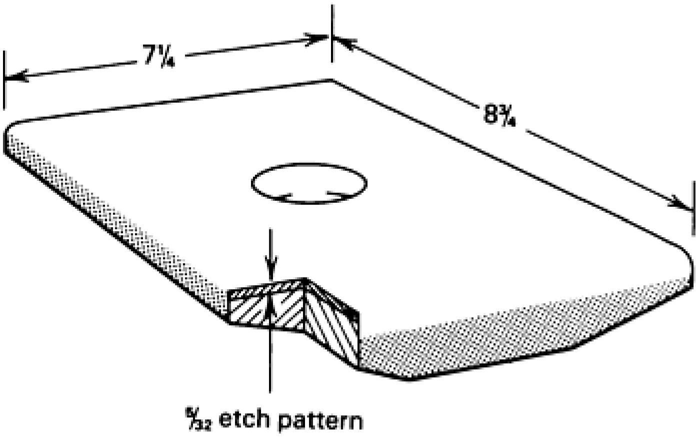


Drop-forged wear blocks of 1040 steel were flame hardened on a conveyor to 53 to 58 HRC (Table 8).

Table 8 Flame hardening of 1040 steel wear blocks

Preliminary operation

Clean blocks until free of scale and rust, preferably by sand or shot blasting.
Loading
Load blocks on one end of conveyor belt.
Flame head
Head contains 2 rows of No. 54 drill size (1.4 mm, or 0.055 in.) flame holes; total of 49 holes, of which 24 are plugged; 150 mm (6 in.) between centers of end holes. Head also contains single row of water-quench holes. Head set at 16 mm ($\frac{5}{8}$ in.) total gap; cone point clearance of flame, 4.8 mm ($\frac{3}{16}$ in.)
Gas pressures
Acetylene, 83 kPa (12 psi); oxygen, 150 kpa (22 psi)
Speed
Conveyor speed, 2.47 mm/s (5.83 in./min); total flame-hardening time, 1.5 min per pad
Hardness and pattern aim
Hardness, 53 to 58 HRC; total depth of hardening to core, 4 mm ($\frac{5}{32}$ in.)



Reference cited in this section

4. G.D. Orr and G.M. Kampitch, Programmable Flame Hardening Through Flow Control, *Heat Treat.*, Sept 1975, p 37-40

Preheating

In flame-hardening parts of large cross section, difficulty in obtaining the desired surface hardness and hardness penetration can often be overcome by preheating. When available power or heat input is limited, the hardened depth can be increased by preheating. The hardness data in Fig. 12 shows the effectiveness of preheating in developing hardness penetration in the ring gear discussed in Table 7.

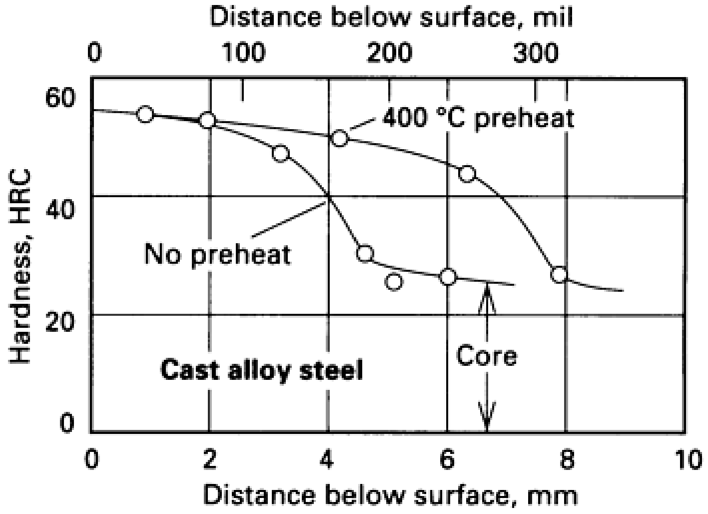


Fig. 12 Effect of preheating on hardness gradient in a ring gear. See Table 7 for preheating procedure.

The flame hardening of prehardened and tempered steels, especially some of the alloy steels, requires careful control of heating to avoid cracking. Preheating the part may be advisable to minimize cracking in such steels. Hardenable cast iron is also susceptible to cracking. In one application, cast iron crane wheels had to be preheated to 480 °C (900 °F) to prevent the rupture of the spokes caused by nonuniform expansion during the spin heating of the tread area.

In another application, the difficulty of heat treating the internal teeth of a planetary-gear housing was overcome by spin hardening. The component had an irregular mass distribution, which led to large distortions when heat treating was done by ordinary flame-hardening or induction-hardening equipment. The case hardening of teeth also failed. The problem was solved by using a specially designed gear wheel spin-hardening machine with close control over heating time and power and by preheating the part with the largest mass and cross section to an accurately predetermined temperature (Ref 3).

Reference cited in this section

3. Surface Hardening Gets Better, *Iron Age Metalworking International*, Dec 1969, p 34-35

Depth and Pattern of Hardness

In some instances, the flame-hardening procedure results in a greater depth of hardness than desired. Figure 5(a), for example, shows that spot hardening a rocker arm pad after heating 4 s at 870 °C (1600 °F) with oxyacetylene flame produces a depth of hardness of 5.1 mm (0.200 in.). If excessive, this depth may be reduced by heating the steel to the same temperature but in a shorter time. Thus, with a reduction in heating time to 3.2 s at 870 °C, the depth of hardening will be 2.5 mm (0.100 in.) (Fig. 5a). Because of the shorter heating period, the cost of hardening each pad will also be reduced.

The problem of excessive depth resulting from a spin-hardening operation may be resolved similarly, as shown in Fig. 5(b). In this operation, heating with an oxyacetylene flame for 13.5 s at 870 °C (1600 °F) produces a hardness depth of 7.6 mm (0.300 in.). Heating at the same temperature for a period of 8 s results in a hardened depth of about 3.8 mm (0.150 in.).

In a progressive-hardening operation with a rate of travel of 1.7 mm/s (4 in./min), a hardness depth of 5.1 mm (0.200 in.) will be produced when the heating time is 12 s at 870 °C (1600 °F), as shown in Fig. 5(c). The flame head contains two

rows of flame holes that produce a heating zone 20 mm (0.8 in.) wide. If the rate of travel is increased 20% to 2 mm/s (4.8 in./min), the heating time is proportionately reduced to 10 s. This results in a hardened depth of about 2.5 mm (0.100 in.).

Variation in depth of hardness may occur in steels of the same nominal composition but from different heats. This is demonstrated in Fig. 13, which shows the variation in depth of hardness obtained in flame hardening hubs made of 1062 steel from three different heats. The inside diameters of these hubs were flame hardened for 12 s to produce a minimum hardness of 59 HRC at a depth of 1.9 mm (0.075 in.).

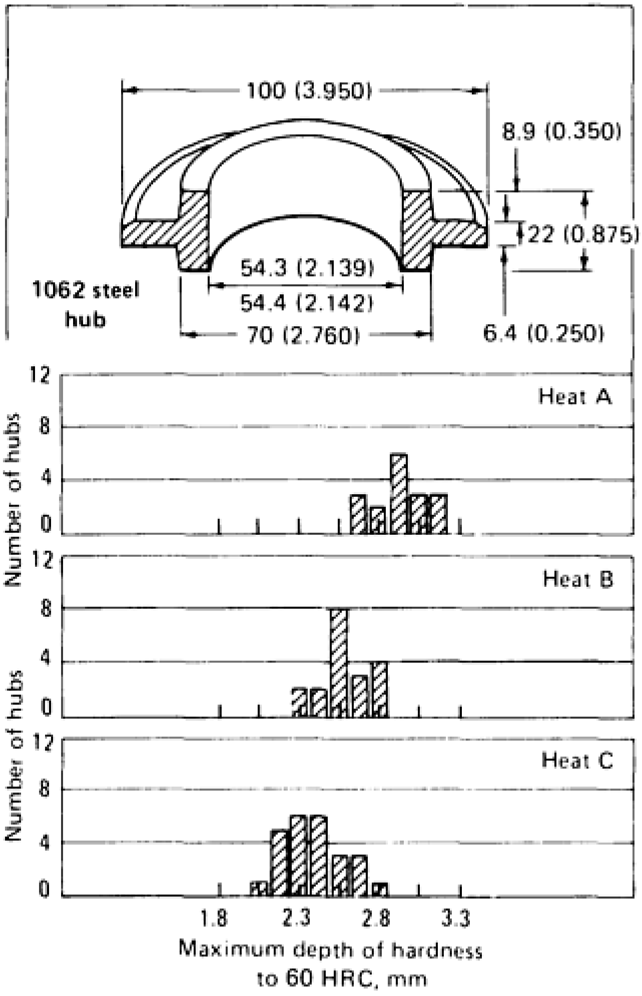


Fig. 13 Heat-to-heat variations in depth of hardness among three heats of 1062 steel hubs flame hardened on the inside diameter to a minimum of 59 HRC at 1.9 mm (0.075 in.) below the surface. Hubs were heated 12 s and quenched in oil. Hardness was measured on cross sections of heated area. Dimensions given in millimeters and, in parentheses, inches

Surface Hardness Pattern. The hardness pattern of any portion of a flame-hardened surface can be determined by lightly blasting the area with fine sand. The hardened portion of the surface will be less affected than the unheated area by the cutting action of the sand. This procedure may also be employed to indicate soft spots when the entire surface has been subjected to flame hardening. (Soft spots may result from nonuniform heating or the interference of scale on the surface.) Another procedure for determining the surface hardness pattern is to etch the area with a 10% nitric acid solution. The hardened area will appear darker than the unhardened area.

These procedures are also applicable to cross sections of hardened areas for an indication of heat penetration, and they are useful as preliminary checks on the performance of the flame-hardening setup.

Variations in the hardness of the surface are exemplified by the data shown in Fig. 14. These hardness readings taken on the surface of races made of 4063 steel cover a one-month period. The races were heated for 9 s to produce a minimum hardness of 59 HRC at 1.3 mm (0.050 in.) below the surface.

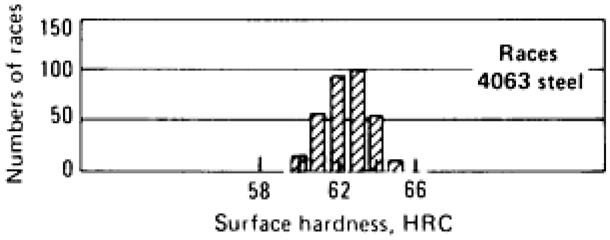


Fig. 14 Distribution of surface hardness. Results obtained during 1 month of testing flame-hardened races (4063 steel) that were heated for a total of 9 s to produce a minimum hardness of 59 HRC at a depth of 1.3 mm (0.050 in.)

Summary. Hardness of the case in flame hardening is a function of the carbon content of the steel and will range up to 65 HRC. Medium-carbon steels with 0.40 to 0.50% carbon are ideal for flame hardening, but steels with carbon contents as high as 1.50% also can be flame hardened with special care. Normally, hardening depth ranges from 1.3 to 6.4 mm (0.05 to 0.25 in.). Heavier sections, such as large rolls and wheels, can have case depths of up to 13 mm (0.5 in.). Manganese-bearing alloys aid in the depth of hardening by decreasing the critical cooling rate, which contributes to deep hardening. Therefore, manganese and free-machining grades of steel are considered excellent for flame hardening.

When hardening depths are required beyond the capabilities of ordinary carbon steels (0.60 to 0.90% Mn), elevated manganese ranges such as 0.80 to 1.10%, 1.00 to 1.30%, or 1.10 to 1.40% can be used efficiently. Wear resistance in many cases is not the only critical design criterion. Under high compressive loading, the hardened layer must be deep enough not only to provide the required wear life of the part, but also to contribute to the support of heavy contact loads. The case must be fully martensitic, and the material supporting the hardened layer must be of sufficient strength. However, increased hardenability may lead to cracking problems, at least with water quenching.

Maintenance of Equipment

Oxy-Fuel Gas Type Flame Heads (Nonferrous). Experience with nonferrous flame heads of three types of construction (drilled face, screw-in tips, and press-in tips) has shown carbon deposit, lack of proper cooling, erosion, and corrosion to be the main causes of maintenance problems common to all.

Carbon Deposit. The intermittent igniting and extinguishing of the flame causes a small deposit of carbonaceous material to build up on the sidewalls of the port, from the retrogression of the burning fuel below the orifice of the port as the flame is extinguished. Although small for each cycle, the deposit builds up gradually until it causes a restriction in the port and thus a variation in the velocity of the gas and therefore in the heating performance. Several thousand cycles may be completed before it is necessary to clean the head.

A slight amount of cleaning can be done without removing the head from the mixer tube. This is done by pushing through the ports a wire of the proper size or a drill one size smaller than the ports. However, care must be exercised to prevent bell mouthing or increasing the size of the port. Cleaning by this method deposits loose carbonaceous material in the fuel chamber, and this material, propelled by the velocity of the oxygen and fuel-gas mixture, may become lodged in other ports.

Flame heads operating on volume production should be removed from the machine and thoroughly cleaned after 40 to 120 h of operation. The interval depends on the installation, the oxygen and fuel gas mixture, and the heating cycle time.

Drilled-port and insert-port heads, when removed, can be cleaned by inserting in the ports a wire of the proper size or a drill one size smaller than the ports and then immersing the heads in a suitable solvent or cleaner that will loosen the carbonaceous deposits. Again, care must be exercised to prevent bell mouthing or enlarging of the port. Also the cleaner

or solvent must not attack the head itself. After cleaning and rinsing in clean water, all traces of dirt and moisture should be blown from the ports, fuel chamber, and water lines. Screw-in tips and heads may be cleaned in the same manner.

Erosion and Corrosion. All types of heads are subjected to the by-products of combustion, which may attack the face of the burner or the tips, causing erosion and corrosion. A flash plate of chromium on the burner face has proved to be helpful in reducing erosion and corrosion. In time, the face of a drilled-port burner may erode to a point at which it is necessary to reface the head by machining and reworking the counterbore. If there is enough space between ports on drilled-port heads, the port can be repaired by drilling oversize and pressing in an insert. These inserts can be removed and replaced when necessary.

Because the oxy-fuel gas type of flame head is water cooled, it may be necessary, in localities where extremely hard water is supplied, to soften the water to keep scale from forming in the cooling passages; commercial water softeners of the zeolite or polyphosphate type may be used. Recirculating systems with heat exchangers are sometimes required.

Air-Gas Type Burners. Failures of air-gas burner liners occur by spalling, erosion, and cracking of the refractory cup or tunnel and outlet. These liners should be inspected periodically, at intervals determined by experience with the individual installation; when conditions are severe, inspection may be required as often as once every shift.

The causes of deterioration of burner liners are thermal shock from repeated rapid heating or cooling (or both) and mechanical shock from work striking the burners. The burner casings deteriorate mainly from prolonged exposure to escaping hot gases that heat the casings locally, causing more or less progressive oxidation, cracking, growth, and, infrequently, burning. If installation space permits the use of water or air cooling, these can usually be expected to increase the life of burners. Shielding, designed to conduct hot gases away from the burners and other parts of the machine, is also valuable in reducing maintenance costs.

Mechanical Components. Because both oxy-fuel and air-fuel gas systems employ pressure gages, pressure regulators, valves, flowmeters, and safety devices, the maintenance problems associated with these accessories are common to both methods of flame hardening. Symptoms and probable causes of trouble with several mechanical components used in flame hardening are listed in Table 9.

Table 9 Maintenance problems in flame-hardening equipment

Component	Symptom of trouble	Probable cause
Pressure gage	Erratic behavior	Mechanical damage to mechanism
Gas supply pressure regulator	Failure to hold pressure setting at outlet	Broken or hardened diaphragm
		Too taut diaphragm
		Sticking stem or valve parts
		Damaged or dirty valve seat or plugged orifices or vents
		Broken or damaged spring
Solenoid valve	Failure to close or open	Defective valve mechanism or wiring
Fuel valve	Flame lingers after shutoff	Dirty seat or stem; damaged seat

Oxygen valve	Flame popping after shutoff	Damaged seat

Air-gas systems also have maintenance problems related to their compressors and blowers. Devices for protection against backfire and explosion should be serviced according to manufacturer instructions.

Electrical Components. Electrical contacts should be cleaned periodically; when the heating cycle is controlled by a timer, periodic checks of the timer are advisable. Generally, if the heating cycle is inaccurate, it will be evident in the inspection of the parts. If the heating cycle is controlled by a thermopile, several items must be checked: Excessive flow of cooling water through the housing will cause condensation on the lens; a deposit of any type on the lens will cause erratic results; and in high-production work, the lens should be cleaned at least twice each shift, and the temperature recorder should be balanced once each shift.

Spindle and Movable Holding Fixtures. It is important that positioning of the parts and the flame head be consistent. Therefore, holding fixtures and spindles should be periodically cleaned, checked, and lubricated. Any worn part should be replaced before it becomes improperly located.

Piping. Types of piping and fittings recommended by underwriters should be used in installing the gas lines from the gas source to the site of use. In long gas lines, means should be provided for purging accumulated condensate from the line before the gas reaches the mixing chamber or torch.

Preventive Maintenance

A typical schedule of preventive maintenance for flame-hardening equipment includes:

Daily

- Check all solenoids for leaks; clean, repair, or replace, as necessary
- Replace damaged screw-in flame tips; clean dirty or clogged tips or ports
- Remove foreign material from surfaces of flame heads and movable machine parts
- Check for stable pilots
- Check for leakage of fuel gas, water, oxygen, and air
- Check level, circulation, and temperature of quench oil
- Clean lens of radiation pyrometer and balance the recorder
- Check oil level and flow of oil to spindle

Weekly

- Check liquid level in backflash arrestor
- Check relief valve on backflash arrestor
- Lubricate all movable parts as required
- Check all fuel-gas, oxygen, and air connections for leaks (using soap solution)

Bimonthly

- Remove and clean flame heads (frequency will vary with installation and use)

Semiannually or annually

- Remove, clean, and repair oxygen and fuel-gas regulators
- Remove, clean, and repair all solenoids
- Check electrical contacts and wiring

- Clean heat exchanger and quench tank
- Check orifice in mixing blowpipe
- Repack motor bearings

Safety Precautions

All fuel gases are explosive when mixed with either air or oxygen within their flammable limits. However, they are widely used throughout industry and are safe when properly handled, stored, and transported in compliance with established laws of safe practice. Stabilized MAPP combines the safety and handling ease of propane with the high heat energy of acetylene.

The following organizations have published information on cylinder storage, cylinder manifolding, acetylene generators, housing and piping systems, equipment, and operating procedures:

- American Gas Association,
- 1515 Wilson Boulevard,
- Arlington, VA 22209

- American Insurance Association,
- (formerly National Board of Fire Underwriters),
- 1130 Connecticut Avenue,
- Washington, D.C. 20036

- Compressed Gas Association,
- Crystal Gateway No. 1,
- Suite 501, 1235 Jefferson Davis Highway,
- Arlington, VA 22202

- Industrial Risk Insurers,
- (formerly Factory Insurance Association),
- 85 Woodland Street,
- Hartford, CT 06102

- National Fire Protection Association,
- Batterymarch Park,
- Quincy, MA 02169

Most state and local governments follow the recommendations of these organizations in adopting regulations pertaining to gases. A study of local regulations should be made to determine whether there is any variance from standard procedures.

Operators should be taught to keep equipment clean, free of grease and oil, and in good condition and to avoid leaks of oxygen or fuel gas by regularly testing them with soapy water free of oil and grease. They should open oxygen or fuel-gas valves slowly and be sure that the lines are purged before igniting. An air hose should be available for dispersing fuel gas that has been bled from the lines. Any spaces in and around the machine in which gases might accumulate should also be purged with the air hose. No flame or other source of ignition should be allowed in proximity to the area where fuel gas or oxygen is released into the air, and good ventilation is of primary importance.

Operators should recognize backfires or backflashes immediately and shut off the gases; the cause and extent of damage must be determined, and corrections made, before the torch is reignited. To prevent major explosions, a backflash arrestor must be installed in the fuel line.

Hand friction lighters should not be used to ignite the gases, except for very small flame heads of low gas capacity. A flame from an acetylene torch or a burner using some other gas should be used. The pilot flame should be very close to the heating head to prevent the accumulation of gas and oxygen before ignition. For automatic flame-hardening machines, the pilot light can be permanently mounted (in which case a flame detector and alarm system should be installed to give warning when the pilot light is extinguished accidently), or electric spark ignition can be used. When operations are stopped for any length of time, the valves in the main supply lines should be closed. These valves must not leak because even a small leak can cause a dangerous accumulation of gas.

Oil or grease may ignite violently in the presence of oxygen under pressure and must be kept away from cylinders, regulators, hoses, and other apparatus. The storage of fuel-gas cylinders must be in accordance with standards established by the Occupational Safety and Health Administration and the National Fire Protection Agency. The allowable amounts of indoor gas storage is limited, and cylinder manifold design must meet the appropriate requirements.

The cylinders in a manifold should be secured with clamps or chain to prevent them from tipping or falling. A fall or any severe bump can detonate acetylene, with disastrous consequences. Propane is not likely to detonate, but any gas under pressure is dangerous if the valve is damaged or knocked off the cylinder. In some instances, noise can be a problem in a gas-air system. Equipment should be designed to keep the noise level within generally accepted limits to avoid injury to nearby personnel.

Quenching Methods and Equipment

The proper application of a suitable quench in flame hardening is as important as proper heating. The quench must remove heat at a rate that will produce the desired structure and assist in controlling the depth of the hardened case.

The method of quenching and type of quenchant vary with the method of flame hardening. In spot hardening, immersion quenching is generally used, but spray quenching may be used.

Quenching after Progressive Heating. Parts heated by the progressive method are usually quenched by a spray integrated into the flame head, although for steels of high hardenability, or when it is desirable to vary or adjust the distance between the heated zone and the quench, a separate spray-quench head is sometimes used. The spray quench should issue from the head at an angle away from the flame head to prevent interference with heating and must provide full coverage over the heated band. The integrated type commonly sprays the quenching medium on the work 19 to 32 mm ($\frac{3}{4}$ to 1 $\frac{1}{4}$ in.) behind the last row of flames. When the surface to be hardened by the progressive method is vertical or overhead, additional cooling may be required after the usual spray quench.

Quenching after Spin Heating. Parts heated by the spinning method can be quenched by several different procedures. In one, the heated part is removed from the heating area and quenched by immersion in a separate quench tank. Another method integrates quenching by making the quench tank a part of the flame-hardening machine. Parts may be heated on the machine spindle or arbor and then quenched by being dropped into a quench tank located immediately below the arbor. Parts that are either too heavy or too fragile to be dropped may be lowered into the quench by means of arms or may be lowered into the quench while still on the arbor. Parts may be removed manually from the quench or automatically by means of a conveyor belt. A spray-quenching ring is sometimes submerged in the quench bath to increase the cooling rate.

Parts heated by the spinning method may also be quenched with quench blocks on the same plane as the flame heads. When the heating cycle is completed and the flames are extinguished, the quench is turned on. The quench blocks should cover the heated band and provide enough quenching liquid to obtain suitable and uniform hardness. There should be enough quench points around the periphery of the block to envelop the area completely with quenchant. Water or a polymer quench solution is usual for this type of quench because of the hazard of contaminating the heating heads with oil. When oil quenching is used, the oil should not contact the heating head. This may be avoided by indexing the heated part to a separate quenching station or by retracting the heating heads into a shielded area.

When air-fuel gas mixtures are employed in spin-hardening operations, the heat pattern developed, in many instances, extends beyond the limits desired. Immersion quenching in such instances could extend the hardening into areas requiring subsequent machining or contribute to an excessive amount of distortion. Localized quenching, such as that provided by quench rings, is a solution to this problem. For example, this quenching method was used in hardening the teeth of large sprockets weighing about 205 kg (450 lb). The entire tooth surface, including the root, was hardened to a depth of 4.8 mm

($\frac{3}{16}$ in.). The 10-min heating cycle completely heated the teeth and backup rim. When quenching was done by rotation of the sprocket in a ring of water spray nozzles, hardening was confined to the desired surfaces and the backup rim remained soft. A similar practice is used for hardening large gears. Parts heated by the combination progressive-spinning method are usually quenched by a spray integrated in the flame heads or by separate quench blocks located below the flame heads.

Quenching Media

With spray quenching, either integrated in the flame head or by separate quench blocks, water or a dilute polymer solution is used as the quenching medium. Quenching oils should not be allowed to come into contact with oxygen or to contaminate equipment using it. As with conventional hardening, the alloy content of the steel determines the type of quench that should be used. The quenchant may be water, a brine solution, the glycol-base polymer quench, or air.

By reducing the pressure of the quenchant, the rate of cooling by spray quenching can be reduced from the maximum for which the integrated or separate quench blocks are designed. Increasing the distance between the last row of flames and the point at which the quenchant impinges will allow the mass of metal below the area to be hardened to extract heat and thus will decrease the severity of quenching.

Quenching distance is another factor the operator must consider because the quenchant must strike the heated area while it is still at the critical temperature to avoid the formation of pearlite or other undesirable transformation products in the microstructure. If the spray head is angled too close to the flame, spotty hardness and blowouts can occur. If the angle of spray is too far away, the case may not be fully hardened.

Forced Air. In progressive hardening operations, forced air is frequently used as the quenchant for steels normally considered to be oil-quenching steels. Water is not used immediately after heating because the fast cooling action would result in surface checks. Because most of these steels have relatively low Ar_3 transformation temperatures, the forced air quickly reduces the surface temperature to a point at which water can be applied without causing surface checks. The resulting hardness is usually close to that obtained with a direct oil quench. For example, 52100 steel quenched with forced air and then with water attains a surface hardness of 60 to 61 HRC.

Forced-air quenching is also used in applications in which intermediate hardnesses are required. One example is the hardening of railroad rail ends to reduce "end-batter" by the impact of car wheels. The rails are indexed under the burners in four preheat stations and one high-heat station (high-temperature, high-velocity burner), which heats the rail to the hardening temperature of 870 °C (1600 °F) in 95 s. In a sixth station, air at 690 kPa (100 psi) is directed against the heated surface. This treatment results in a hardened structure of fine pearlite that provides wear resistance and sufficient ductility to withstand the impact of moving wheels. Water is unsuitable in this application because the high-carbon rail steel is susceptible to cracking. Rail lengths for curves, crossovers, and switches are similarly hardened; however, for these, hardening is done progressively, using oxy-gas burners and air quenching.

Immersion quenches vary in type in relation to the metal used, the hardness and depth desired, and the mass, design, and dimensional tolerances of the part. The quenching medium can be a caustic or brine solution, water, a soluble-oil emulsion, or any of a large variety of oils or simulated oils such as polymer quenches.

Self-Quenching. During any type of flame hardening other than through hardening, the mass of cold metal underneath the heated layer aids quenching by withdrawing heat. Thus, cooling rates are very high compared with rates for conventional quenching. During the progressive hardening of the teeth of gears made from medium-carbon steels such as 4140, 4150, 4340, and 4640, for example, the combination of rapid heating and the temperature gradient between the surface and the interior of the gear results in a subsequent self-quench that is equivalent to quenching in oil.

For uniform quenching, a coolant can be used at some distance from the tooth being heated. In one application involving hardening the teeth of 4150 steel gears in the size range of 4 to 12 pitch, one tooth at a time was heated and cooled by conduction. The coolant was directed at the body of the gear. With this procedure, the hardness of the teeth was 50 to 55 HRC after the gears had been tempered at 200 °C (400 °F).

Flame-Hardening Problems and Their Causes

Problems that may occur in flame hardening and their causes are:

Overheating

- Controlling pyrometer set too high
- Millivolt compensator of controlling pyrometer set incorrectly
- Heating cycle too long
- Flame heads too close to work
- Oversize flame ports
- Excess oxygen in flame
- Excessive fuel-gas pressure
- Improper pattern of flame tip

Hardness below minimum required

- Controlling pyrometer set too low
- Millivolt compensator of controlling pyrometer set incorrectly
- Heating cycle too short (underheating)
- Severity of quench too low
- Delay before quenching too long
- Part not thoroughly quenched
- Material hardenability too low for quench
- Surface decarburized

Spotty or uneven hardening

- Nonuniform heating
- Time interval between heating and quenching too short
- Quenching medium not sufficiently agitated
- Water in quenching oil
- Scale on work
- Improper quenching medium
- Surface decarburized

Distortion

- Shape of part or relationship of portion to be hardened to remainder of section not well adapted to flame hardening
- Metallurgically unsuitable prior structure
- Heating cycle too long
- Nonuniform heating
- Nonuniform quenching
- Excessive rate of quenching
- Material hardenability excessive

Shallow depth of hardening

- Material of low hardenability
- Excessive rate of gas flow; check for oxidizing flame
- Flame-port velocity too high
- Controlling pyrometer set too low
- Millivolt compensator of controlling pyrometer set incorrectly
- Short heating cycle or excessive scanning speed
- Severity of quench too low

- Delay before quenching too long

Excessive depth of hardening

- Low flow rate of gas; check for reducing flame
- Excess fuel gas in flame
- Controlling pyrometer temperature set too high
- Millivolt compensator of controlling pyrometer set incorrectly
- Flame port velocity too low

Excessive scaling

- Heating cycle too long
- Rates of gas flow too low
- Flame velocity too low
- Delay before quenching too long
- Improper arrangement of flame heads around periphery; overheating or banding

Tempering of Flame-Hardened Parts

It is usually desirable to temper parts that have been flame hardened; the need for tempering martensite is the same regardless of the heat-treating method used to produce it. Flame-hardened steel will respond to a tempering treatment in the same manner as it would if hardened to the same degree by any other method. Standard procedures, equipment, and temperatures can be used. However, for work that is flame hardened because it is too large to be heated in a furnace, flame tempering may be the only feasible method of tempering available.

Flame Tempering. Large articles are usually hardened by the progressive method and can be tempered immediately by reheating the hardened surface with a flame head placed a short distance behind the quench. The reheating or tempering flame head must be designed correctly in regard to number and size of orifices or tips (flame ports) to produce the desired work temperature and temperature gradient in the flame-hardened zone at the flame-hardening speed.

Exact final adjustments can be made by varying the flow of gases through the flame head and by adjusting the distance between flame head and work surface. Tempering flame heads must have smaller heat outputs than hardening flame heads because the too-rapid heating of the hardened zone can cause cracking and because, for tempering, the temperatures required are lower and temperature control is usually more critical.

Self-Tempering. On large parts flame hardened to depths of about 6.4 mm ($\frac{1}{4}$ in.) or more, the residual heat present after quenching may be sufficient to accomplish satisfactory relief of hardening stresses, and subsequent tempering in a separate operation may be unnecessary. Air-fuel gas heating, because of its lower rates of heat transfer, promotes the development of the deep-seated heat required for self-tempering.

When residual heat cannot be used and it is desirable to eliminate the separate tempering operation, the use of a lower-carbon steel is suggested if hardness requirements permit. The preheating of heavy parts increases the residual heat available for tempering. For this purpose, preheating may be accomplished by either heating the part in a furnace, if feasible; or by spinning the part in the burner ring with the burners firing at reduced or idling input. The choice depends on the availability of equipment and the economics involved. The exact preheat temperature will vary, depending on the size and configuration of the part and the degree of stress relief or temper desired. In each application, the exact schedule may be established on a trial basis as a preliminary step.

Surface Conditions

For wrought and cast steel parts, the surface conditions likely to be detrimental to successful flame hardening are, in general, those that interfere with heating or quenching, cause localized overheating, initiate cracking, or result in the presence of a soft surface skin after proper heating and quenching.

Table 10 summarizes the more common defects or conditions, their origins, and the detrimental effects to be expected when they are present on flame-hardened areas. The extent of these defects determines the amount of difficulty they may cause.

Table 10 Surface conditions detrimental to flame hardening of steel parts

Defect or condition	Probable origin of condition	Detrimental effects to be expected on flame-hardened areas
Laps, seams, folds, fins (wrought parts)	Rolling mill or forging operations	Localized overheating (or, at worst, surface melting), with consequent grain growth, brittleness, and greater hazard of cracking
Scale (adherent)[(a)]	Rolling or forging; prior heat treatment; flame cutting	Insulating action against heating, with resulting underheated areas and soft spots
		Localized retardation of quench, causing soft spots
Rust, dirt[(a)]	Storage and handling of material or parts	Similar to scale condition as noted above left
		Severe rusting may result in surface pitting that will remain after hardening.
Decarburization	Present in as-received steel bar stock; heating for forging or prior heat treatment of parts or stock	In severely decarburized work, no hardening response will be found when parts are tested by file or other superficial means[(b)].
Pinholes, shrinkage (castings)	Casting defects	Localized overheating (or, at worst, surface melting), with consequent grain growth, brittleness, and greater hazard of cracking
Coarse-grain gate areas (castings)	Casting gates located in areas to flame hardened (avoid, if possible)	Increased cracking hazard during quenching, compared with nongated areas; shrinkage defects also likely in these areas
Improper welds	Parts welded with an alloy dissimilar to base metal	Weld zone reaction dissimilar to base-metal reaction. Weld may separate, requiring rewelding or scrapping of the part[(c)].

(a) In addition to having detrimental effects on flame-hardened surfaces, scale, rust, or dirt in the path of the flame may become dislodged and cause fouling of oxy-fuel gas burners or react chemically with ceramic air-fuel gas burner parts (causing rapid deterioration). When such materials enter a closed quenching system, they may clog strainers, plug quench orifices, and cause excessive wear of pumps.

(b) Partial decarburization lowers surface hardness as a direct function of actual carbon content of stock lost at surface, provided that steel was adequately heated and quenched.

(c) To avoid these and other problems, it is mandatory that the flame hardener be given accurate and complete information on any changes in composition and past processing of the part. For example, previously hardened parts should never be flame hardened unless they have been

annealed; otherwise, cracking is inevitable.

Reference cited in this section

1. N.J. Fulco, Flame Hardening, *Heat Treat.*, Aug 1974, p 14-17

Dimensional Control

Because of its ability to heat specific areas of a part selectively, flame hardening in many applications affords greater control of dimensional stability than is obtainable by furnace heating and quenching. The magnitude of the dimensional changes that occur in flame hardening is influenced by such factors as size and shape of the part, area heated, depth of heating, hardenability, and quenching medium. Figure 15, for example, shows the various dimensional changes that occurred from the flame hardening of converter gear hubs.

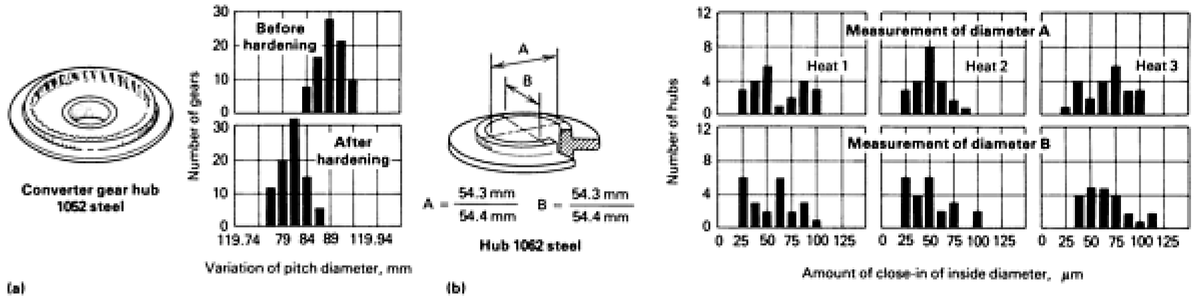


Fig. 15 Distribution of dimensional change as a result of flame hardening. (a) Change in pitch diameter of converter gear hubs made of 1052 steel. Gear teeth on inside diameter were heated for a total of 9.5 s, before being quenched in oil to provide a depth of hardness of 0.9 mm (0.035 in.) above the root. (b) Close-in of inside diameters of converter hubs made of 1062 steel. Inside diameter was heated for a total of 12 s and then oil quenched to harden to 59 HRC min at a depth of 1.9 mm (0.075 in.) below the surface. Inside diameter was finish ground after hardening.

Selection of Process

Flame hardening is basically adaptable to surface hardening and to the through hardening of selected areas. Manufacturing specifications often call for the heat treatment of an entire part, but in many cases this is not necessary. Crane wheels, mill rolls, and gears are examples of items for which flame hardening can be used to harden only the working surfaces. Dies often require hardening only along parting lines or in forming areas.

Other hardening processes that may be applicable for accomplishing the same purposes include:

- Induction hardening for surface or through hardening
- Carburizing, nitriding, and other furnace processes in which surface composition is altered to permit hardening of the case
- Application of hard facing materials to surfaces
- Through hardening of selected sections by partial immersion in molten lead or salt baths

Table 11 lists the different processes in use and describes the benefits realized from each.

Table 11 Relative benefits of five hardening processes

Carburizing	Hard, highly wear-resistant surface (medium case depths); excellent capacity for contact load; good bending fatigue strength; good resistance to seizure; excellent freedom from quench cracking; low-to-medium-cost steels required;

	high capital investment required
Carbonitriding	Hard, highly wear-resistant surface (shallow case depths); fair capacity for contact load; good bending fatigue strength; good resistance to seizure; good dimensional control possible; excellent freedom from quench cracking; low-cost steels usually satisfactory; medium capital investment required
Nitriding	Hard, highly wear-resistant surface (shallow case depths); fair capacity for contact load; good bending fatigue strength; excellent resistance to seizure; excellent dimensional control possible; good freedom from quench cracking (during pretreatment); medium-to-high-cost steels required; medium capital investment required
Induction hardening	Hard, highly wear-resistant surface (deep case depths); good capacity for contact load; good bending fatigue strength; fair resistance to seizure; fair dimensional control possible; fair freedom from quench cracking; low-cost steels usually satisfactory; medium capital investment required
Flame hardening	Hard, highly wear-resistant surface (deep case depths); good capacity for contact load; good bending fatigue strength; fair resistance to seizure; fair dimensional control possible; fair freedom from quench cracking; low-cost steels usually satisfactory; low capital investment required

Source; Ref 5

Induction hardening and flame hardening are the most effective methods for selectively hardening portions of a part (gear teeth, for example) without affecting other areas. A 4150 steel shaft, 760 mm (30 in.) long, with a 25 mm (1 in.) long gear at one end, can be core hardened to 26 to 32 HRC all over (a good machining hardness), and the gear can be hardened to 55 to 60 HRC by flame or induction hardening. If carburizing or nitriding were used instead, the main shaft would have to be masked with copper, which would have to be stripped away after hardening.

The differences between these three basic types of surface-hardening processes can be small enough for certain applications that their feasibilities overlap. For example, a ring gear used in almost identical applications has been made for four customers using four different surface-heating procedures: induction hardening a 4150 steel gear, with or without separate core hardening, depending on the specific application; flame hardening the teeth of a 1045 steel gear; carburizing an 8620 or 9310 steel gear, and then finish grinding; and core hardening a 4150 steel gear to 32 to 34 HRC and then nitriding.

Careful analysis, however, would no doubt show that one of the four variations would be most economical. Examples of false economy are common. A company might save 25¢/kg on steel but have to pay twice that amount for hot or cold straightening to correct the distortion caused by the lower heat treatability of the lower-cost steel.

In selecting a flame-hardening process, consideration must be given to the method of applying the flame to the work and to the choice of gas mixture. Oxy-gas equipment differs significantly from air-gas equipment in the design of the systems that control, deliver, and burn the gas mixtures.

The heating characteristics of the combustion mixture largely determine the degree to which the hardening and heat-affected zones can be localized in the workpiece. Shallow hardness patterns (less than 3.2 mm, or $\frac{1}{8}$ in., deep) can be obtained with oxy-gas mixtures because the higher-temperature flames produced will provide a sufficiently rapid heat transfer to localize the heat pattern effectively. Deeper hardness patterns may permit the use of either oxy-gas or air-gas mixtures. With oxy-gas mixtures, the heat is localized, but care is required in controlling the heat release rate to avoid overheating the surface during the development of the deeper-seated heat.

Air-gas mixtures, because of the lower rate of heat transfer obtained with them, reduce the tendency toward surface overheating but generally extend the heat-affected zone well beyond the desired hardness pattern. For this reason, air-gas flame hardening is generally limited to those applications in which the portion to be hardened may be through heated or in which materials of shallow hardenability are used. In the latter instance, the depth of the hardness pattern is primarily controlled by quenching rather than by heating intensity. Because of potential excessive distortion, the deeper-seated heat developed in a part by air-gas flames may preclude the use of this heating medium.

In view of these considerations, the success of air-gas flame hardening largely depends on the configuration of the part insofar as that configuration favors heat localization with its lower rates of heat transfer. In selective through hardening of gear and sprocket teeth, flanges, ribs, edges, and similar projections, air-gas flame heating may be applied. On the other hand, the surface hardening of gear teeth, rolls, journals, shaft areas, machineways, wear areas of forming dies, inside and outside diameters of hubs, and massive sections is usually done with oxy-fuel flame equipment. Small parts frequently require the very small, easily controllable flame characteristics obtainable with oxy-fuel burning equipment.

When more than one mode of flame application or combustion-gas mixture can be used for a flame-hardening operation, the selection of process and equipment becomes primarily an economic consideration. The equipment may then be chosen on the basis of the expected cost involved in meeting immediate and anticipated production requirements.

Whether or not a flame-hardening process is selected in preference to other hardening processes for a specific application is commonly determined on the basis of the suitability of the process for producing the required results, control of distortion, and cost. A specific example of the selection of flame hardening as a method of hardening is described below.

Example 2: Flame Hardening versus Induction Hardening of Sprocket Teeth.

Because of service failures and to avoid a design change, a sprocket manufacturer changed from induction hardening to flame hardening of sprocket teeth (Fig. 16). When induction hardened, the sprockets were failing in the web area. Failure was attributed to high stress concentration resulting from the induction through hardening of the teeth and rim. Continued use of induction hardening would have required major redesign of the part and remaking of a costly forging die.

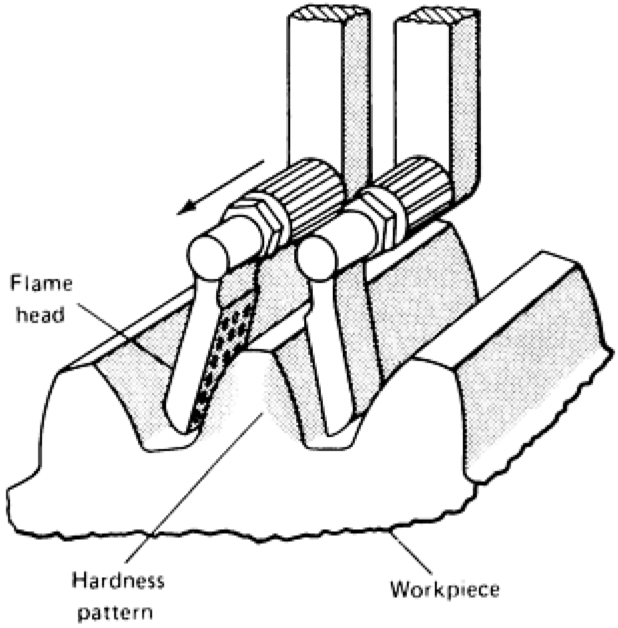


Fig. 16 Hardness pattern developed in sprocket tooth when standard flame tips were used for heating. When space permits the use of this methods, hardening one tooth at a time results in low distortion.

For flame hardening, the sprocket was indexed on a small positioner, and standard flame-hardening tips were moved across the face of the tooth by means of a small flame-cutting dolly. Warm-water quenching was used to eliminate the slight surface checks that had developed with cold-water quenching. Figure 16 shows the hardness pattern developed by the standard flame tips. Failures were eliminated, sprockets hardened by this method had excellent wear qualities, and the cost of hardening was not increased.

Reference cited in this section

5. R.F. Kern, Selecting Steels for Heat-Treated Parts, Part II--Case Hardenable Grades, *Met. Prog.,* Dec 1968, p

Selection of Material

The use of flame hardening is limited to hardenable steels (wrought or cast) and cast irons. Typical hardnesses obtained for various grades of these materials by flame heating and quenching in air, oil, or water are given in Table 12.

Table 12 Response of steels and cast irons to flame hardening

Material	Typical hardness, HRC, as affected by quenchant		
	Air[a]	Oil[b]	Water[b]
Plain carbon steels			
1025-1035	. . .	. . .	33-50
1040-1050	. . .	52-58	55-60
1055-1075	50-60	58-62	60-63
1080-1095	55-62	58-62	62-65
1125-1137	. . .	. . .	45-55
1138-1144	45-55	52-57[c]	55-62
1146-1151	50-55	55-60	58-64
Carburized grades of plain carbon steels[d]			
1010-1020	50-60	58-62	62-65
1108-1120	50-60	60-63	62-65
Alloy steels			
1340-1345	45-55	52-57[c]	55-62
3140-3145	50-60	55-60	60-64
3350	55-60	58-62	63-65
4063	55-60	61-63	63-65

4130-4135	. . .	50-55	55-60
4140-4145	52-56	52-56	55-60
4147-4150	58-62	58-62	62-65
4337-4340	53-57	53-57	60-63
4347	56-60	56-60	62-65
4640	52-56	52-56	60-63
52100	55-60	55-60	62-64
6150	. . .	52-60	55-60
8630-8640	48-53	52-57	58-62
8642-8660	55-63	55-63	62-64
Carburized grades of alloy steels[d]			
3310	55-60	58-62	63-65
4615-4620	58-62	62-65	64-66
8615-8620	. . .	58-62	62-65
Martensitic stainless steels			
410, 416	41-44	41-44	. . .
414, 431	42-47	42-47	. . .
420	49-56	49-56	. . .
440 (typical)	55-59	55-59	. . .
Cast irons (ASTM classes)			
Class 30	. . .	43-48	43-48

Class 40	. . .	48-52	48-52
Class 45010	. . .	35-43	35-45
50007, 53004, 60003	. . .	52-56	55-60
Class 80002	52-56	56-59	56-61
Class 60-45-15	. . .	. . .	35-45
Class 80-60-03	. . .	52-56	55-60

(a) To obtain the hardness results indicated, those areas not directly heated must be kept relatively cool during the heating process.

(b) Thin sections are susceptible to cracking when quenched with oil or water.

(c) Hardness is slightly lower for material heated by spinning or combination progressive-spinning methods than it is for material heated by progressive or stationary methods.

(d) Hardness values of carburized cases containing 0.90 to 1.10% C

Maximum hardness is not the sole criterion used in selecting flame hardening as a heat treatment. Proper steel selection is essential to minimize distortion, for example. Plain carbon steels should be used, if possible, instead of steels whose deep-hardening characteristics are more likely to incur higher internal stresses.

Some flame hardeners feel it is important to stress relieve all alloy steels and other steels with more than 0.40% carbon at 175 to 245 °C (350 to 475 °F), depending on customer specifications. This low-temperature tempering decreases hardness, but it also removes internal stress and restores toughness and ductility.

Selective heating has the disadvantage of developing residual tensile stresses in the surface. As one area of a piece of metal is heated while the remainder stays cold, the hot metal expands; if restraint is sufficient, the heated metal will upset itself. Upon cooling, this upset metal becomes short. As it cools to room temperature, it often stabilizes in a state of tension, which can be high enough to crack the part.

When a part is to be induction or flame hardened, the materials engineer should work closely with the designer to keep the level of hardness, and the necessary carbon, as low as possible, while still meeting engineering requirements. Carbon content is the most important factor determining the level of hardness that can be attained in steels by induction or flame heating. It controls hardness level, the tendency of the part to crack, and the magnitude of the part to crack, and the magnitude of residual surface stresses.

The practical level of minimum surface hardnesses attainable with water quenching for various carbon contents is shown in Fig. 17. The curve is applicable for induction hardening as well as for flame hardening. It applies also for alloy steels, except those containing stable carbide formers such as chromium and vanadium.

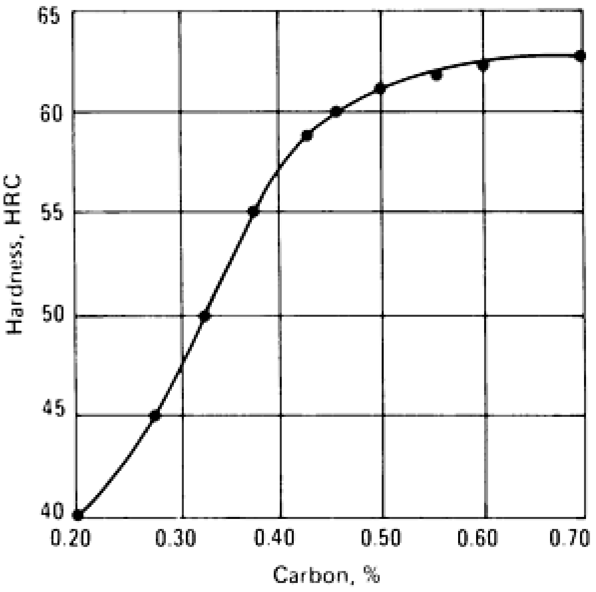


Fig. 17 Relationship of carbon content to minimum surface hardness attainable by flame or induction heating and water quenching. Practical minimum carbon contents can be determined from this curve.

For best results, steels to be induction or flame hardened should be as-rolled, normalized (particularly from a high temperature), air-blast quenched, or quenched and tempered. These preferred heat treatments result in microstructures conducive to rapid and complete austenitization and full hardening. In selecting steels for either induction or flame hardening, it is important that the necessary steps be taken to ensure that the areas to be hardened are free of decarburization. Depending on stock size, steel grade, producing mill, and several other factors, the depth of decarburization for as-rolled bar may run from near 0 to 3.2 mm (0.125 in.). It should not be assumed that turned and polished bar is free of decarburization unless it is specifically ordered with this requirement. Carbon-restored and cold-finished bar is available from mills in various carbon and alloy grades.

When maximum resistance to fatigue is desired, the hardened surface should contain residual compressive stresses; a recommended level is 172 MPa (25 ksi). Because surfaces hardened to depths of less than 1.9 mm (0.075 in.) are commonly residually stressed in tension, it is suggested that depth of hardening be at least 2.7 mm (0.105 in.) to ensure that residual stresses are compressive. This depth is particularly appropriate for manufacturers not equipped with residual stress-measuring equipment. Further, microstructure should be at least 90% martensite, with no ferrite visible at a magnification of 500×.

Carbon Steels. Plain carbon steels in the range of 0.37 to 0.55% C are the most widely used for flame-hardening applications. They can be through hardened in sections up to 13 mm ($\frac{1}{2}$ in.). This response permits the use of carbon steel for selectively flame-hardened small gears, shafts, and other parts of small cross section in which uniform properties are needed throughout the section. These same steels can be used for larger parts in which hardness is necessary only to shallow depths from 0.8 to 6.4 mm ($\frac{1}{32}$ to $\frac{1}{4}$ in.).

Carbon steels 1035 to 1053 are suitable for flame hardening; 1042 and 1045 are the most widely available and are recommended for all flame-hardening applications except when they would be incapable of meeting requirements, for example:

- Failure of a 1045 steel part to harden with a given quench would necessitate the use of a steel of higher hardenability, for example, one with higher carbon or manganese or both, or possibly an alloy steel
- If increased depth of hardening is required, 1042 or 1045 may be inadequate where heavy sections are progressively hardened; therefore, the substitution of 1541, 1552, or an alloy steel would be necessary
- In applications in which wear resistance is of prime importance, it might be advisable to use a steel with

0.60% C or more to produce maximum surface hardness. Steels this high in carbon content are often quenched in oil or simulated oil to avoid the possibility of cracking due to water quenching. Thus, greater hardenability may be needed with the higher carbon content

- When a severe quench in brine or caustic is required for hardening 1042 or 1045 steel and such quenching causes cracking, a steel of higher hardenability--either carbon or alloy, which can be hardened by a less severe quench--should be selected

Alloy Steels. The use of alloy steels for flame-hardening applications is justified only when:

- High core strength is required (through heat treatment before flame hardening) and carbon steels are inadequate to achieve this strength in the section sizes involved
- The mass and shape of a part, restrictions on distortion, or the hazard of cracking preclude the use of carbon steel quenched in water
- Certain alloy grades may be more readily obtainable than carbon grades (particularly the higher-manganese carbon grades) appropriate for the application. Steels such as 4135H, 4140H, 6150H, 8640H, 8642H, and 4340H are typical of the more readily obtainable alloy steels

Carbon and alloy steel castings are widely used for flame-hardening applications. The selection of a specific composition or grade is made on much the same basis as for wrought carbon and alloy steels.

Cast Iron. Gray cast irons, ductile irons, and pearlitic malleable irons having combined carbon contents of 0.35 to 0.80% can be flame hardened and will respond the same as steel.

Cast irons having less than 0.35% combined carbon will not respond readily to flame hardening because of the inability of austenite to dissolve graphite during the extremely rapid heating that occurs during flame hardening. Flame hardening these irons produces a typical hardness of about 40 HRC. Malleable iron, in which all the carbon is in graphitic form, is not amenable to flame hardening for this reason.

Cast irons having combined carbon contents greater than 0.80% are difficult to flame harden because of their inherent brittleness and susceptibility to cracking when heated and quenched rapidly. The low melting point of cast iron and the presence of graphite in the microstructure make cast iron susceptible to "burning" or even localized melting during flame hardening; therefore, extreme care must be taken to reduce the rate of heating when cast iron is hardened using equipment designed specifically for flame hardening steel. For example, the distance between the inner cone and the workpiece can be increased, or the flame velocity can be decreased. The use of a flame head with smaller orifices will also decrease the heating rate.

Perhaps the most significant factor in the response of cast irons to flame hardening is prior microstructure. Irons without free ferrite in their microstructure respond almost instantly to flame or induction heating and require very little holding time at the austenitizing temperature in order to be fully hardened. With a moderate amount of free ferrite, the response may be satisfactory, but an entirely ferritic matrix, typical of grades with high ductility, requires several minutes at 870 °C (1600 °F) to be fully hardened by subsequent cooling. A matrix microstructure of fine pearlite, readily obtained by normalizing, has a rapid response to surface hardening and provides excellent core support for the hardened case.

Other Materials. Flame hardening can be applied to other hardenable ferrous materials, for example, alloy cast irons, martensitic stainless steels, and tool steels. The nature of flame hardening, however--especially the relatively high-temperature gradients and higher-than-normal surface temperatures--may cause the retention of excessive amounts of austenite in many of the highly alloyed materials, with possible low hardness and transformation to untempered martensite in service, which is accompanied by brittleness.

Carburized parts made of plain carbon or alloy steels can be flame hardened to provide a hard case of high carbon content. The depth of carburized case may vary from a few hundredths of a millimeter to 1.6 mm ($\frac{1}{16}$ in.) or more. The flame-hardening procedure is adjusted to heat the carburized case to its full depth for hardening. Because the core of low-

carbon steel thus treated does not harden substantially, the method provides a means of accurately controlling the depth of hardened case.

Flame Annealing

The chemical reaction between oxygen and steel during flame cutting evolves intense heat, raising the temperature of the cut edge to the melting point on the surface and above the transformation temperature to a shallow depth. If the carbon or alloy content of the steel is high enough, hardening results when the heated zone is cooled rapidly.

Carbon steels containing 0.30% C or less do not harden sufficiently to prevent the use of flame-cut pieces in structures or in subsequent fabrication where bending is involved. When cut by flame, steels containing alloying elements and steels containing more than 0.30% C may harden sufficiently to prevent the use of flame-cut pieces for some purposes.

When hardening is likely to occur along a cut edge, oxyacetylene flames applied by suitable equipment can be used either to prevent hardening or to soften an already hardened cut surface. The term flame annealing is applied to this process and to the selective flame softening of areas of hardened steel parts. Tool steels and certain highly alloyed steels will crack during flame cutting, or very soon after, unless they are heated to temperatures ranging from 200 to 425 °C (400 to 800 °F) before being cut.

Laser Surface Hardening

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Introduction

LASER SURFACE HARDENING of ferrous materials is an established process used to enhance the mechanical properties of highly stressed machine parts, such as gears and bearings. Surface hardening increases the wear resistance of the material, and under favorable circumstances, increases the fatigue strength caused by residual compressive stresses that are induced in the workpiece surface by the transformation hardening process. The surface hardening process is not fundamentally different from conventional through hardening of ferrous materials. In both processes, increased hardness and strength are obtained by quenching the material from the austenite region to form hard martensite. Surface hardening differs from conventional through hardening in that only a thin surface layer is heated to austenitization temperatures prior to quenching, leaving the interior of the workpiece essentially unaffected.

Because ferrous materials are fairly good heat conductors, it is necessary to use very intense heat fluxes to heat the surface layer to austenitization temperatures without unduly affecting the bulk temperature of the workpiece. This heat input is commonly obtained by the use of very hot flames or by high-frequency induction heating. By selectively heating the workpiece surface to austenitization temperatures, desired surface hardening is obtained by application of a quench medium to the hot surface, or by self-quenching. Self-quenching occurs when the cold interior of the workpiece constitutes a sufficiently large heat sink to quench the hot surface by heat conduction to the interior at a rate high enough to allow martensite to form at the surface.

In recent years, industrial lasers have become available for metalworking uses, including surface hardening. A laser can generate very intense energy fluxes at the workpiece surface, and the resulting temperature profiles in the workpiece usually can be made steep enough to negate the need for external quench media. The laser beam is a beam of light, which is essentially independent of the workpiece, easily controlled, requires no vacuum, and generates no combustion products. However, laser surface hardening also has some disadvantages that might limit its practical use in a heat-treating shop. These disadvantages may include the need for complex optics and the use of coatings because of the low infrared absorption characteristics of steel. In Europe, work has focused on an alternate technique using a Brewster-angle treatment without coatings.

Fundamentals of Laser Surface Hardening

When a laser beam impinges on a surface, part of its energy is absorbed as heat at the surface. If the power density of the laser beam (usually given in watts per square centimeter) is sufficiently high, heat will be generated at the surface at a rate higher than heat conduction to the interior can remove it, and the temperature in the surface layer will increase rapidly. In a very short time, a thin surface layer will have reached austenitizing temperatures, whereas the interior of the workpiece

is still cool. Even with a relatively moderate power density of 500 W/cm^2 (3200 W/in.^{2}), temperature gradients of 500 °C/mm (25 °F/mil) can be obtained. By moving the laser beam over the workpiece surface (see Fig. 1), a point on the surface within the path of the beam is rapidly heated as the beam passes. This area is subsequently cooled rapidly by heat conduction to the interior after the beam has passed. By selecting the correct power density and speed of the laser spot, the material will harden to the desired depth.

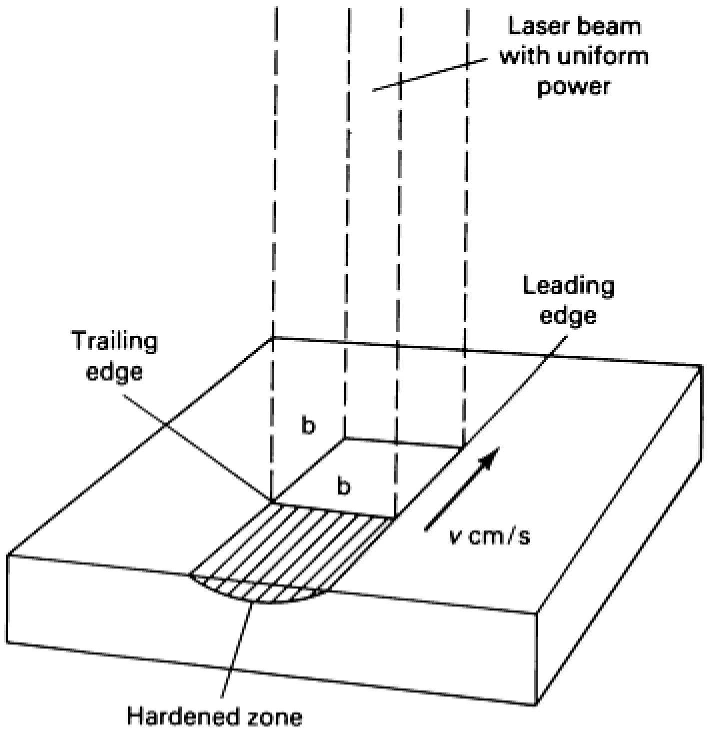

Fig. 1 Square laser beam with uniform power density on a flat plate

A relatively broad area beam, often in the shape of a square or a rectangle, is used in the laser hardening process. The power density of a focused laser beam used for hardening is much lower than the power density of the small, intense focused spots used for welding and cutting. The power density is typically in the 1000 to 2000 W/cm^2 (6400 to 13,000 W/in.^{2}) range, occasionally as high as 5000 or as low as 500 W/cm^2 (32,000 to 3200 W/in.^{2}).

The resulting depth of case will depend on the hardening response of the material, but it will rarely be more than 2.5 mm (0.1 in.). For steel with low hardenability, such as low- and medium-carbon steel, the depth of case obtainable is much smaller, varying from perhaps 0.25 mm (0.01 in.) in mild steels to 1.3 mm (0.05 in.) in a medium-carbon steel. Because of the very high heating and cooling rates obtainable, it is possible to harden steels not normally considered hardenable, such as SAE 1018. For the same reason, the hardness obtainable by the laser hardening process can, in some instances, be slightly higher than that considered possible with conventional methods.

Ferrous materials are not good absorbers of infrared and far-infrared electromagnetic radiation. For instance, polished pure iron has an absorptivity of about 4% at room temperature. Grit-blasted cast iron has an absorptivity of 25% at room temperature, and this value increases to about 40% at 800 °C (1470 °F) in an inert atmosphere. The formation of oxides on the ferrous surface can increase absorptivity beyond these values, but efficient use of the laser energy demands the introduction of a controlled high-value absorbing coating on the material surface. Chemical coatings, such as manganese phosphate and paints of graphite, silicon, and carbon, have all been used successfully. Some of these coatings may burn off during the heating process, and some may leave a residue which in itself can be an indicator of the maximum surface temperature reached. In any event, the absorptivity of these coatings at the beginning of the heating cycle is high (90% or better) and continues to be higher than that of the bare material throughout the temperature excursion. The overall absorptivity of these coatings, applied like a spray paint, is typically about 80%.

For shorter wavelengths (1.06 μm near-infrared radiation), the room-temperature absorptivity may be as high as 60% (as would be the case in yttrium-aluminum-garnet, or YAG, laser transformation hardening), but an absorbing coating is still recommended for efficient use of the laser energy.

The major advantages of laser surface hardening include: close control of the power input with metal-working lasers; the laser can provide high power density in selected areas, which in turn minimizes the total energy input, and thereby, dimensional distortion; and the ability of the laser to reach normally inaccessible areas on the workpiece surface. Because no vacuum or protective atmosphere enclosure is needed, and the distance from the workpiece to the last optical element of the laser system can be quite long, it is possible to process very large or irregular-shaped workpieces. The laser beam can also be optically shaped or split to accommodate different geometries.

On the negative side, the depth of case obtainable is limited to about 2.5 mm (0.1 in.), usually less than half of this, and the capital cost of the equipment may be high. Therefore, careful analysis of a potential application for laser hardening is needed to ascertain the cost-effectiveness of the process.

Metallurgy of Laser Hardening

As stated earlier, the surface hardening process is not fundamentally different from the conventional hardening processes because the same metallurgical reactions occur. In surface hardening, however, the heating portion of the process cycle must, out of necessity, be much shorter than that of conventional hardening. This is particularly true for laser hardening, where heating to the austenitizing temperatures occurs within seconds or even fractions of a second. In fact, in laser surface hardening the heating period is frequently shorter than the cool-down time.

The response of ferrous materials to rapid cool-down from the austenite region has been studied in great detail for many decades and is well understood. The same cannot be said for the heating period of the process. Basically, the problems associated with these high heating rates are that the formation of austenite as well as the redistribution of carbon, necessary to form a homogeneous γFe-C solid solution, are processes that require small but definite time intervals. The kinetics of these processes under very high heating rates are still somewhat uncertain, making the design of a laser surface hardening process more difficult than that of a conventional through hardening procedure.

The basic reaction taking place during the heating period is the transformation of the bcc (α) iron into fcc (γ) iron. This occurs by nucleation and growth of the new phase in the matrix of the old phase. In slow heating, the process will start at A_1 (723 °C, or 1335 °F) in a carbon steel and will be complete at the A_3 line. However, when the heating rate is high, the system is far from equilibrium conditions and the A_3 line will tend to be displaced upward to higher temperatures. Thus, although the temperature may be sufficiently high to form austenite under conditions of slow heating, the same temperature level may be insufficient even to initiate austenitization under high heating rates. Laser hardening parameters are, therefore, usually designed to give peak temperatures well above those employed in conventional hardening to ensure austenitization, but not high enough to initiate surface melting.

The equilibrium room-temperature structure of iron and steel will contain carbon in the form of iron carbide or graphite as a separate phase. To bring about hardening upon quenching, this carbon must be uniformly dissolved in the austenite. To do so, the carbon must be redistributed by diffusion into areas that originated from practically carbon-free ferrite.

This requires time, even at the high temperatures used in laser hardening, and under certain conditions, laser processing may occur too rapidly to allow for complete diffusion. This problem is obviously most prevalent when the carbon molecules have larger molecular distances to travel in order to dissolve evenly in the iron matrix, such as in coarse pearlitic structures, structures containing proeutectoid cementite, spheroidized materials, and cast irons, particularly cast iron with a high content of free ferrite. Figure 2 shows the structure of a ductile cast iron after laser processing. The extent of carbon diffusion that occurred during the processing is clearly revealed by the region of martensite surrounding the graphite nodules.

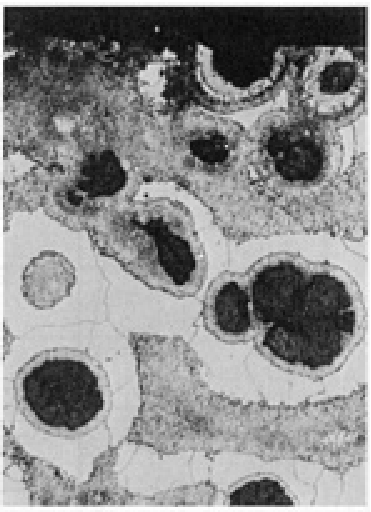

Fig. 2 Structure of laser-hardened ductile cast iron. 250×

The intrinsically high heating rates associated with laser hardening, combined with the need to allow sufficient time above the A_3 point to form homogeneous austenite, necessitate high peak temperatures. Retained austenite is found in laser hardened materials as revealed by x-ray analysis, and it appears that the amount of retained austenite increases with increasing maximum processing temperatures. Attempts to increase the case depth by increasing the energy input may therefore result in an undesirable structure if carried too far.

The upper limit for the surface temperature in laser processing is set by the melting point of the material because surface melting is undesirable in most instances. On simple plane surfaces, this is easy to avoid, but on workpieces with more complex design the surface temperature may vary across the beam-impingement area, even if the power density over the beam cross section is uniform. This can occur when the surface is curved, and in particular when the beam strikes an area with abrupt angles. The projected power density will then be nonuniform, and the heat flow uneven, so that part of the illuminated surface may reach the melting point before the remaining area has reached adequate temperatures to austenitize to a sufficient depth. Sharp edges and corners can be troublesome because they tend to concentrate the heat flow and lead to blunting of the edges by melting.

Another problem associated with some laser surface hardening applications is the necessity to overlap hardening passes. This may occur at the closure of a path around a cylindrical workpiece, or in the overlap zone between parallel paths being processed sequentially. Because lateral heat flow from the moving laser spot is unavoidable, backtempering will take place by the heat flow into areas already hardened by previous passes, or, in the case of closed paths, at the start of the pass. The lower the processing speed, the more pronounced the effect because relatively more heat will have time to diffuse into the previously hardened area. Even at high speeds and with the application of external heat sinks or water cooling, this effect cannot be entirely eliminated. Figure 3 shows the hardness profile across the boundary between parallel hardened tracks. As the figure shows, leaving a space between the tracks results in unreacted, and therefore soft, material in the boundary. If, on the other hand, the tracks are overlapping, backtempering will occur, as shown on the right side of the boundary in the bottom curve. The use of special optics may eliminate the necessity of forming overlap areas. However, this will always entail illuminating the entire width of the work area with laser radiation, and the available power of the laser limits the size of the workpiece that can be processed by the use of such optics. In some applications, the formation of a backtempered zone is not detrimental, provided that the processing is done in such a way that the backtempered area is located in a position of low service stresses or wear. Thus, for example, the interior walls of internal combustion engines may be hardened by straight or spiral laser passes, leaving unhardened material between the passes without harmful effects.

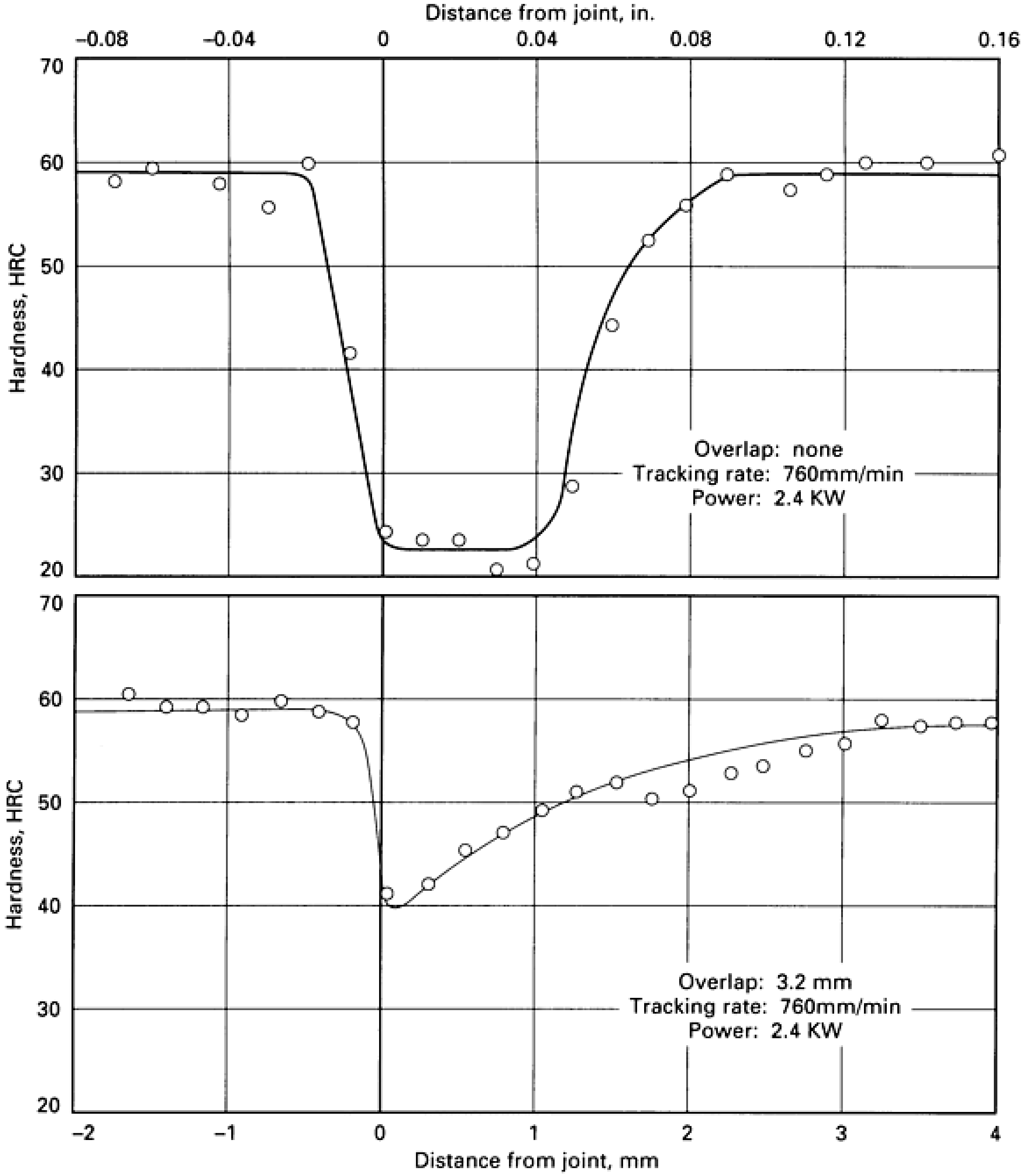

Fig. 3 Overlap zones between parallel laser tracks. Square laser spot size 12.7 mm × 12.7 mm

Heat Flow in Laser Hardening

In laser surface hardening, thermal energy is generated by absorption of the laser radiation at the surface. The increase of temperature in the interior of the workpiece is by way of conduction only; no sources of thermal energy exist below the surface. Thus, if the rate of absorbed power and the thermal properties of the material are known, it is possible, at least in principle, to calculate the temperature distribution in the workpiece. This is of considerable value, because it is then possible to predict the results of laser processing in advance and to calculate the optimum processing parameters, such as power density, processing speed, and spot size.

The long wavelength electromagnetic radiation (infrared) from a typical carbon dioxide laser is not efficiently absorbed by ferrous metals at room temperatures. It is, therefore, necessary to coat the workpiece with a substance that will aid in absorbing the laser energy or to use a Brewster-angle treatment without coatings. Commonly used coating materials are

manganese phosphate, graphite, or carbon-black paint. The paint, in the form of flat, black spray paint, is by far the most convenient coating to use. It is easy to apply and is fairly insensitive to variation in coating thickness.

When laser energy is absorbed at the surface at a rate of 500 W/cm^2 (3200 W/in.^{2}) or more, surface temperature rises very rapidly because the conduction of heat to the interior cannot keep up with the influx of energy to the surface. The higher the input flux, the more rapidly the temperature rises in the surface layer, and as a consequence, the temperature gradient in the workpiece will be steeper. The maximum surface temperature allowable is the melting point of the material, although in practical applications temperatures should be held well below this value. This clearly acts as a constraint on the depth of austenitization that can be achieved. If lower laser power density is used and the processing speed is correspondingly decreased, the surface temperature will rise more slowly and the temperature gradient will be less steep. This allows austenitization to a greater depth, as shown in Fig. 4. However, the rate of cooling by self-quenching will be slower, and it may be insufficient to trap the dissolved carbon in a martensitic matrix without some carbon precipitation. This would not allow the material to harden fully. Thus, the two physical limitations of melting temperature (T_m) and necessary cooling rates act to impose a limit on the obtainable depth of case regardless of the power available for the processing.

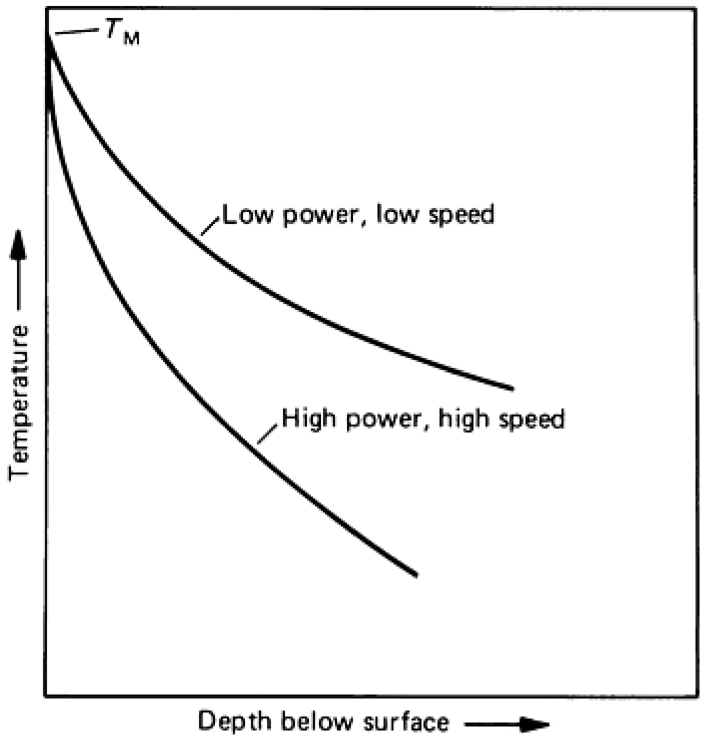

Fig. 4 Influence of processing parameters on heat penetration in laser surface transformation hardening

To obtain good self-quenching, it is generally necessary to use high power density and high processing speed for steels of low hardenability. Steels of high hardenability can be processed to greater depth by relatively low power densities and low processing speed. For many such steels, the slow processing rate will be necessary to give the material time to form homogeneous austenite. Thus, deep case depth in plain carbon steels may be difficult to achieve. It is possible to use external quench procedures, thereby obtaining deeper case depths in steels of low hardenability. This is achieved at the cost of greater dimensional distortion because the total power input increases with decreasing speed for constant maximum surface temperature.

Temperature Distribution. If the absorbed power density, laser spot dimensions, processing speed, and thermal properties of the material are known, the temperature distribution in the workpiece can be calculated by means of several expressions found in the literature. The simplest expression is obtained if it is assumed that heat only flows normal to the workpiece surface, that is, one-dimensional heat flow. If the workpiece is large in this direction, the temperature is given by:

$$T = T_0 + 2Q / K\sqrt{a\,t_D}\,ierfc\frac{d}{\sqrt{a\,t_D}} \qquad \textbf{(Eq 1)}$$

where T is temperature in celsius, T_0 is room temperature in celsius, Q is absorbed power in W/cm^2, K is thermal conductivity in W/cm · °C, αis thermal diffusivity in cm^2/s, δis depth below the surface in cm, and t_D is dwell time in s.

Dwell time is the amount of time a given spot on the surface will be exposed to the laser beam. This is, therefore, equal to the length of the laser spot in the direction of travel divided by the speed of travel. The expression ierfc(x) is the integrated complementary error function defined by:

$$ierfc(x) = \int_x^{\infty} erfc(f)\,df$$

where erfc(f) is the error function complement:

$$\text{erfc}(f) = 1 - \text{erf}(f)$$

and the error function erf(f) is given by:

$$erf(f) = \frac{2}{\sqrt{p}}\int_0^m e^{-m^2}\,dm$$

These functions are tabulated in many sources and can easily be evaluated. Figure 5 shows a plot of ierfc(x).

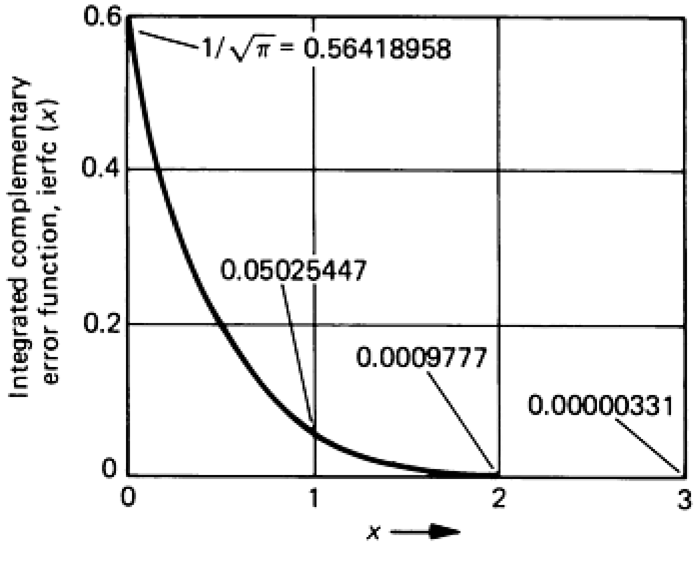

Fig. 5 The integrated complementary error function

If we apply Eq 1 to a moving laser spot on a plane surface, it becomes clear that as the leading edge of the spot reaches a given spot on a plane surface, the temperature will rapidly start to increase, and the maximum temperature will be reached at the trailing edge of the spot, as shown in Fig. 6. A similar, but smaller, temperature increase will be experienced at points below the surface. If Eq 1 is solved for various values of the depth δ under the trailing edge of the spot, a temperature-profile can be constructed representing the maximum temperature conditions in the vicinity of the surface (see Fig. 7). Knowing the transformation temperature A_3, it is then a simple matter to determine the largest obtainable depth of hardened case δ.

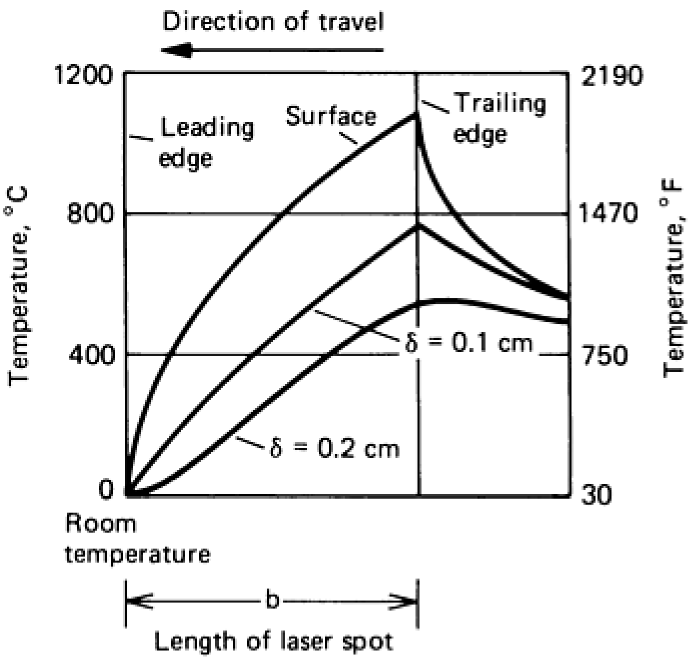

Fig. 6 Temperature distribution along the centerline of a 1 cm × 1 cm (0.4 in. × 0.4 in.) laser spot. Power density, 1200 W/cm^2 (7700 W/in.^{2}); speed, 1 cm/s (0.4 in./s)

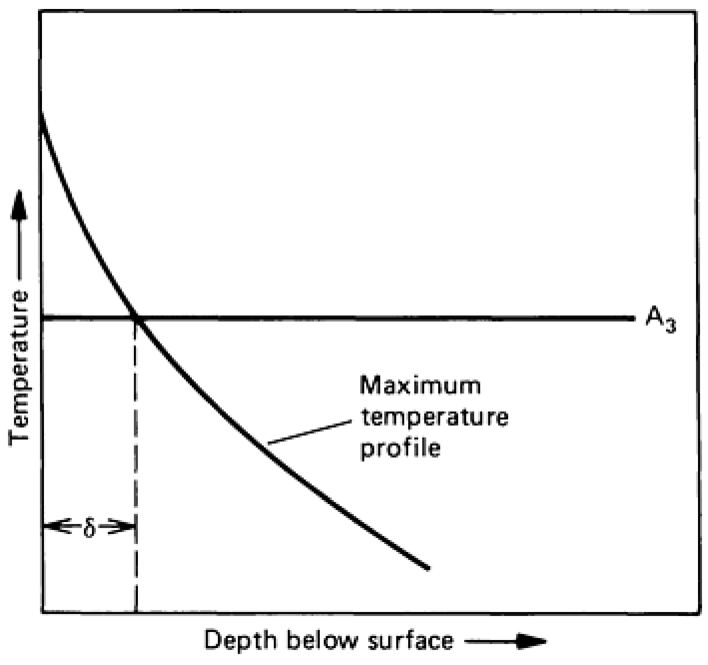

Fig. 7 Predicting depth of case in laser transformation hardening

In reality, heat diffuses in all directions into the workpiece from the moving laser spot, not only normal to the surface. Furthermore, heat is lost by radiation from the surface, and the thermal properties are not constants but are temperature dependent. Finally, in many instances, the workpiece is not large enough to be considered infinite, as Eq 1 assumes. All of these factors can contribute to make the estimates obtained from Eq 1 unreliable. Nevertheless, at high processing speeds (that is, low dwell time, t_D) and for reasonably thick specimens and large laser spots, Eq 1 gives a good estimate for depth of obtainable case. It is possible to develop expressions that take into account the three-dimensional nature of the heat flow. Such expressions can take the form of complex analytical solutions to the heat flow equation, or are based on finite-element analysis. The practical application of such analysis requires the use of computers.

Cooling Rates. By a relatively simple expansion of Eq 1, the cooling rate of any given point in the workpiece can be estimated if only one-dimensional heat flow is considered. This is done by means of the expression:

$$T = T_0 + 2Q/K\left\{\sqrt{a\,t_D}\,ierfc\frac{d}{2\sqrt{a\,t_D}} - \sqrt{a\,(t-t_D)}\,ierfc\frac{d}{2\sqrt{a\,(t-t_D)}}\right\} \quad \textbf{(Eq 2)}$$

In this equation, the symbols have the same meaning as in Eq 1, except that t is the time elapsed since the leading edge passed over the spot for which we need to know the temperature; and t - t_D is the time elapsed since the trailing edge passed over the spot, that is, the time elapsed after cooling by self-quenching began. When using this equation, it is very important that the workpiece be large enough to provide an adequate heat sink.

Equation 2 can be used in conjunction with C-T diagrams to predict whether or not the cooling rate by self-quenching will be adequate for hardening under a given set of circumstances. To aid in the use of Eq 1 and 2, Fig. 8 gives the values of the thermophysical constants for hypoeutectoid carbon steels. The plotted values are the integral average values from room temperature to 1000 °C (1830 °F) and are given in units convenient for calculation of temperatures by Eq 1 and 2 when the power input (Q) is in W/cm^2. It should be noted that Q is not the applied power density but the estimated absorbed power in W/cm^2.

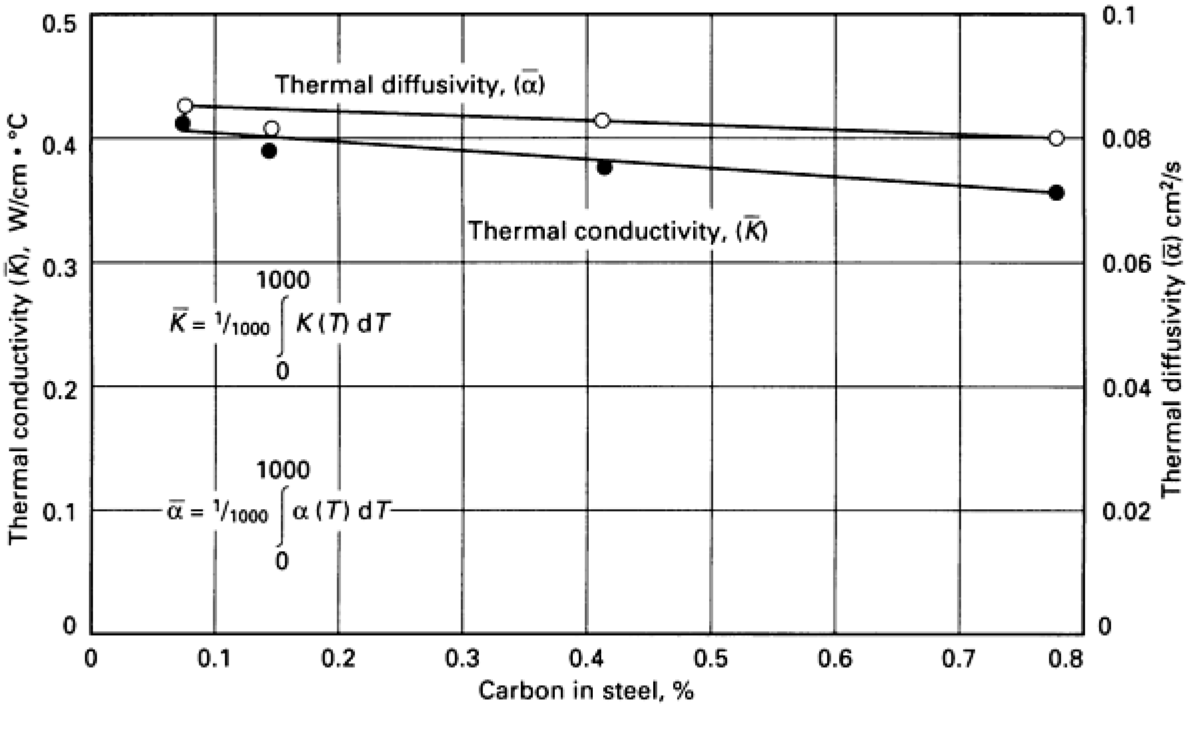

Fig. 8 Thermophysical constants of carbon steels (integral averages between 0 and 1000 °C)

Processing Parameters

Many factors influence the results of laser surface transformation hardening including size of the laser spot, power density, uniformity of power density, processing speed, thermal properties of the material, and laser hardenability of the material. The last factor encompasses the material's response to rapid eating and quenching and is, in part, dependent on the starting condition of the material--that is, whether the material is normalized, annealed, and so on.

The parameters of principal interest are power density, its uniformity, and processing speed. It is obvious that processing speed should be as high as possible to attain high production rates. However, the speed at which the laser spot moves over the surface is not a good measure of the production rate by itself because the dimensions of the spot normal to the direction of travel are equally important in determining the area coverage rate. Another important factor in determining the results of processing is the dwell time. The relative dimensions of a rectangular spot do not influence the coverage rate as long as the power density stays constant. Therefore, the area of the laser spot that will give a specific result is limited

by the available power. An exception to this is when the spot is very narrow in the direction of travel and/or when the speed is very low. Under such conditions, lateral heat losses become large and the spot dimensions influence the results. The conditions under which this effect becomes noticeable is:

$$B = vb/4\alpha < 6$$

where b is the spot dimension in the direction of travel, v is the speed of the spot, and α is the diffusivity, all in cgs units.

The following are general guidelines for choice of processing conditions:

- Usable power densities in laser surface hardening are in the 500 to 5000 W/cm^2 (3200 to 32,000 W/in.^{2}) range. Corresponding dwell times are in the range 0.1 to 10 s. For carbon steels, the power density is usually from 1000 to 1500 W/cm^2 (6400 to 9700 W/in.^{2}), and the dwell time 1 to 2 s
- Materials with high hardenability can be processed at low power density and high dwell time (low speed), whereas materials with low hardenability should be processed at high power density and low dwell times
- Rectangular, square, or sometimes round laser spots with uniform power density are suitable in obtaining uniform hardened case
- High power density and low dwell time give shallow case, but high cooling rates. The reverse is true for low power densities
- Maximum surface temperature is approximately proportional to the square root of the processing speed. Hence, a doubling of the power density requires a quadrupling of the speed to obtain equivalent maximum surface temperatures. Figure 9 shows the results of laser treatment of SAE 1078 steel at various power levels and speeds
- Increasing the power density results in lower total energy input for the same maximum surface temperature
- Steel with normalized, annealed, or spheroidized structures; steel with proeutectoid cementite; cast irons and steels with stable alloy carbides require longer dwell times than steels that have been hardened and tempered
- Small workpieces will require higher power densities and lower dwell times than large pieces, unless external quenching media are used

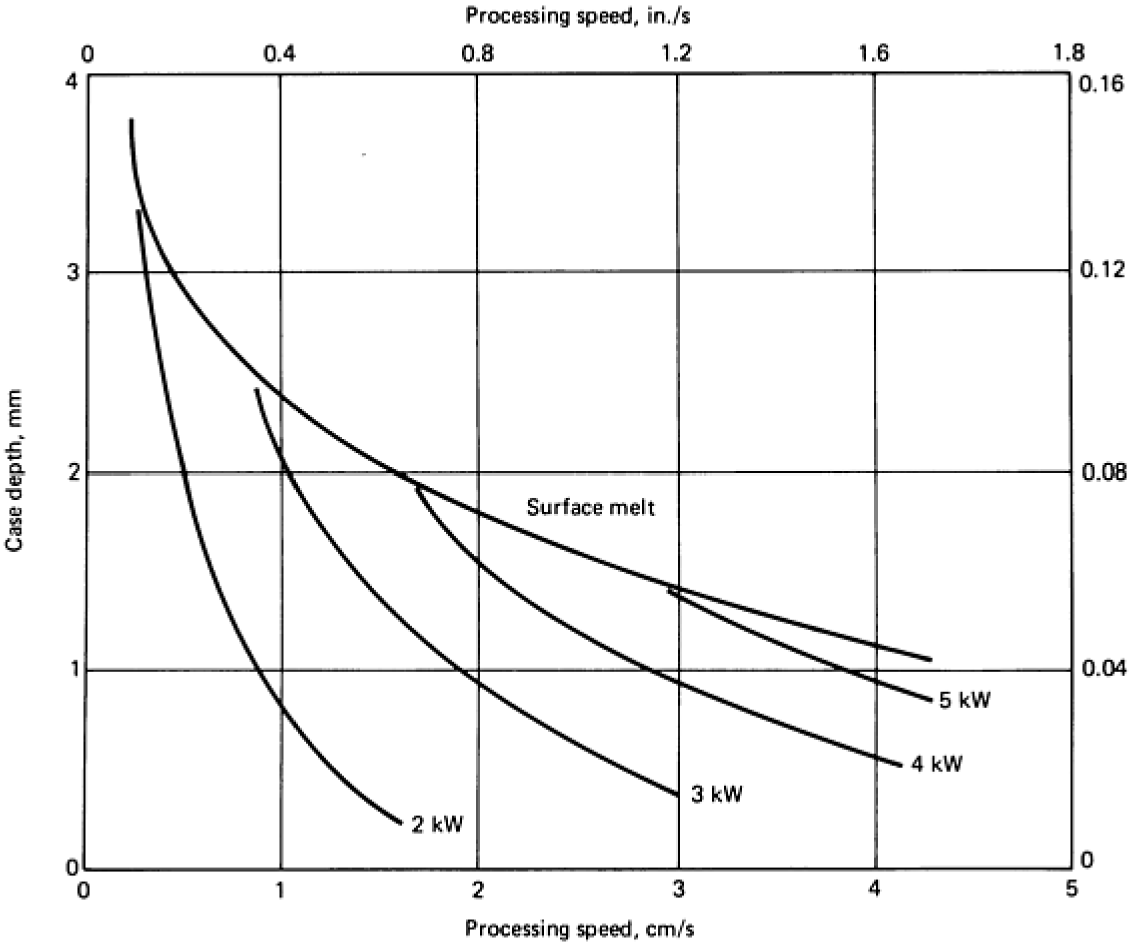

Fig. 9 Laser surface transformation hardening of SAE 1078 using optical integrator with 1.27 cm × 1.27 cm (0.5 × 0.5 in.) laser spot

Metalworking Lasers

Several models of metalworking lasers of both domestic and foreign manufacture are commercially available. The majority of these are of either the Nd:YAG solid-state type, or the carbon dioxide gas type. These lasers may have pulsed or continuous output power. Both types, whether pulsed or continuous wave, can be used for surface hardening.

The power output of metalworking lasers at the present time is in the 50 W to 25 kW range. Capabilities and operating ranges for CO_2 and Nd:YAG lasers are shown in Tables 1 and 2. The minimum size of a laser system for a potential industrial application is determined on the basis of such factors as required production rate, minimum practical spot size, and power density necessary to achieve the desired results. The laser is also a versatile tool, which can be used for a number of metalworking processes such as welding, cutting, and hardfacing.

Table 1 Process capabilities of CO_2 lasers by power range

	200-300 W	**300-500 W**	**500-800 W**	**800-1500 W**	**1500-3000 W**	**>3000 W**
Seam welds, spot welds, maximum penetration, mm (in.)	0.75 (0.030)	1.3 (0.050)	2.0 (0.080)	3.2 (0.125)	6.4 (0.250)	19.0 (0.750)
Cutting, maximum thickness, mm (in.)	1.5 (0.060)	5.0 (0.20)	9.5 (0.375)	12.7 (0.500)	19.0 (0.750)	<25.0 (<1.00)

Heat treating case depth, mm (in.)	. . .	. . .	0.75 (0.030)	1.3 (0.050)	1.3 (0.050)	1.3 (0.050)
Cladding, surfacing, glazing, annealing	. . .	. . .	Yes	Yes	Yes	Yes

Table 2 Process capabilities of Nd:YAG lasers by power range

	<100W	**150-200 W**	**200-400 W**
Microwelding, soldering, marking	Yes	. . .	. . .
Seam welds, spot welds, maximum penetration, mm (in.)	. . .	1.3 (0.050)	2.0 (0.080)
Cutting, maximum thickness, mm (in.)	. . .	5.0 (0.2)	38 (1.5)
Drilling, maximum thickness, mm (in.)	. . .	5.0 (0.2)	38 (1.5)

Lasers emit electromagnetic radiation in the infrared portion of the spectrum, and the laser beam from these machines is invisible. The carbon dioxide laser emits radiation with 10.6 μm wavelength, and this radiation is easily absorbed in a variety of nonmetallic substances. A thin sheet of lucite between the operator and the beam/workpiece interaction zone can absorb potentially harmful stray radiation. The output of the YAG laser has a much shorter wavelength (1.064 μm), and therefore, the operator is required to wear protective eyeglasses for the shorter wavelength. YAG lasers are limited to relatively low power levels. Therefore, in metalworking processes requiring more than 500 W of power, the carbon dioxide laser is usually employed because it can deliver much higher continuous output, although YAG lasers as powerful as 1800 W (continuous wave) have recently been brought to market (MARTEK).

Although many applications utilize defocused beams, the primary output beam from the laser is more often focused in metalworking applications. The output beam is directed and shaped by optical systems to generate a laser spot of the desired size and shape on the workpiece surface. Such an arrangement allows substantial flexibility in the use of a laser system. Because the coherent radiation from a laser has low loss of power with distance (depending on ambient conditions such as humidity), the laser itself can be situated at a considerable distance from the work area. Furthermore, different types of metalworking applications can be performed with the same laser by changing the optical system. Several jobs can be performed simultaneously with one laser by using several work stations (Fig. 10), each with its own optical system designed for a specific application. In most multiple work stations, each work station has its own control console, allowing manual or automatic control of beam power, duration of power delivery to the workpiece, rate of increase of power at the start of the run, rate of decrease at the end (ramp-up and ramp-down), and manipulation of the workpiece fixture and protective gas flow, if required. The laser power is automatically maintained at the desired level by a feedback control device in the laser. Positive feedback from temperature sensors, monitoring the temperature in the beam workpiece interaction zone, also can be used. The entire operation can be controlled by microprocessors. By directing the laser beam to the individual work stations in sequence and utilizing the time when the power is used at another station for workpiece manipulation, maximum usage of the laser can be achieved.

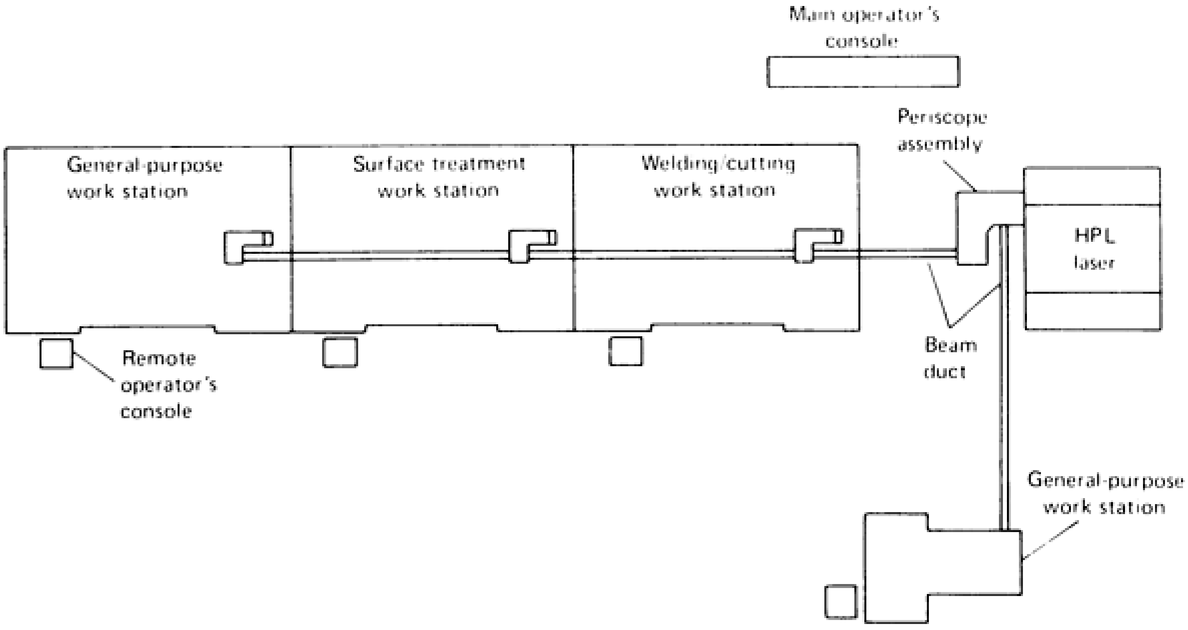

Fig. 10 Metalworking laser with multiple work stations

Optical Systems

In laser welding and cutting operations, a focused beam of intense power is used. For laser transformation hardening, this focused spot is replaced with a broad beam of much lower power density, partly because the hardening process requires lower power densities and partly to obtain reasonable rates of area coverage.

The simplest way to obtain such a spot is to position the workpiece surface in such a way that it intercepts the beam some distance from the focal plane of a converging beam. However, the power density distribution of a spot obtained in this manner is rarely sufficiently uniform and at the same time large enough to give satisfactory results.

The most suitable laser spot for surface hardening is a square or rectangular spot with uniform power density, sometimes referred to as top hat profile (see Fig. 1). Such a laser spot requires reshaping of the output laser beam that is attained by the use of various optical systems.

Transmissive optical elements, such as lenses and windows, can be used. However, because of the long wavelength of the radiation typical for CO_2 lasers, these elements must be made from special materials such as zinc selenide to avoid excessive absorption.

Depending on the laser power, reflective optical components are less fragile and better adapted to industrial environments. They consist of flat, spherical, or parabolic mirrors made from copper or molybdenum, which have excellent reflective characteristics to laser radiation. By the use of these mirrors, the beam can be reshaped and redirected to suit the particular application requirement.

The simplest way of creating uniform power density in the focused beam is with the use of so-called "binary optics." Another simple way to form a square or rectangular beam is to use mirrors or lenses to form a focused spot and then to scan this spot rapidly back and forth in two perpendicular directions, as shown in Fig. 11. If scanning is done at a sufficient rate, the result will be equivalent to spreading the power of the focused spot over the area being scanned, because the thermal lag of the metal will act to even out the power input to a uniform power density. The scanning can be performed conveniently by electromechanical vibration of one or more of the mirrors in the optical system. In this way, it is possible to generate spots of desired size and shape on the workpiece surface.

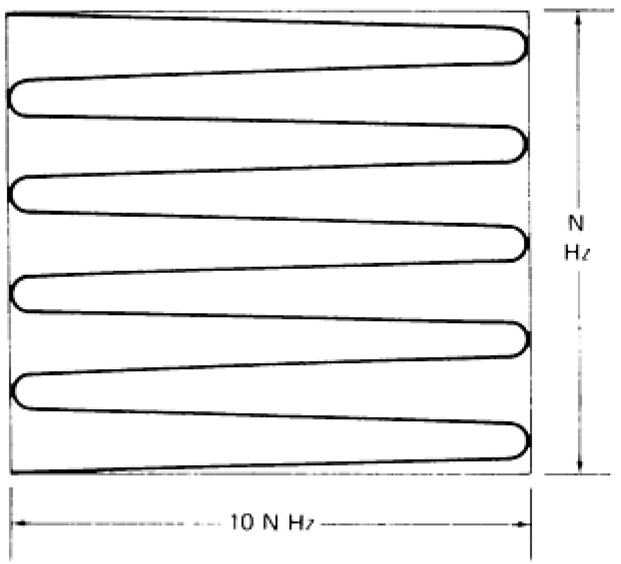

Fig. 11 Scanning a small focused laser spot to generate a square, broad area beam

Devices that scan in only one direction are line sources The width of the line is equal to the diameter of the focused laser spot that is being scanned. This can be varied by defocusing. The length of the line can also sometimes be varied by changing the scan amplitude. Such devices are therefore quite flexible, and because they form laser spots with high power density, they are very useful when only shallow cases are required. In particular, such devices are used when the workpiece has low mass and can only support self-quenching if the total energy input is low. Figure 12 shows two types of scanners used to generate high-intensity line sources.

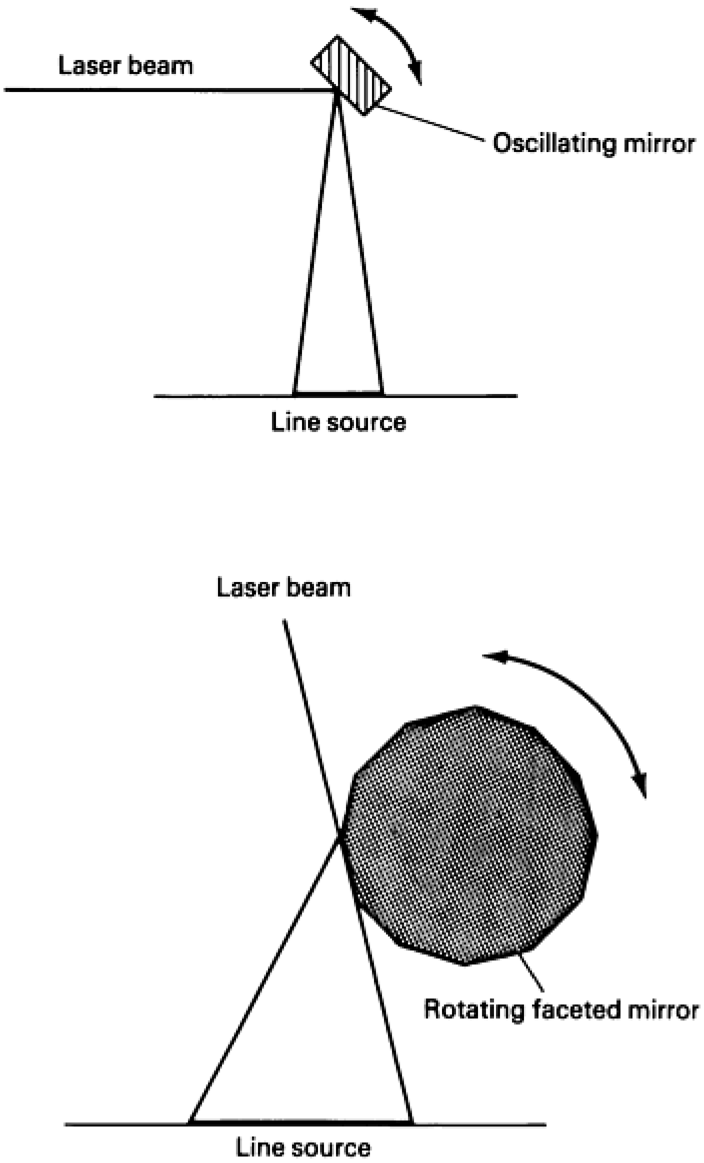

Fig. 12 Laser beam scanners for generating line sources

Another method of forming a square or rectangular beam is to use a device known as an optical integrator. This device, shown in Fig. 13, is an array of flat mirrors mounted on a spherical surface placed to intercept the output laser beam. Each mirror forms an image of the part of the output beam that it intercepts, and all of the images from the array will be formed in the same position. In this way, the output beam is reshaped to form the desired square or rectangular spot in the focal plane of the integrator, having uniform power density over the illuminated area on the workpiece surface.

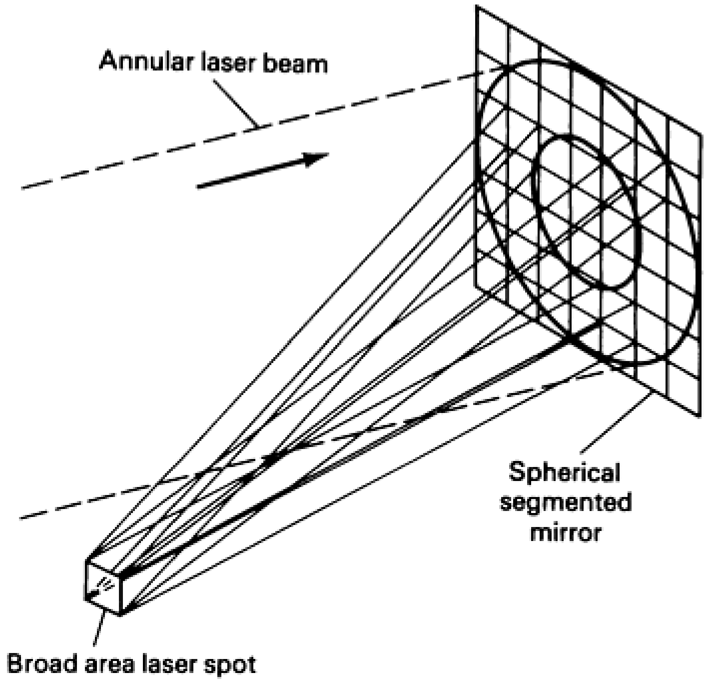

Fig. 13 Optical integrator

Presently, new techniques are being developed, both in Europe and the United States, for generating laser spots with "programmed" power density. Computer-generated patterns can be transferred to metal mirrors that allow the formation of a variety of laser spot shapes in the focal plane, and the power density of such laser spots can be given desired power density distributions.

One application of this technique is in generating a square spot with a higher-than-normal power density in the leading edge of the spot. Traversing such a spot over a steel surface will, if the power density ratio between the edge and the rest of the spot is about two to one, result in a very rapid temperature increase followed by a period of nearly constant temperature increase until the trailing edge is reached. This allows the material to be kept at austenitizing temperatures longer than is the case for a spot with uniform power density with equal maximum processing temperature, as shown in Fig. 14. The longer austenitizing time available with the "hot" leading edge is particularly useful for laser hardening of nodular cast irons and low- or medium-carbon steels with relatively large amounts of free ferrite. The increased time above the transformation temperature allows for the diffusion of carbon to occur in such cases, which is necessary for the formation of homogeneous austenite.

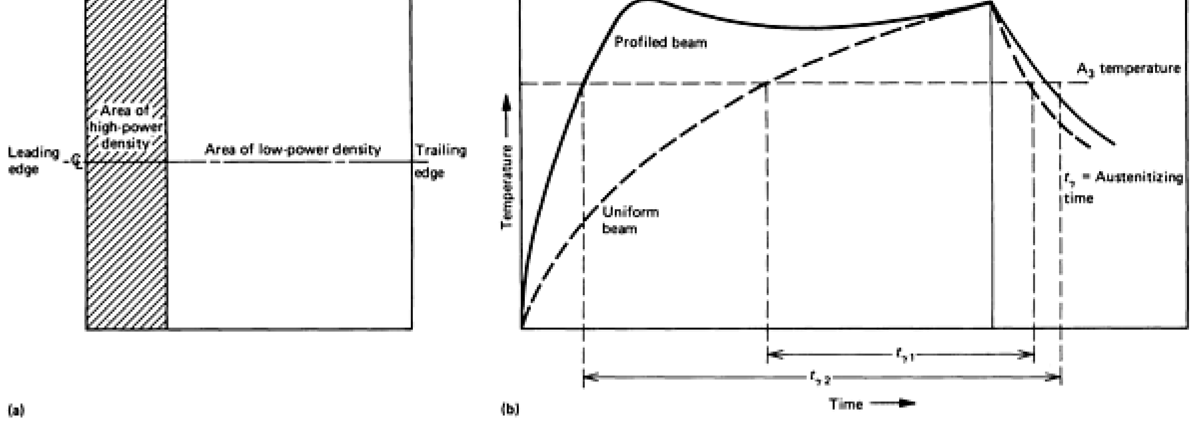

Fig. 14 Laser surface transformation hardening with a profiled laser beam. (a) Power density distribution in the profiled laser spot. (b) Temperature profiles along the centerline of the laser spot

Both scanning optics and integrator optics form beams that can be redirected by flat mirrors or refocused by appropriately curved mirrors (Fig. 15). In this way, the laser spot can be generated in the exact shape at desired location. The complexity of this use of optics, however, can prevent the use of lasers in a heat treat shop.

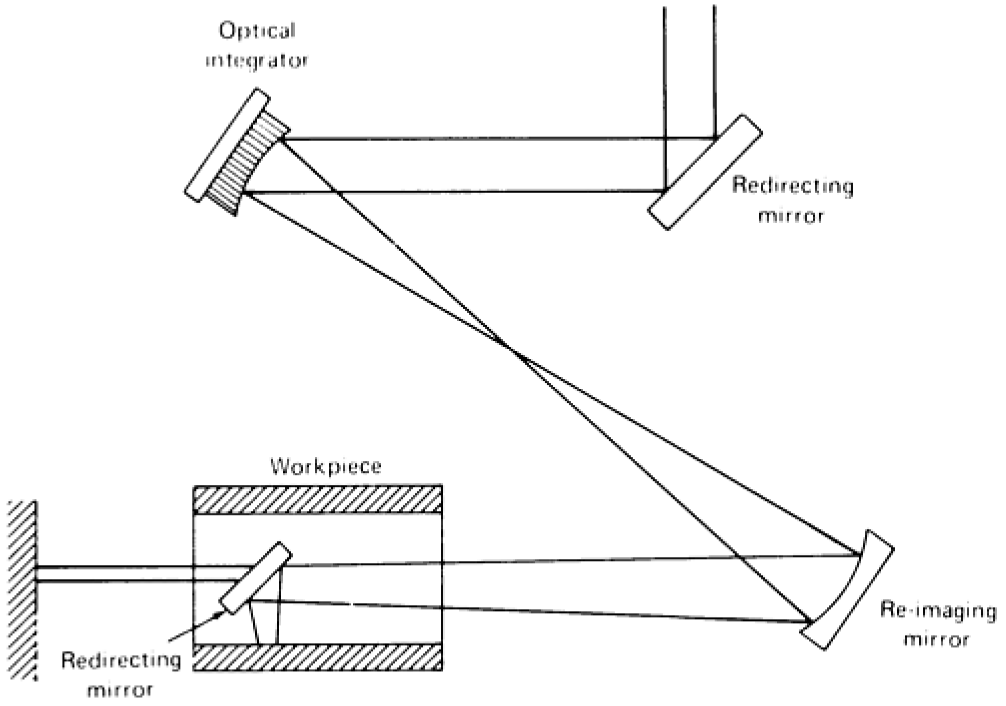

Fig. 15 Optical system for laser heat treatment of the inner surface of a cylinder

For workpieces of cylindrical design, special optical components called toric mirrors can be used. These mirrors take advantage of the fact that the output beam from the laser can be made hollow or annular in cross section. Directing the beam by suitable mirrors onto the workpiece causes a continuous band of laser irradiated surface to form around the periphery of the workpiece, either on the inner surface of a hollow cylinder or on the outer surface of a cylinder, as shown in Fig. 16. The complete surface can be laser treated by moving the workpiece in the axial direction through the ring-shape laser spot. No backtempering is encountered because no start/stop or parallel spiral zones are generated. The relatively large area of the ring-shape laser spot limits the size of workpieces that can be processed with this technique to about 25 mm (1 in.) diameter for each 8 kW of power available.

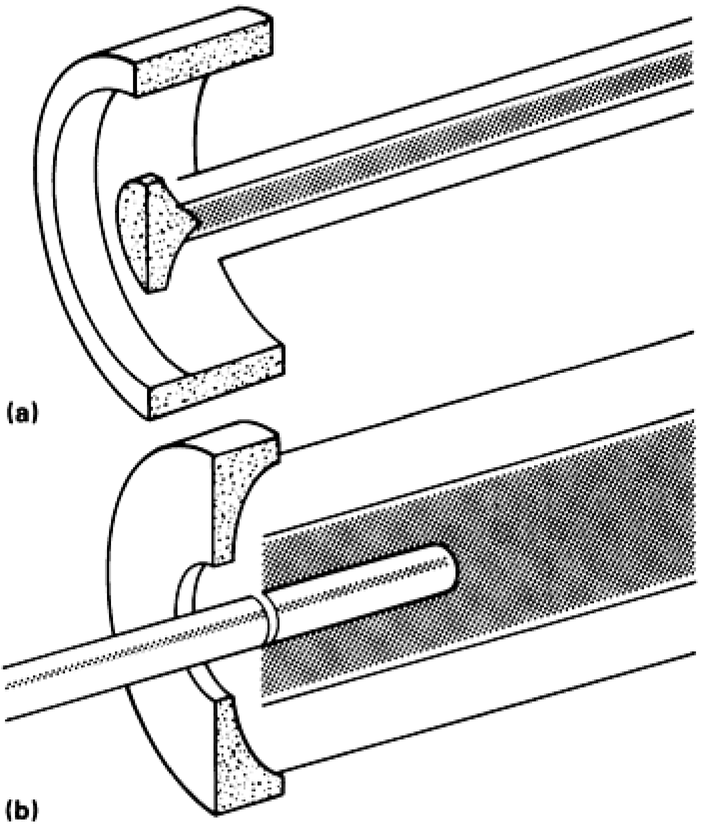

Fig. 16 Toric mirrors for treating cylinders. (a) Outer surface of cylinders. (b) Inner surface of hollow cylinder

Another technique that can be used for nonplanar surfaces is beam splitting. The laser beam is split into two equal parts by a copper prism, and the individual parts of the beam are directed at different angles to the workpiece surface by suitable reflective mirrors. Figure 17 shows the application of this technique to heat treating a wide semi-circular groove. If only a single beam, normal to the bottom of the groove, had been used, the angle of incidence of the laser beam at the left and right top of the groove would have been too shallow to generate sufficient heat. By using two beams as shown, this problem can be overcome.

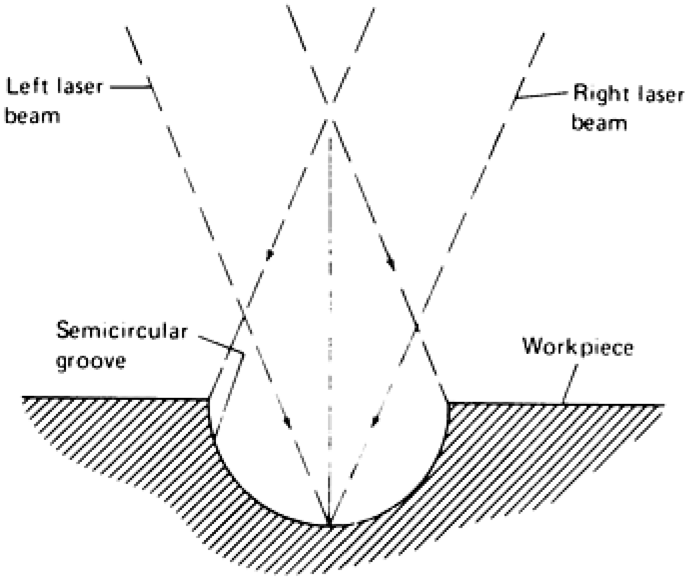

Fig. 17 Using two equal laser beams to surface harden a semicircular groove

Application

Lasers have become commonplace in many fields, but their use in surface treatments is relatively limited. This is probably due to the high cost of the large lasers that are required for most metalworking operations. Lasers are also not very efficient from the energy standpoint. The output energy may be only 10% of the input energy from flashlamps or arc sources. This is another reason why lasers can be expensive.

Nonetheless, the flexibility of laser delivery systems, low distortion, and high surface hardness have made lasers very effective in selective hardening of wear and fatigue-prone areas on irregularly shaped machine components such as camshafts and crankshafts. Molian (Ref 1), for example, has tabulated the characteristics of 50 applications of laser transformation hardening. The materials hardened include plain carbon steels (1040, 1050, 1070), alloy steels (4340, 52100), tool steels, and cast irons (gray, malleable, ductile). The energy-absorbing coatings are listed, and typical case depths for steels are 250 to 750 μm and for cast irons about 1000 μm.

Some of the techniques used in laser hardening applications are described in the following three examples. These examples do not necessarily convey predominant commercial usage but rather the type of systems required in a particular application. Further information on laser systems and their application in metalworking is given in the Selected References listed at the end of this article.

Laser Surface Hardening of 4140 Cylinder with Conical Top. The object was to surface harden the conical part of the workpiece shown in Fig. 18 to increase the wear resistance. The minimum required case depth was 1.1 mm (0.044 in.); the hardness at this depth should be 45 HRC. The workpiece had been hardened and tempered to 40 to 42 HRC prior to laser processing to obtain strength and ductility.

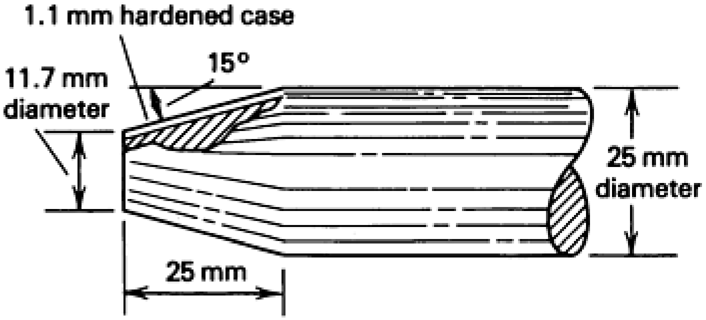

Fig. 18 Laser hardening of conical SAE 4140 workpiece

Because the workpiece was cylindrical and had a maximum diameter of 25 mm (1 in.), a toric mirror could be used in conjunction with a 15 kW CO_2 laser. The processing arrangement is shown in Fig. 19. In this fixture, the workpiece was rotated at 1300 rev/min under the ring-shape laser spot formed by the toric mirror. This was done to ensure uniform power density around the periphery of the workpiece. The ring-shape spot had a width of 5 mm (0.2 in.), and hardening of the desired area could be obtained by moving the workpiece in the axial direction. In this way, the entire area could be covered without forming any overlap zones.

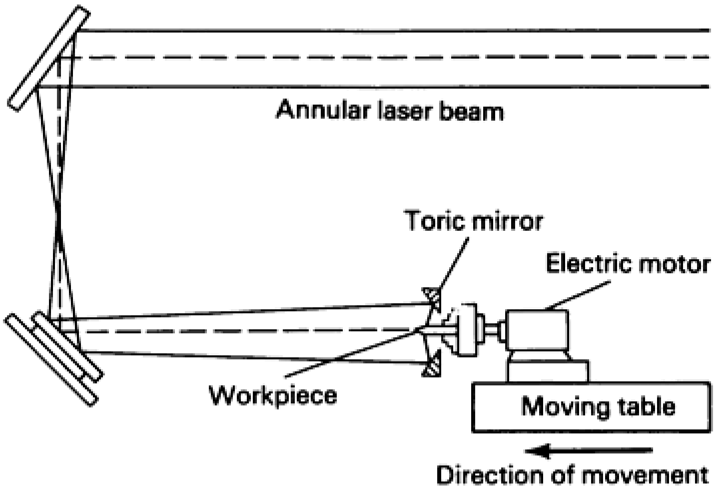

Fig. 19 Arrangement for laser heat-treating SAE 4140 cylinder with conical tip

Because the area under the ring-shape laser spot will increase as the beam sweeps from the tip of the cone to the cylindrical part of the workpiece, the power input had to be increased linearly with the distance in order to maintain constant power density.

Theoretical calculations, using Eq 1 with a thermal conductivity of 0.35 W/cm · °C (0.49 W/in. · °F) and a thermal diffusivity of 0.070 cm^2/s (0.01 $in.^2/s$), showed that a processing speed of 229 mm/min (9 in./min) and a power density of 1620 W/cm^2 (10,450 $W/in.^2$) would give a surface temperature of 1360 °C (2480 °F). This is only an estimate, as Eq 1 assumes a plane workpiece rather than a cylindrical one. To process at a slower rate and at lower power density would give deeper heat penetration, but the self-quenching rate would be lower. On the other hand, processing at higher speed and power would lead to shallower heat penetration.

The workpiece was coated with flat, black spray paint and processed at the following parameters:

- Axial speed: 221 mm/min (8.7 in./min); or 3.8 mm/s (0.15 in./s)
- Power: 3500 W at the tip, increasing to 7600 W at the cylindrical portion
- Rate of power increase: 620 W/s

The hardened case obtained ranged from 1.65 mm (0.065 in.) at the tip to 2 mm (0.08 in.) at the tip to 2 mm (0.08 in.) at the cylindrical portion of the workpiece. The surface hardness was 58 to 59 HRC.

Laser Surface Hardening of 4140 Cylinder Using a Square Laser Spot. When the use of toric mirrors is not practical because of laser beam shape (not annular) or because the diameter of the bar to be hardened is too large, the treatment can be performed with a square beam, as shown in Fig. 20.

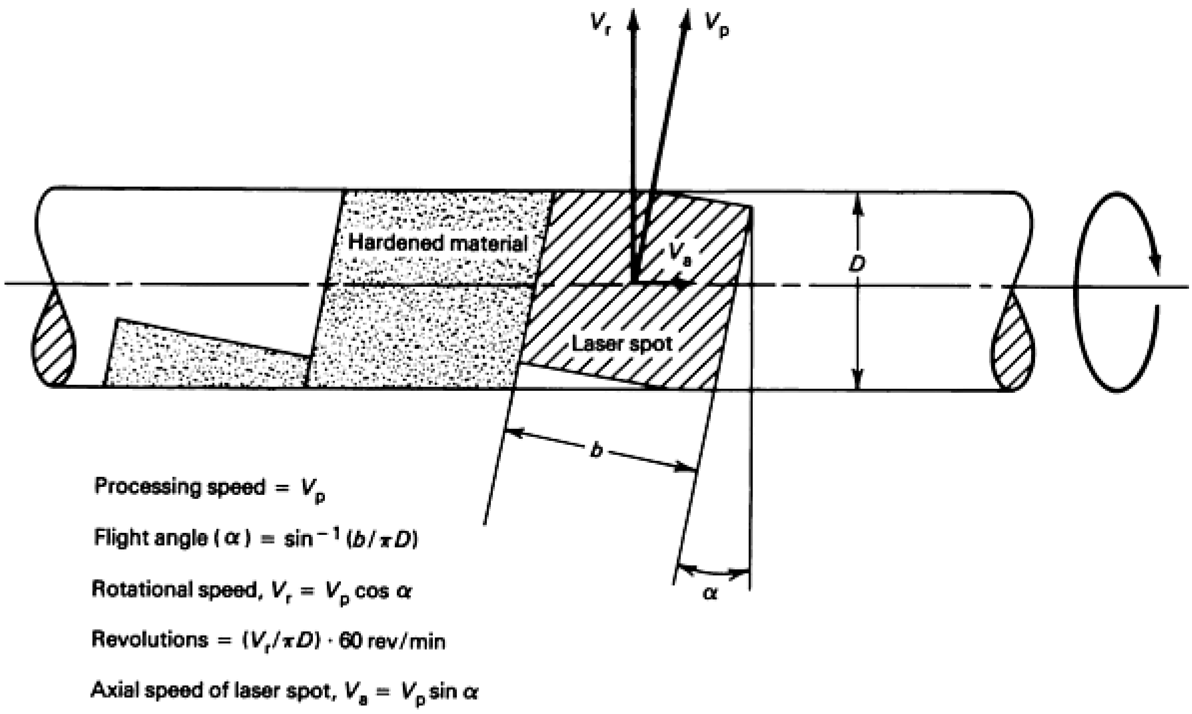

Fig. 20 Laser hardening of SAE 4140 steel bar using a square laser spot

Such spiral pattern "candystriping" can be used on any bar of reasonable size, but the zones between flights of the spiral pattern will have low hardness due to lack of closure, or, if positive overlap is used, due to back tempering.

In this processing, the laser spot must be angled in order to obtain uniform heat input to all spots on the surface of the bar. The angle depends on the size of the laser spot and the diameter of the bar.

In the present example, the bar had a diameter of 1.59 cm ($\frac{5}{8}$ in.) and the laser spot was 1.27 cm (0.5 in.) square. The tilt angle of the laser spot was 14.75°, and the desired processing speed was 2.12 cm/s (0.835 in./s) at 3.6 kW power. The axial translation speed of the laser spot was then calculated to be 0.53 cm/s (0.2 in./s), and the rotational speed was 2.05 cm/s (0.807 in./s) or 25.46 rev/min.

The resulting case was 1.8 mm (0.07 in.). This is much deeper than would be expected from using the prediction model described earlier. In this case, such a simple model cannot be used due to the geometry of the workpiece.

Laser Surface Hardening of Cast Iron Camshaft Lobes. The surface of the lobes of an automotive camshaft made from ductile cast iron (see Fig. 21) was to be surface hardened to increase wear resistance. The desired case depth, defined as the depth where the hardness was 50 HRC, was 0.5 to 1.0 mm (0.02 to 0.04 in.).

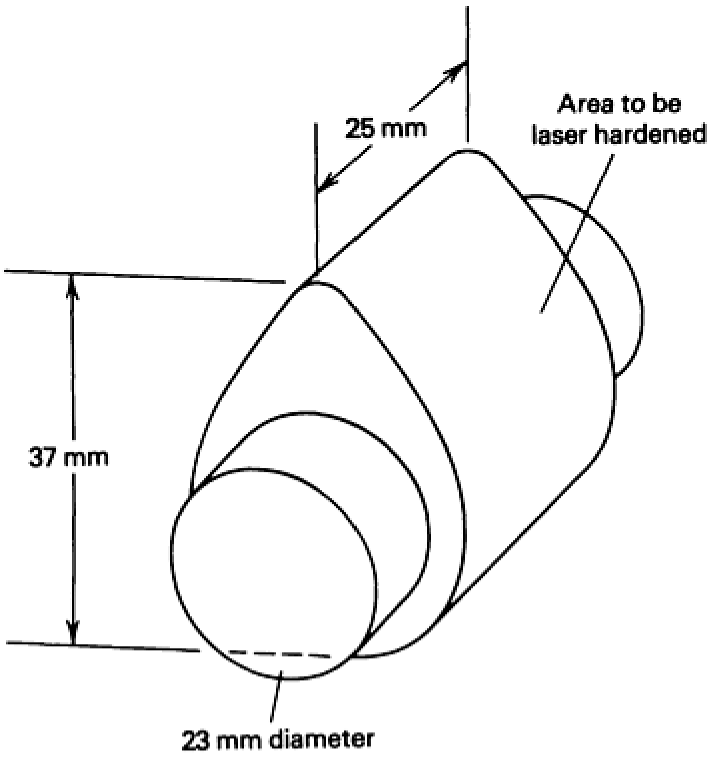

Fig. 21 Ductile cast iron cam from automotive camshaft

A 15 kW CO_2 laser was used for the processing. The optical system delivered a focused spot, with a diameter of 10 mm (0.4 in.) to the workpiece. This spot was scanned over a distance of 22 mm (0.9 in.) normal to the direction of processing and 25 mm (1 in.) in the direction of processing. The frequency of scanning was 125 Hz in the normal direction and 700 Hz in the processing direction, forming a rectangular spot 22 mm by 25 mm (0.9 in. by 1.0 in.) on the camlobe surface.

To obtain an even hardened case around the periphery of the camlobe, it was necessary to vary the angular speed of rotation of the lobe under the laser beam. The reason is that the angle of incidence of the laser beam to the workpiece changed during rotation, from nearly normal incidence at the cylindrical portion of the lobe to a grazing incidence of only 20 to 30° at the flat portion. Furthermore, at constant rotational speed, the linear speed of processing would vary as the lobe rotated. This was obtained by mounting the workpiece on a rotary table. The speed of rotation was varied by means of an electromechanical controller in a pre-determined manner.

The camlobe was laser hardened using a manganese phosphate coating to increase energy absorption. Because of the design of the workpiece, it was difficult to predict the optimum processing parameters by calculations and the parameters were, therefore, evaluated by trial and error. The results were:

Power input	9 kW
Power density	1600 W/cm^2 (10,300 W/in.^{2})
Linear speed of processing	

at the cylindrical portion	760 mm/min 30 (in./min)
at the flat portion	180 mm/min (7 in./min)
Depth of case	0.55 mm (0.022 in.)

The hardness profile of the surface layer of the camlobe is shown in Fig. 22.

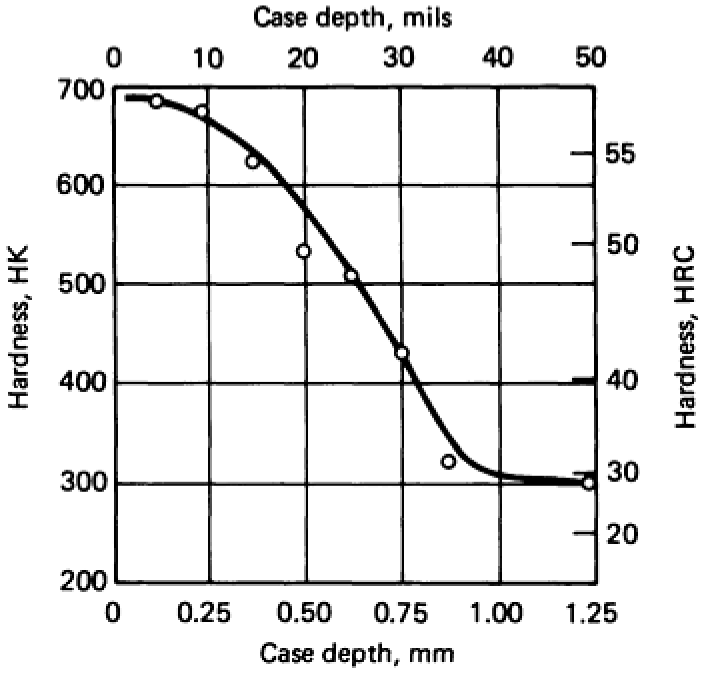

Fig. 22 Hardness profile of laser surface hardened cast iron camlobe

Laser Surface Hardening of a Large Gear. The gear, made from SAE 1045 steel, had a diameter of 28 cm (11 in.) and a thickness of 10 cm (4 in.). The gear had 34 teeth and a diametral pitch of 3.35. To increase fatigue and wear properties, a hardened case of 1 mm (0.04 in.) was desired, extending in a continuous manner from the tip of one tooth to the tip of an adjacent tooth, as shown in Fig. 23.

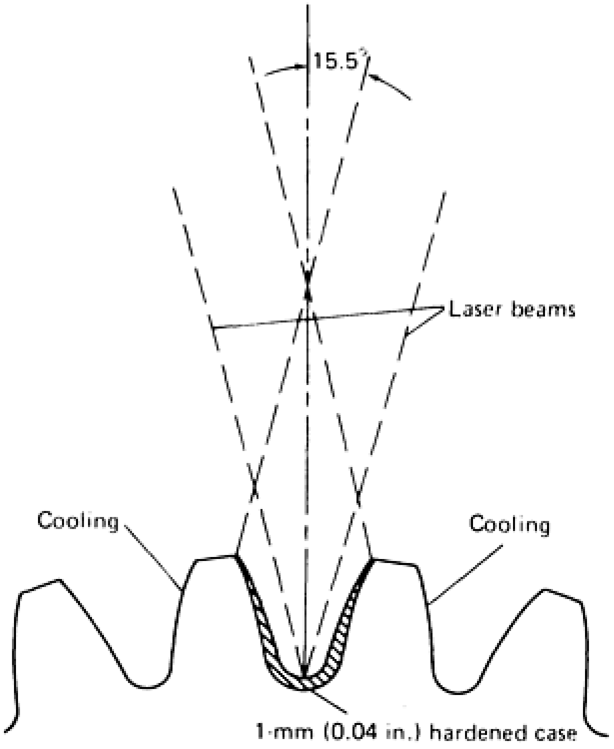

Fig. 23 Laser hardening of SAE 1045 gear

In this application, two laser beams had to be directed toward the surface of the gear teeth at an angle of 15.5° from the normal to the root area, as shown in Fig. 23. These two beams must be abutting but not overlapping at the root between the teeth. A single beam with normal incidence to the root area could not be used because the angle of incidence at the adjacent fillets would be too shallow to generate a hardened case in this critical area, where fatigue cracks are likely to originate.

The output beam from a 15 kW CO_2 laser was split into two equal parts by a reflective copper wedge. Each beam was then directed to the workpiece surface in the form of a 12.5 mm by 12.5 mm (0.5 in. by 0.5 in.) spot by two optical integrators, as shown in Fig. 24. The projected area of each beam on the workpiece surface was approximately 12.5 mm by 25.4 mm (0.5 in. by 1 in.); thus, the total irradiated area was 3.18 cm^2 (0.5 $in.^2$).

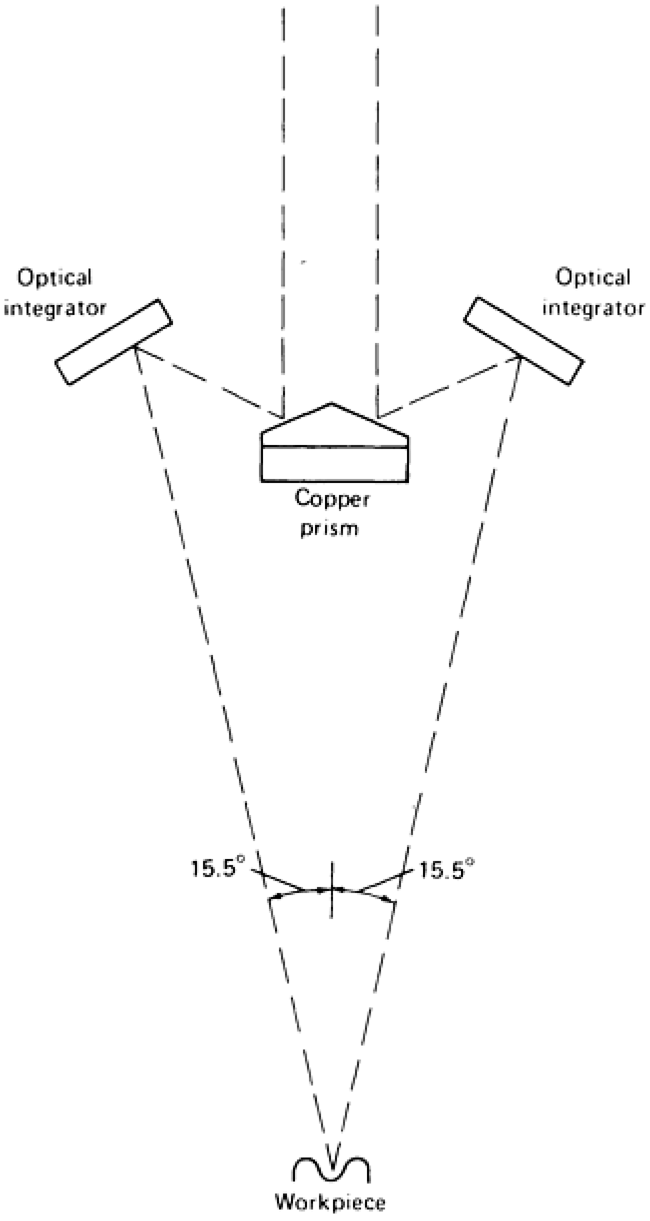

Fig. 24 Dual beam optics for laser gear heat treating

After surface preparation with flat, black spray paint, the gear was laser processed at a total power input of 8.8 kW and with a translation speed of 500 mm/min (20 in./ min). The calculated overall power density was 1380 W/cm^2 (8900 W/in.^{2}), but the actual power density varied somewhat over the interaction area because of the variation of incidence angle to the curved surface.

Sequential runs were made on teeth 120° apart to minimize heat distortion. Water cooling was used on tooth flanks adjacent to the processing area to prevent backtempering of previously processed teeth. The obtained case depth (45 HRC) was 1.2 to 1.3 mm (0.046 to 0.052 in.) at mid flank and at the root and 1 mm (0.04 in.) at the fillets. Surface hardness was 59 to 60 HRC.

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Electron Beam Surface Hardening of Steels

S. Schiller and S. Panzer, Forschungsgesellshaft für Elektronenstrahl-und Plasmatechnik mbH, Dresden B. Furchheim, Sächsische Elektronenstrahl, GmbH, Chemnitz, Germany

Introduction

ELECTRON BEAM HARDENING TREATMENT (EBHT) is a short surface hardening procedure for martensitically hardenable ferrous materials. Austenitizing occurs through the energy transferred by electron beams. Precise application of the energy with respect to workpiece location and elapsed time using a focused and deflectable electron beam makes it the process of choice, especially for the partial hardening of highly stressed surface regions in components. The austenitizing process advances from the surface toward the inner core regions of the component via heat conduction, thus allowing for a defined adjustment of the hardness penetration by selecting a suitable energy transfer duration. Typical hardening depths obtained by the EBHT process range from 0.1 to 1.5 mm (0.004 to 0.006 in.). The rapid cooling of the austenite required for martensite formation occurs through a self-quenching process that is dependent on the thermal conductivity and starts after the energy transfer has ceased. Depending on the material selected, the workpiece thickness required should be at least 5 to 10 times the austenitizing depth.

Although developed in 1970 (Ref 1), this technique has only recently found practical application in the metals industry. Because it offers the advantages of extremely low hardening distortion and relatively low energy consumption, electron beam hardening provides the metallurgist with an additional option to conventional hardening techniques. For certain specialized applications, electron beam hardening is competitive with both case hardening and induction hardening processes in the heat-treating marketplace.

Reference

1. W. Hiller and R.M. Silva, 2nd Electron Beam Processing Seminar, Frankfurt, Universal Technology Corporation, Dayton, OH, 1972, p 3g1-3g32

Energy Absorption and Heat Conduction

As shown in Fig. 1, the electrons of the beam hit the component surface and penetrate into the metal surface. Because of the intense interaction between the beam electrons and the atoms of the material being bombarded by the beam, the electrons lose their energy rapidly. The majority of the energy lost by the electrons is transformed into heat in the absorption volume. Approximately 75% of the power generated by an electron beam is converted to heat when the beam is incident perpendicular to a steel surface (Ref 2). Substantial energy losses are incurred chiefly by the backscattering of incompletely decelerated electrons. The efficiency of this energy conversion is independent of the optical properties of the workpiece surface and the temperature of the material. When the incident beam is inclined to the steel surface, energy losses are increased because of enhanced electron backscattering.

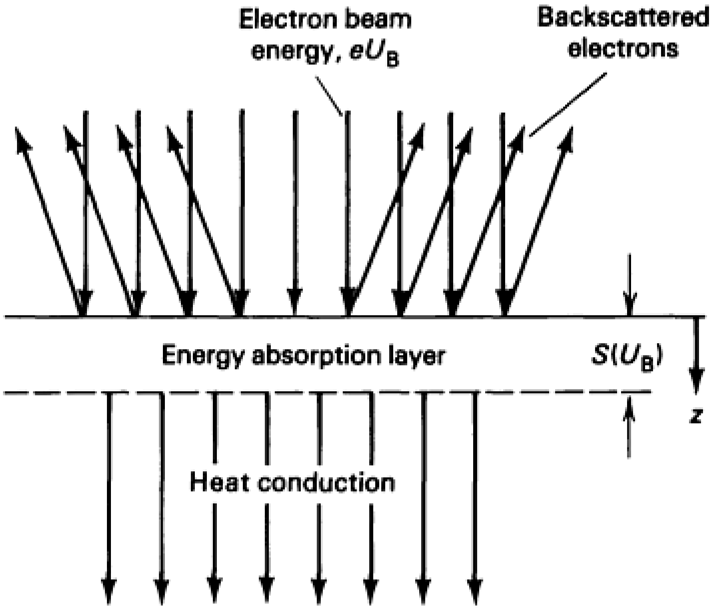

Fig. 1 Energy absorption zone and heat conduction zone generated by an electron beam on the surface of a workpiece

The thickness of the energy absorption layer is fixed by the electron range, *S* (in µm), which is given by the equation:

$$S = 2.1 \text{ x } 10^{-8}\left(\frac{U_B^2}{r}\right) \qquad \textbf{(Eq 1)}$$

where the constant 2.1 × 10^{-8} is dimensionless, U_B is the acceleration voltage of the electron beam in volts, and ρ is the density of the material in g/cm^3 (Ref 2). For ferrous metals, typical acceleration voltages of the beam range from 60 to 150 kV and typical electron range values are 10 to 50 µm (0.0004 to 0.002 in.).

As a result of the energy transfer, it is the material in the energy absorption volume which is heated first. This results in a temperature gradient toward the interior of the component. Because of the heat conduction in the direction of this gradient, the regions adjacent to the absorption volume are heated accordingly. The longer the duration of the energy transfer, the farther the heated zone of the material extends beyond the actual energy absorption volume. The temperature field, *T* (*x*, *y*, *z*, *t*), that results is described by the heat conductivity equation:

$$\left(\frac{\partial}{\partial t} - a\frac{\partial^2}{\partial r^2}\right)T$$

$$T = \left\{ {}_0\frac{v(x,y,z,t)}{rc} \; for \; 0 \le t \le t_H, a = \frac{l}{rc} \right\} or \; t>t_H \qquad \textbf{(Eq 2)}$$

where **r** is a vector in space defined by $|\mathbf{r}|^2 = (x^2 + y^2 + z^2)$ and *a* is the temperature diffusivity resulting from the heat conductivity (λ), the specific heat (*c*), and the density (ρ) of the material. The term *v* (*x*, *y*, *z*, *t*) describes the heat source distribution in the energy absorption volume which extends over the energy transfer duration, $t = 0$ to $t = t_H$. The solution to the equation of heat conduction (Eq 2) for different source distributions *v*and various boundary conditions is available in technical literature covering thermodynamics (Ref 3).

However, one general result of the resolved heat conductivity equation (Eq 2) shall be dealt with here in more detail because it is of great significance for electron beam hardening. This is the sudden energy transfer which occurs within a time $t_H \rightarrow 0$. In this case, the energy absorption layer is heated and gives an energy accumulator that discharges at a time constant:

$$t \approx \frac{S^2}{a} \quad \textbf{(Eq 3)}$$

because of the heat conduction. This means that the energy absorption layer maintains the energy transfer into the interior of the workpiece for a certain time even after the pulsed beam action has ceased. As a result, it is immaterial whether a particular energy flow density is transferred to the surface either continuously or pulsed, provided the timed pulse spacing lies within the time τ given by Eq 3 for the generation of the temperature field in a distance $z > S$ to the surface. Because of the interdependence of Eq 1 and Eq 3, however, the heat-retaining capacity of the energy absorption layer and the discharge time constant will strongly increase with the acceleration voltage of the electron beam. Depending on the acceleration voltage and material, this results in values of τ in a range of a few μs to a few hundred μs.

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Energy Transfer and the Temperature-Time Cycle

The energy transfer mechanism to the workpiece surface with respect to location and time determines the time-dependent spatial thermal profile in the workpiece and, therefore, both austenitizing and martensite formation in the material is quite extensive. Two important cases of the transferred areal energy and its effects on the thermal profile in the outer layer of the workpiece are shown in Fig. 2. The energy flow densities were chosen so that the surface is kept just below the melting temperature. With a time-invariant energy flow density, the surface temperature varies directly with the square root of the action time and attains the allowable ultimate temperature only at the end of the transfer duration t_H (see Fig. 2a). With an adequate degressive energy flow density, the surface can be kept at the permissible temperature throughout the energy transfer duration (see Fig. 2b). (However, because the energy flow density diverges as $t \rightarrow 0$, this case can be implemented in practice only approximately.) Such an isothermal energy transfer offers the advantage of a rather high rate of temperature rise desired for austenitizing at the highest possible energy utilization for this process.

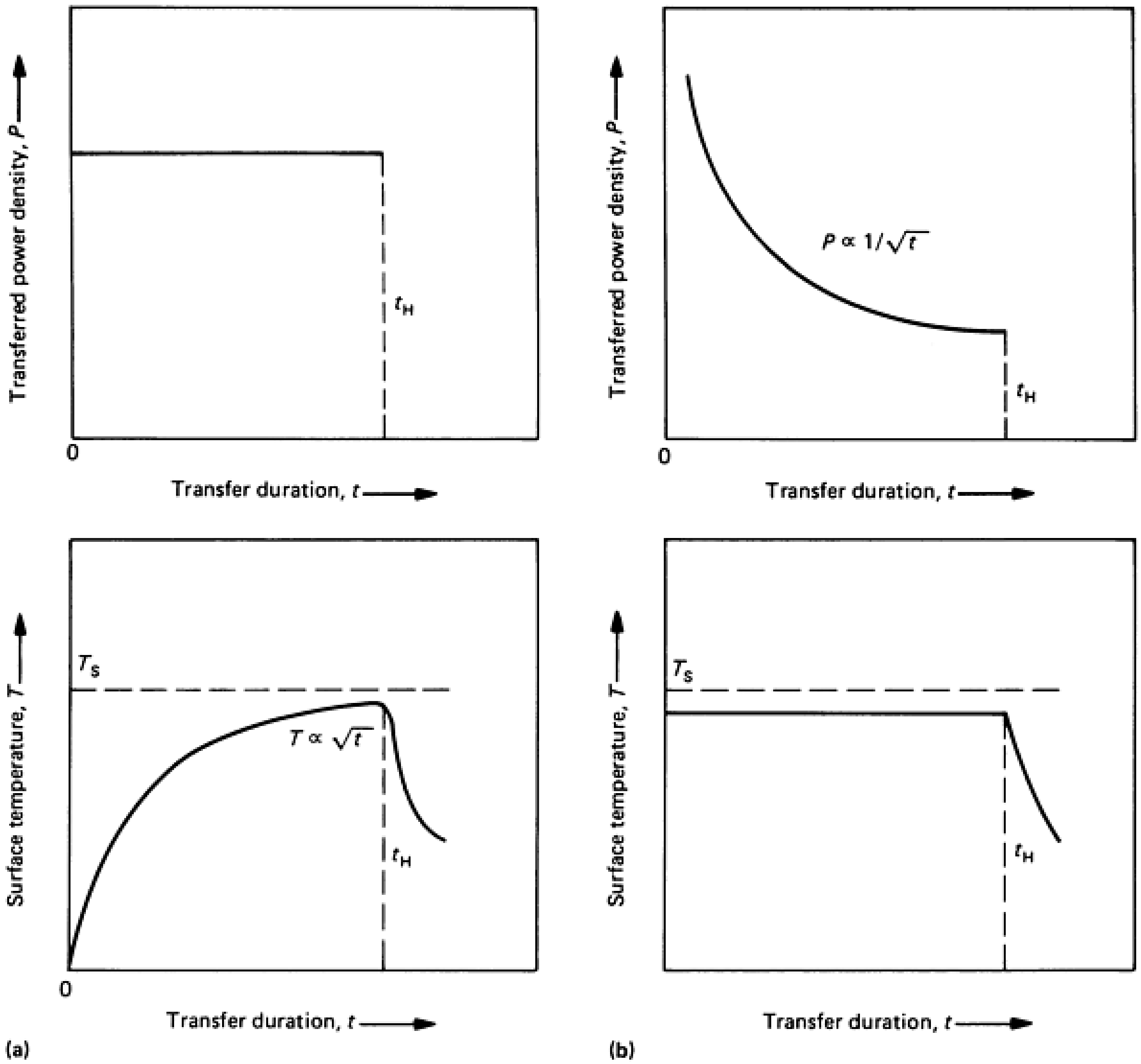

Fig. 2 Relation between time response of the transferred power density, *P*, and the surface temperature, *T*, for two cases. (a) Constant power density, where *P* does not vary but *T* varies directly with $\sqrt{t}$. (b) Isothermal energy transfer, where *T* does not vary but *P* is inversely proportional to 1/ $\sqrt{t}$ Melting temperature, T_s

Pulsed Energy Transfer. When the energy is transferred to the surface in a pulsed mode, a temperature oscillation occurs in the rhythm of a pulse train both in the energy absorption volume and on the surface itself. If the energy pulses have been chosen so that the allowable maximum temperature on the surface, T_S, is attained just at the pulse end, the surface temperature will oscillate between this temperature and a time-dependent minimum. The time dependence of this minimum surface temperature is illustrated in Fig. 3 for various pulse spacings, Δt, and electron ranges, *S*. The effect of both parameters on the rise of the minimum surface temperature up to the tolerable final value of approximately (T_S - 100) °C or (T_S - 212) °F becomes clearly evident. At a given electron range and energy transfer duration, or austenitizing depth, there is a minimum rate for the energy transfer. Below this value, the temperature oscillation cannot be tolerated.

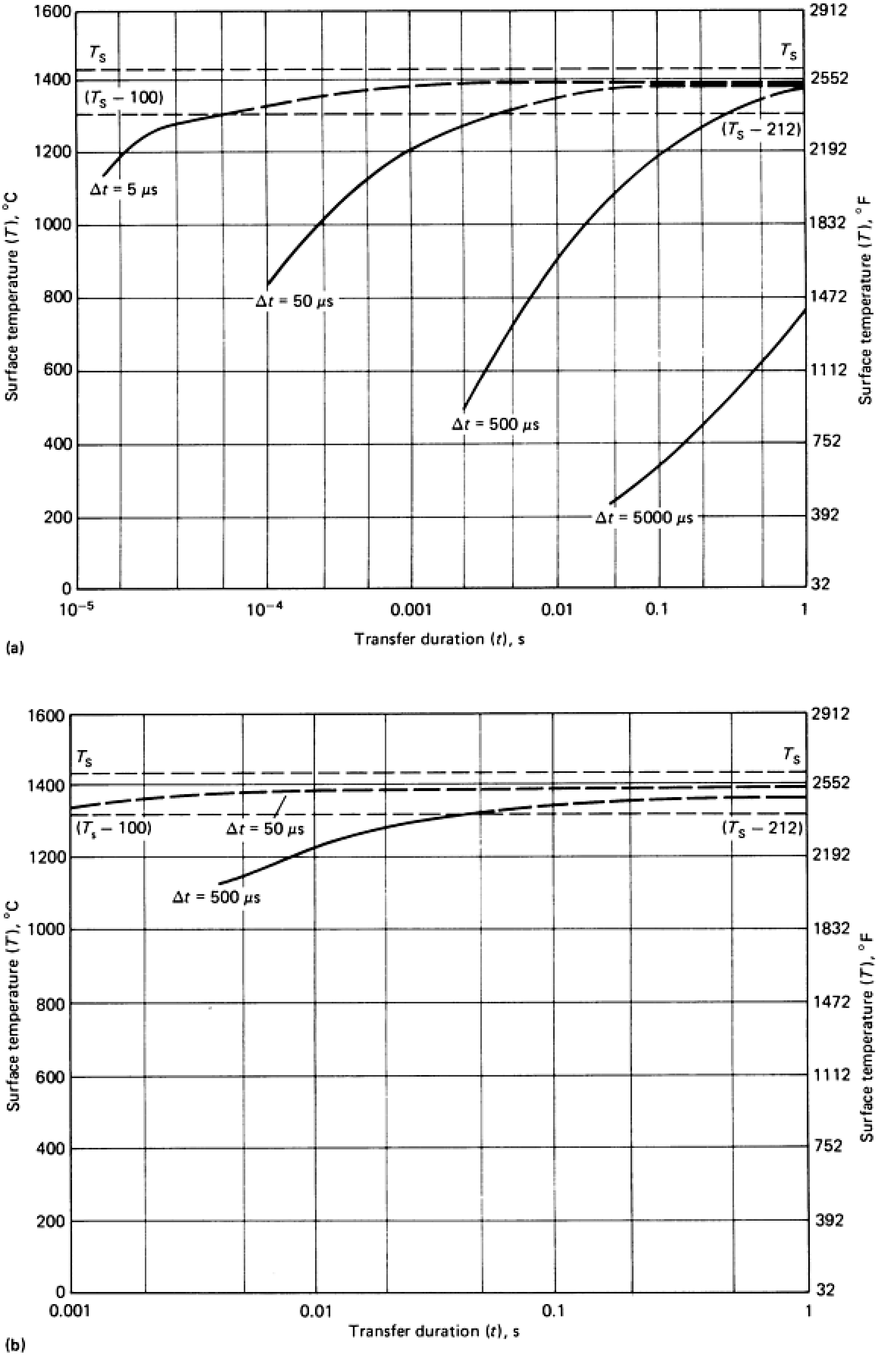

Fig. 3 Plot of surface temperature, T, below the melting point, T_S, versus transfer time, t, for selected pulse spacings, Δt, of 5, 50, 500, and 5000 μs and two selected electron ranges, S, of (a) 10 μm and (b) 50 μm. Data

are for the minimum surface temperature obtained for the pulse energy transfer obtained at the Δ*t* values used.

For the simple experimental determination of the necessary minimum rate of the energy transfer, it is suggested to use a transferred energy density, e_F, as a function of the pulse rate which still prevents the surface from incipient fusing. Figure 4 shows the result obtained for an extreme case of a line-scanned electron beam at a workpiece motion normal to the direction of scan (Ref 4). From the data in Fig. 3 and 4, it is possible to derive coinciding pulse rate requirements for the hardening problem described in Fig. 3.

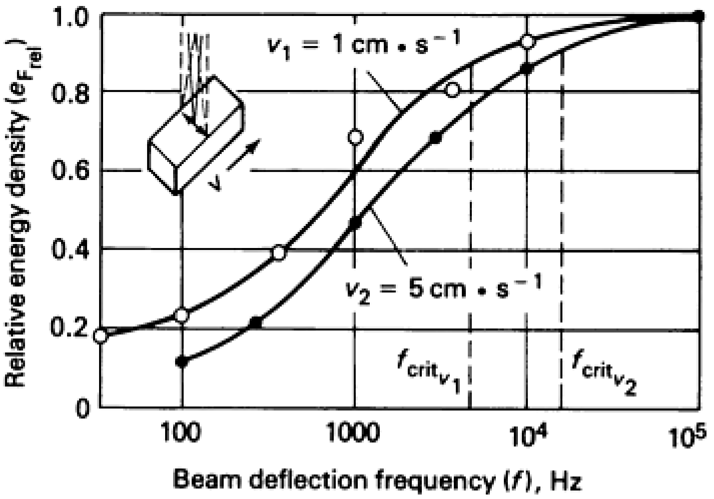

Fig. 4 Relative energy density, eF_{rel} **=** e_F**(f)/**e_F**(100 kHz), transferable without superficial fusing as a function of the beam deflection frequency, *f*, for two different moving rates,** v_1 **and** v_2**, in C 45 steel. Electron energy, 60 keV; beam spot, 0.3 mm (0.01 in.) deflection; triangular function; and critical frequency at selected moving rates,** $fcrit_{v1}$ **and** $fcrit_{v2}$

Thermal Profile of the Workpiece. In the case of electron beam hardening with isothermal energy transfer, the surface temperature is practically constant throughout the energy transfer duration and is chosen such that it lies just below the melting temperature. As the distance to the surface increases, the temperature rise and the maximum temperature obtained will differ as shown in Fig. 5. At a specific distance below the surface, z_o, the austenitizing temperature is attained. At a greater distance, however, such is not the case. Therefore, different austenitizing conditions exist at different distances below the surface of the steel.

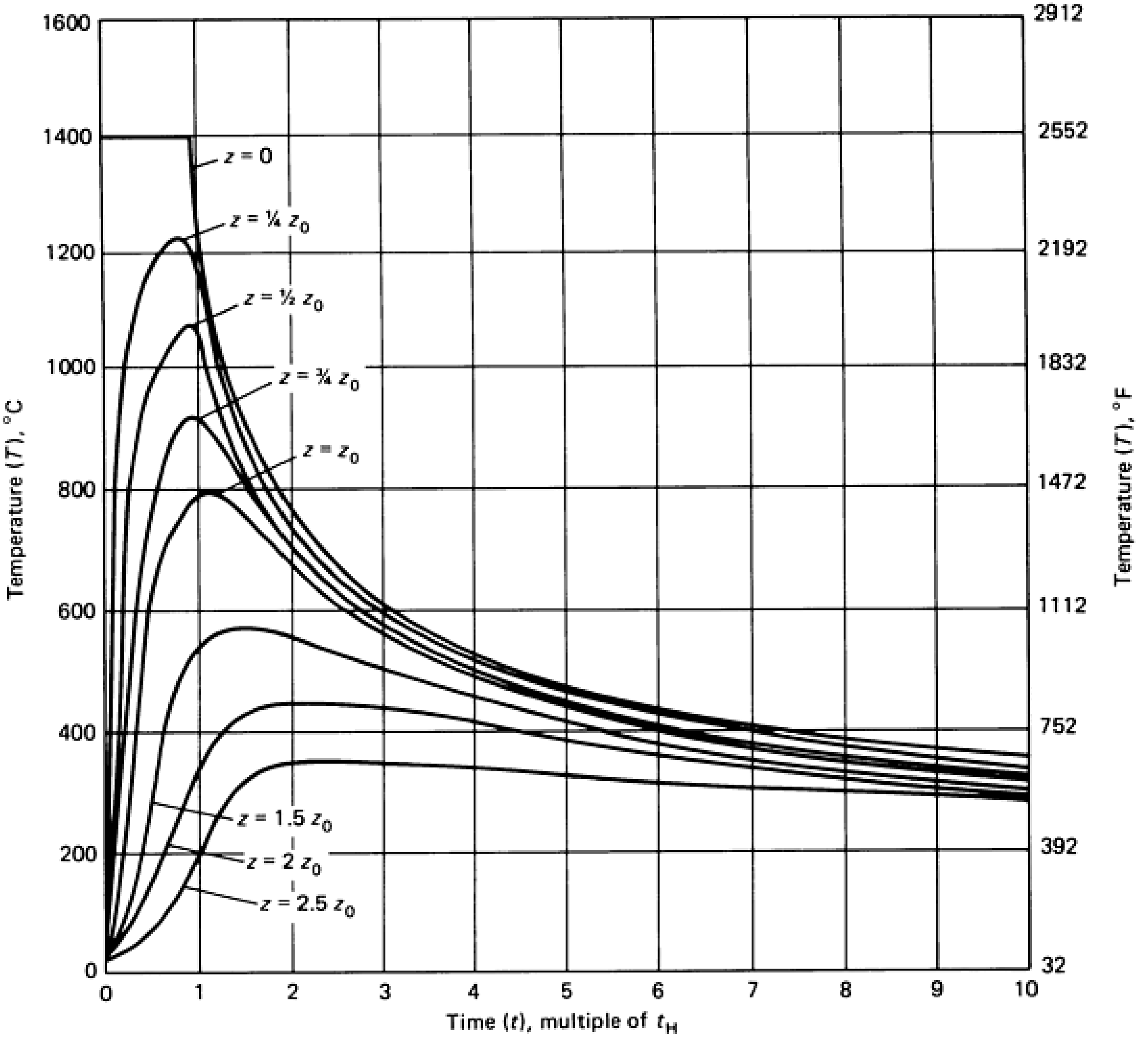

Fig. 5 Plot of temperature versus time, *t*, expressed as a multiple of the energy transfer duration, t_H, as a function of distance from the surface, *z*, for the isothermal energy transfer in steel. Depth is expressed with *z* being a fraction or multiple of the austenitizing depth, z_o.

After the energy transfer duration t_H has elapsed, cooling takes place so that the surface-distant regions of the material are always at a lower temperature level than the near-surface regions. In contrast to hardening techniques that use quenching by an external medium, cooling occurs in the component from the inside core toward the outside surface.

The austenitizing depth determines the thickness of the hardened layer. Heating of the material beyond the austenitizing depth represents an unavoidable internal energy loss that is due to the mechanism of heat conduction. The temperature gradient on the austenitizing boundary obtained at the end of the heat-up duration and the relative share in the internal energy loss are determined by the time behavior of the surface temperature. With an isothermal energy transfer and a surface temperature close to the melting temperature, the maximum austenitizing depth is obtained at a minimized internal energy loss under otherwise given conditions. The slope of the temperature gradient on the austenitizing boundary is reduced with increasing austenitizing depth.

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Control of Beam Location and Duration

In the case of an areal energy transfer, electron beam hardening requires energy flow densities on the order of 10^3 to 10^4 W/cm^2 (3×10^6 to 3×10^7 Btu/ft$^2 \cdot$ h). At the focus of the beam, however, the energy flow density ranges from 10^6 to 10^7 W/cm^2 (3×10^9 to 3×10^{10} Btu/ft$^2 \cdot$ h).

Beam Defocusing Method (Ref 5). A simple solution for matching the energy flow density to specific requirements is a technique called beam defocusing. Figure 6 shows computer-controlled deflection used to raster (move) the defocused electron beam over the surface of the workpiece into a shaped pattern of a microenergy dot array. This provides a precise local heating to the austenitizing temperature. When heating ceases, the surface layers rapidly transform into martensite by self-quenching, producing surface hardness values approximately 1 to 2 HRC higher than that obtained in furnace heat treated components.

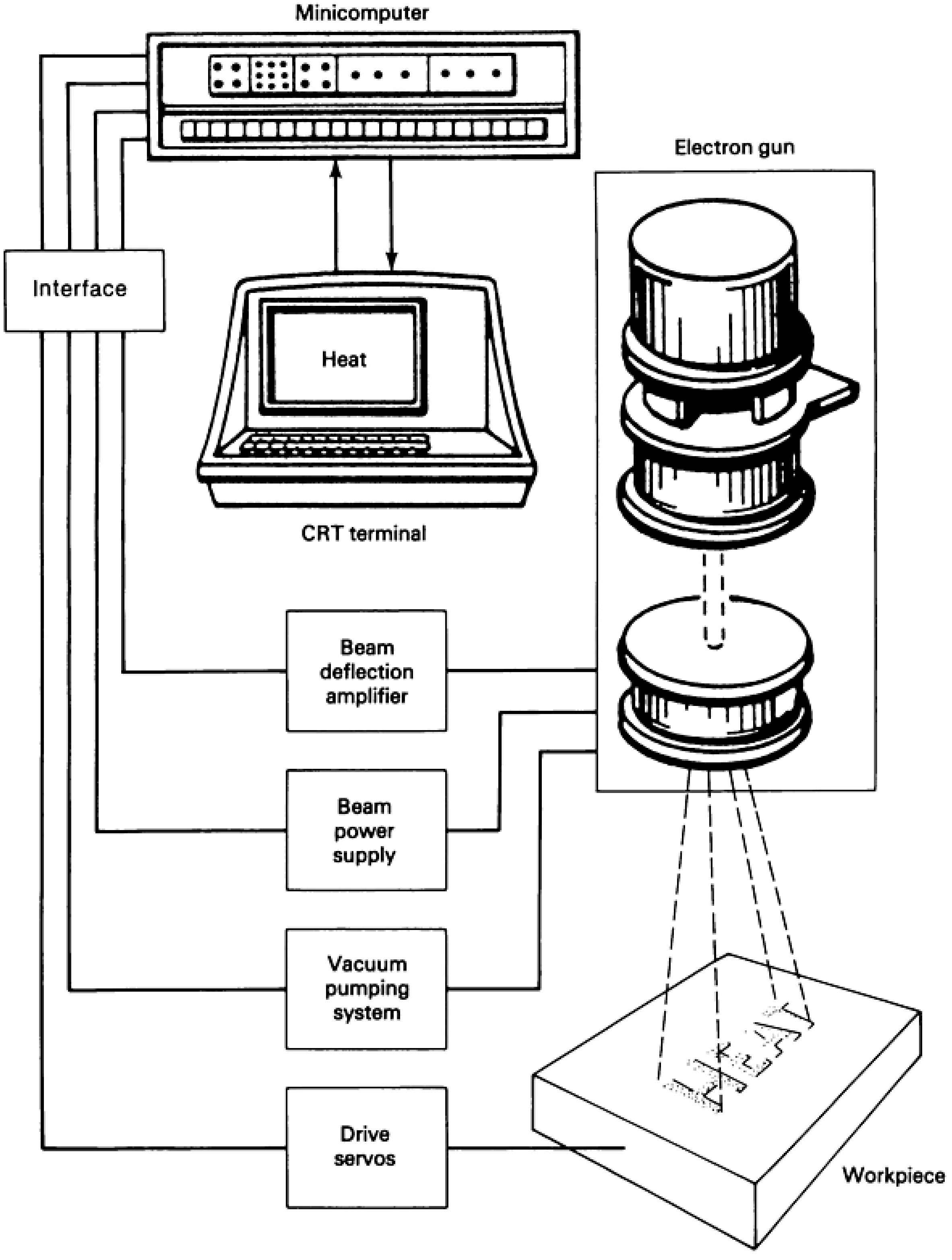


Fig. 6 Schematic of a computer-controlled electron beam hardening installation incorporating the beam defocusing method

Although this method is practical for some applications, it will not be emphasized in this article because it overlooks the principle of very precise energy transfer to a specified location.

In terms of location and time, the most significant beam control is obtained by means of a beam focused onto the component surface (see Fig. 7). Several versions of this technique are used. In variant A (see Fig. 7a), the beam acts on

the neighboring surface locations point-by-point and in a timed sequence. The action time is determined by the austenitizing depth required. Using a time-degressive flow of the beam current, it is possible to obtain an isothermal energy transfer at the center of the corresponding site of the surface. However, the occurrence of temper zones on neighboring sites not heated in a timed sequence is a drawback of this procedure. To avoid the incipient fusing of the surface, the beam power must be limited to approximately several hundred watts. As a result, this procedure is cost-effective only for the hardening of very small surfaces.

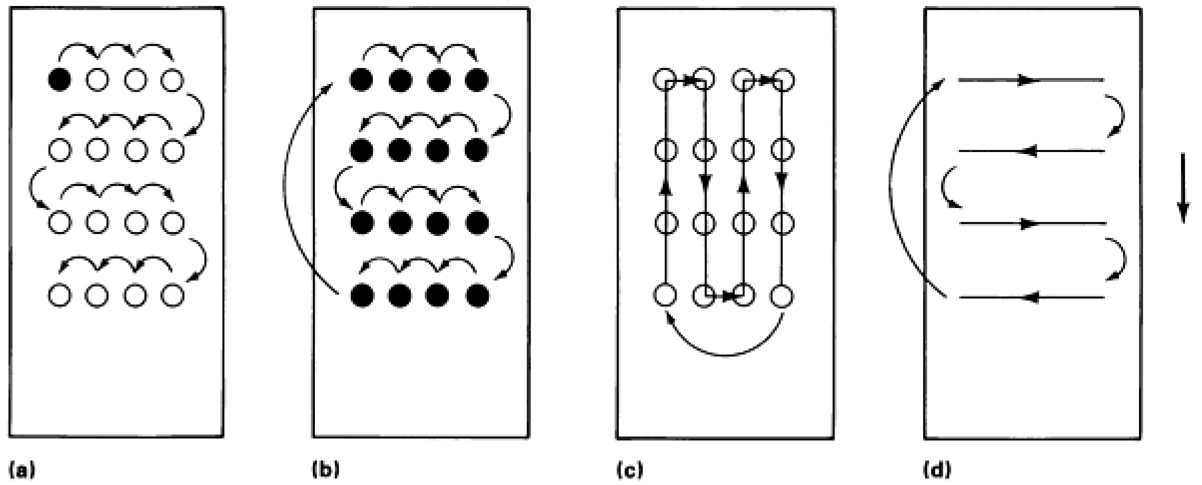


Fig. 7 Beam guidance for surface hardening with respect to location and time. (a) Variant A, point by point in succession. (b) Variant B_1, point by point in repetition. (c) Variant B_2, rate-controlled in line-shaped repetition. (d) Variant C, rf line raster in repetition on a moving workpiece

In variant B_1, the energy transfer also occurs in a dot raster, but the beam is guided in a rapid cyclic sequence from point to point in a jump-like manner (Fig. 7b). Referenced to a given surface location, the energy transfer takes place in a pulsed mode. One decisive advantage of the pulsed mode is that the energy input can be easily matched to the conditions of heat dissipation present at the work site. To this end, the proportional dwell time of the beam within a deflection cycle is chosen so that it is greater at the boundary and corner points of the energy transfer field than on its inner points (Ref 6). Again, a degressive beam current/time dependence is required to obtain an isothermal energy transfer.

Compared to variant B_1, the beam guidance variant B_2 (see Fig. 7c) excels in its ability to guide the electron beam continuously and repeatedly over the energy transfer field. Thus, the risk of overheating at the raster points linked with local surface fusing is notably reduced. The matching of the energy dose to the varying conditions of heat dissipation is achieved by using a site-dependent beam deflection rate.

The beam guidance variants B_1 and B_2 are recommended wherever an energy flow density has to be transferred. This strongly depends on treating site conditions. For example, this holds for cases in which the slope of the surface to the beam axis changes within the energy transfer field. Moreover, curved and limited energy transfer fields can be easily implemented in this way. Hence, the processing variants B_1 and B_2 are recommended for the hardening of surfaces whose accessibility to the beam scan field is limited because of the configuration of the part. Depending on the size of the surface to be hardened, the power consumption of a focused electron beam amounts to several kilowatts. In the beam guidance variant C, the beam is radio frequency (rf) scanned in a line raster (see Fig. 7d). The workpiece is moved normal to the direction of the scan, preferably at a constant speed relative to the energy transfer field that is fixed in space. Thus, the energy transfer duration is determined by the ratio of the raster field extension in the direction of motion to the travel speed of the component surface. Thus, an isothermal energy transfer can be readily implemented by a corresponding choice of the raster line spacings (see Fig. 8). The advantage of this beam guidance version is that the dwell time of the scanned beam on a given surface location is extremely short. With scan rates at 1 to 10 km/s (3000 to 30,000 ft/s), beam dwell times as low as 10 ns can be obtained. Under these conditions, the energy absorption layer acts as a heat accumulator. The oscillations on the component surface temperature become very low. Figure 9 can be used to estimate the temperature oscillation on the surface as a function of several beam parameters and the scan rate. For example, when U_B is 100 kV, dF_x is 0.05 cm, v_y is 4×10^5 cm $\cdot$ s^{-1}, and P is 20 kW, a ΔT value of 53 K is obtained (see Fig. 9). Table 1 lists the composition of C 45 steel and other steels discussed in this article.

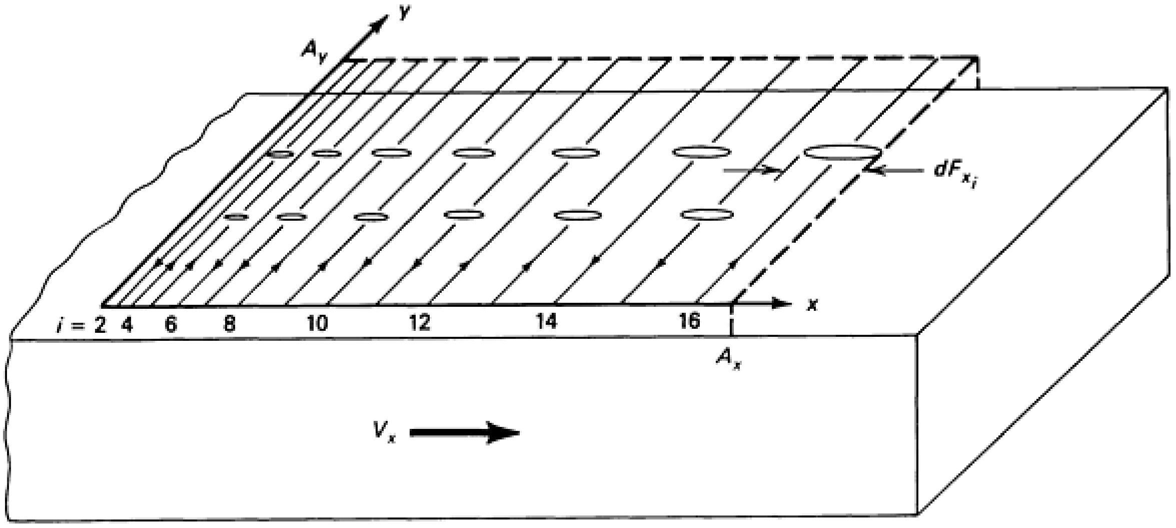
Table 1 Steels commonly used in electron beam hardening applications

Material			Composition, wt %											
AISI	UNS No.	DIN[(a)]	C	Si	Mn	P	S	Cr	Mo	Ni	V	Al	Cu	Ti
Carbon and low alloy														
4140	G41400	42 CrMo 4	0.38-0.45	0.17-0.37	0.50-0.80	0.035 max	0.035 max	1.90-1.20	0.15-0.25	0.30 max	0.06 max	. . .	. . .	. . .
1340	G13400	42 MnV 7	0.38-0.45	0.17-0.37	1.60-1.90	0.035 max	0.035 max	0.31 max	0.10 max	0.30 max	0.07-0.12	. . .	. . .	. . .
E52100	G52986	100 Cr 6	09.95-1.05	0.17-0.37	0.20-0.45	0.027 max	0.020 max	1.30-1.65	. . .	0.30 max	. . .	. . .	0.25	. . .
1015	G10150	C 15	1.12-0.19	0.17-0.37	0.35-0.65	0.040 max	0.040 max	0.50 max	0.10 max	1.30 max	. . .	. . .	. . .	. . .
1145	G10450	C 45	0.42-0.50	0.17-0.37	0.50-0.80	0.040 max	0.040 max	0.50 max	0.10 max	0.30max	. . .	. . .	. . .	. . .
1070	G10700	Ck 67	0.65-0.72	0.25-0.50	0.60-0.80	0.035 max	0.035 max	0.35 max	. . .	0.35 max	. . .	. . .	0.35	. . .
. . .	. . .	55 Cr 1	0.52-0.60	0.17-0.37	0.5-0.8	0.035 max	. . .	0.2-0.5	. . .	0.3 max	. . .	0.02-0.05	0.3 max	0.015
. . .	. . .	50 CrV 4	0.47-0.55	0.4 max	0.7-1.1	0.035	0.03 max	0.9-1.2	. . .	. . .	. . .	. . .	. . .	0.1-0.2
Tool steels														
O2	T31502	90 MnV 8	0.85-0.95	0.15-0.35	1.80-2.00	0.030 max	0.030 max	. . .	. . .	. . .	0.07-0.12	. . .	. . .	. . .
W1	T72301	C 100 W1	0.95-1.14	0.15-0.30	0.15-0.25	0.020 max	0.020max	0.20 max	. . .	0.20 max[(b)]	. . .	. . .	. . .	. . .

Source: Ref 7, 8

(a) Deutsche Industrie-Normen.

(b) 0.25 max Cu.



i	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
$\frac{x_i}{A_x} \cdot \frac{1}{1024}$	2	10	26	50	82	122	170	226	290	362	442	530	626	730	842	962
$\frac{dF_{x_i}}{A_x} \cdot \frac{1}{100}$	0.4	1.2	2.0	2.7	3.5	4.3	5.1	5.9	6.6	7.4	8.2	9.0	9.8	10.6	11.3	12.1

Fig. 8 Location of *y*-deflection tracks in the *x*-*y* beam deflection field assigned to the workpiece for isothermal energy transfer. Data are for relative numerical values of x_i/A_x and dF_{xi}/A_x for $N = 16$, as the number of scan lines within the deflection field and dF_{xi} as the extension of the beam spot normal to the scan direction; v_x is the moving rate of the workpiece relative to the deflection field

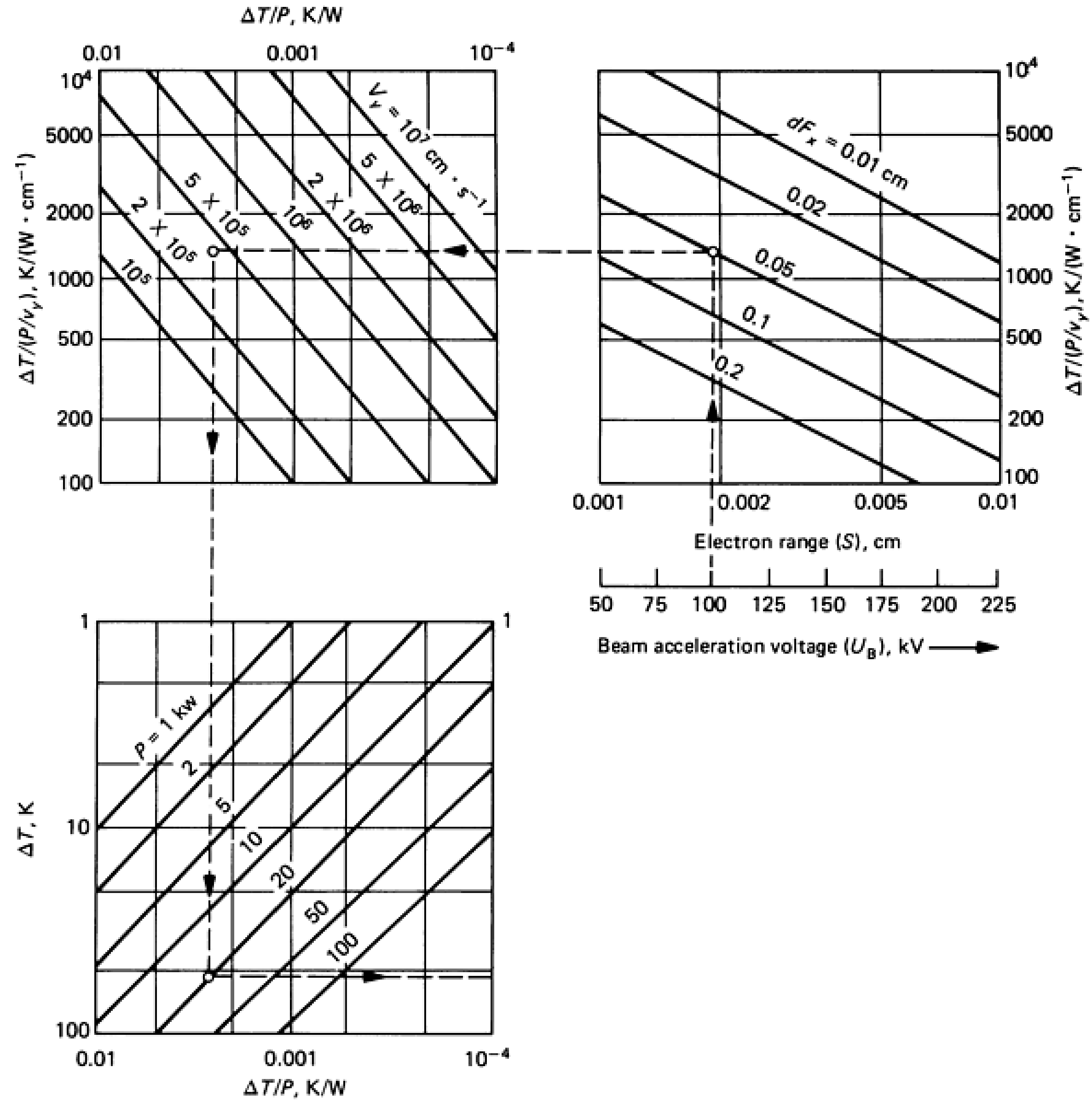


Fig. 9 Determination of on-site temperature jump of an electron beam as a function of various process parameters [$S(U_B)$, dF_x, v_y, and P] for C 45 steel

Beam guidance version, variant C, uses extremely high beam power consumption in the kilowatt range and provides the highest process productivity in terms of the hardenable surface per unit of time (see Fig. 10). Because each surface location passes the same temperature-time cycle, the lateral homogeneity properties of the hardness layer are very good.

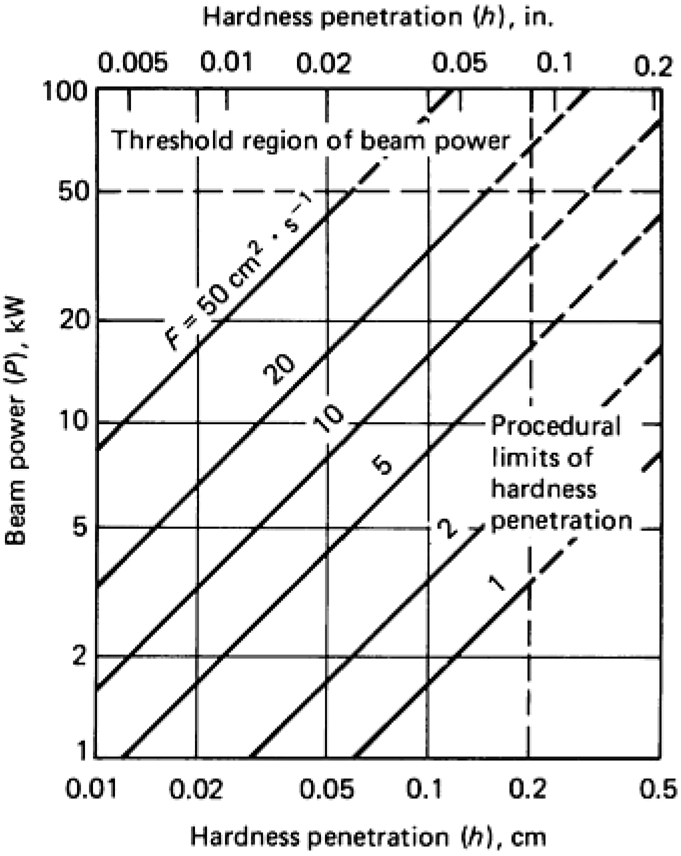


Fig. 10 Plot of beam power, *P*, versus hardness penetration, *h*, for selected values of areal throughput, *F*. Data are for isothermal energy transfer of C 45 steel.

If the reversing points of the beam's deflection are not well defined, tracks of incipient fusing are obtained on the edges of the hardness track. The energy flow density in the raster direction can be selected at random simply by choosing a corresponding raster line spacing. Difficulties are encountered in terms of maintaining the density in the direction of the scan lines without sacrificing the advantage of a high deflection rate.

Beam guidance version C is especially useful for applications such as the hardening of larger surfaces on plane and cylindrical components.

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Properties of the Hardened Layer

When a material undergoes austenitizing and self-quenching heat treatments, a hardened surface layer is produced because of heat conduction. The properties of the hardened layer depend on the mode of energy transfer and the composition and microstructure of the material. This section will discuss process-specific properties of the hardened layer in greater detail. The results are based on isothermal energy transfer data obtained using the high-speed scan technique (see Fig. 8) and a surface temperature that is close to the melting temperature of the material being tested.

Hardness Penetration and Energy Density Transfer. Figure 11 shows the effect of different thermal pretreatments on a carbon steel and a low-alloy steel. The scattering of the data points attests to the variation in the material properties of the two steels. The following conclusions can be drawn from the data in Fig. 11:

- At a given temperature, the transfer energy density, e_F, is a representative measure of the hardening depth
- The relation between the energy density, e_F, and the hardening depth is linear
- At a given surface energy, the hardening depth obtained depends on the material composition
- Based on the material composition of both steel types, the thermal pretreatment state has a low to dominant effect on the hardening depth. The latter holds true especially for high alloying contributions, especially chromium

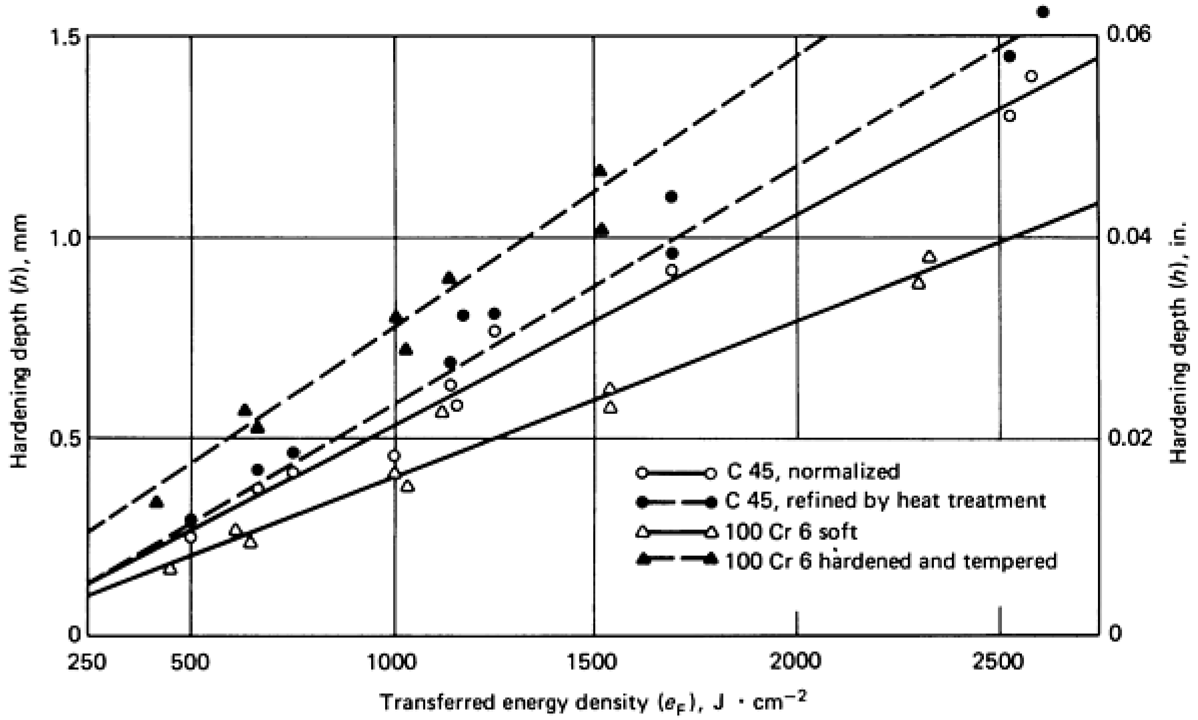


Fig. 11 Plot of hardening depth, *h*, as a function of the surface energy density, e_F, lost via isothermal energy transfer near the melting temperature of C 45 and 100 Cr 6 for selected preheating conditions. Source: Ref 9

Based on these conclusions, it can be assumed that it is possible to mathematically determine the effect of thermal heat treatments on the hardening depth of a material at selected temperatures prior to experimentally determining the conditions required.

Cross-Sectional Profile of the Hardened Layer. A significant feature of the energy transfer principle illustrated in Fig. 8 is that, on each surface location within the hardness track, an equal energy density is applied in the same time regime. However, a constant hardening depth across the hardness track can be expected only for those track regions in which identical conditions of heat dissipation exist (that is, wherever the isotherms run parallel to the surface). This holds true in cases where the width of the energy transfer track either coincides with or exceeds the width of the workpiece.

On the other hand, if the width of the workpiece is greater than the width of the energy transfer track, other heat dissipation variables determine the marginal zones. At the track edge, the isotherms are bent toward the surface. Thus, a constant hardening depth exists at the exact center of the track that, depending on the ratio of the track width to hardening depth, is flanked by marginal zones where the hardening depth continually reduces to zero. As a rule, this effect, although caused by the heat conduction mechanism, cannot be fully eliminated by a higher energy input at the marginal zones of the track. Figure 12 shows the typical cross-sectional profile of a hardness track with a track width-to-hardening depth ratio of 50:1. With its pronounced range of constant hardening depth, it significantly differs from the cross-sectional

profiles obtained with other energy transfer techniques. The drop in hardening depth is limited to a narrow marginal zone of which the width is less than twice the hardening depth.

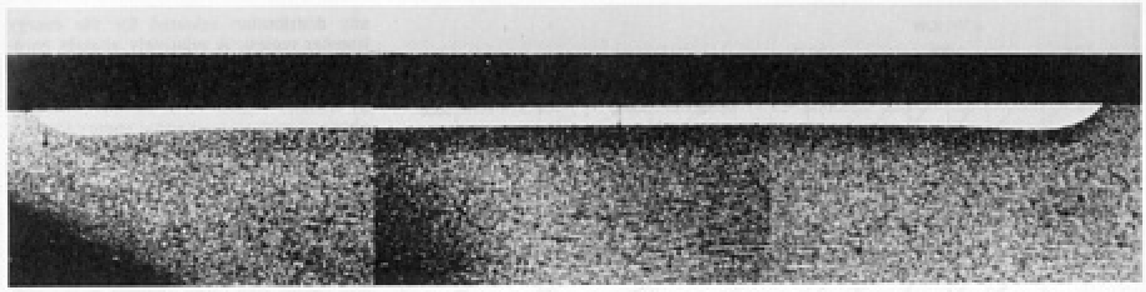


Fig. 12 Cross-sectional profile of a hardness track in Ck 67 steel refined by heat treatment. Hardening depth, 0.4 mm (0.016 in.); width of hardness track, 20 mm (0.8 in.); energy input, 600 J · cm^{-2}

Hardness Gradient in the Hardened Layer. As predicted by the energy transfer principle and as corroborated by other researchers (Ref 10), hardness measurements that are taken on the surface in the direction of the track and transverse to the track resulted in constant hardness values. At the track edges, however, the hardness values drop abruptly to the base material value and then the temper zone value. In accordance with the properties of the material, the surface hardness may also depend on the hardening depth within certain limits. This is attributable to the dwell time increasing with the hardening depth to keep the surface at a higher temperature while simultaneously reducing the quench rate.

The hardness profile measured normal to the workpiece surface is determined by the effect of the rapidly changing temperature cycle with distance to the surface. Depending on the morphology of the material and the kinetics of the austenitizing process, this temperature change has a bearing on the hardness gradient. The finite temperature difference, $TA_{c3} - TA_{c1}$, between the completion and the beginning of austenitizing, which is related to the slope of the temperature gradient in this transformation range, also provides a finite slope of the hardness gradient between the hardened layer and the base material. In the case of a base material that has been quenched and tempered, the inevitable heat-up of the material beyond the austenitizing depth usually produces a tempered boundary layer having a corresponding drop in hardness. Figure 13(a) shows the hardness profile normal to the surface at selected hardening depths for C 45 steel refined through heat treatment. A relatively constant maximum hardness value (800 to 900 HV) over a wide range of layer thickness values to 0.50 mm (0.02 in.) is typically followed by a steep drop in hardness value of the base material that levels off at 350 HV with increasing distances to the surface of the material. The slope of this drop in hardness in the transition region is reduced proportionately with the increasing hardening depth as the transfer energy density is increased. The scatter in the measured values about the plotted curve is negligible. Figure 13(b) shows the corresponding hardness profiles for the same material following normalization. The spread of the measured microhardness values is remarkably wide and can be attributed to the inhomogeneity of the initial state that has both ferritic and pearlitic zones. This scattering of hardness values clearly reflects the known strong effect a thermal pretreatment of the material exerts on the hardness values in the case of a short-time hardening.

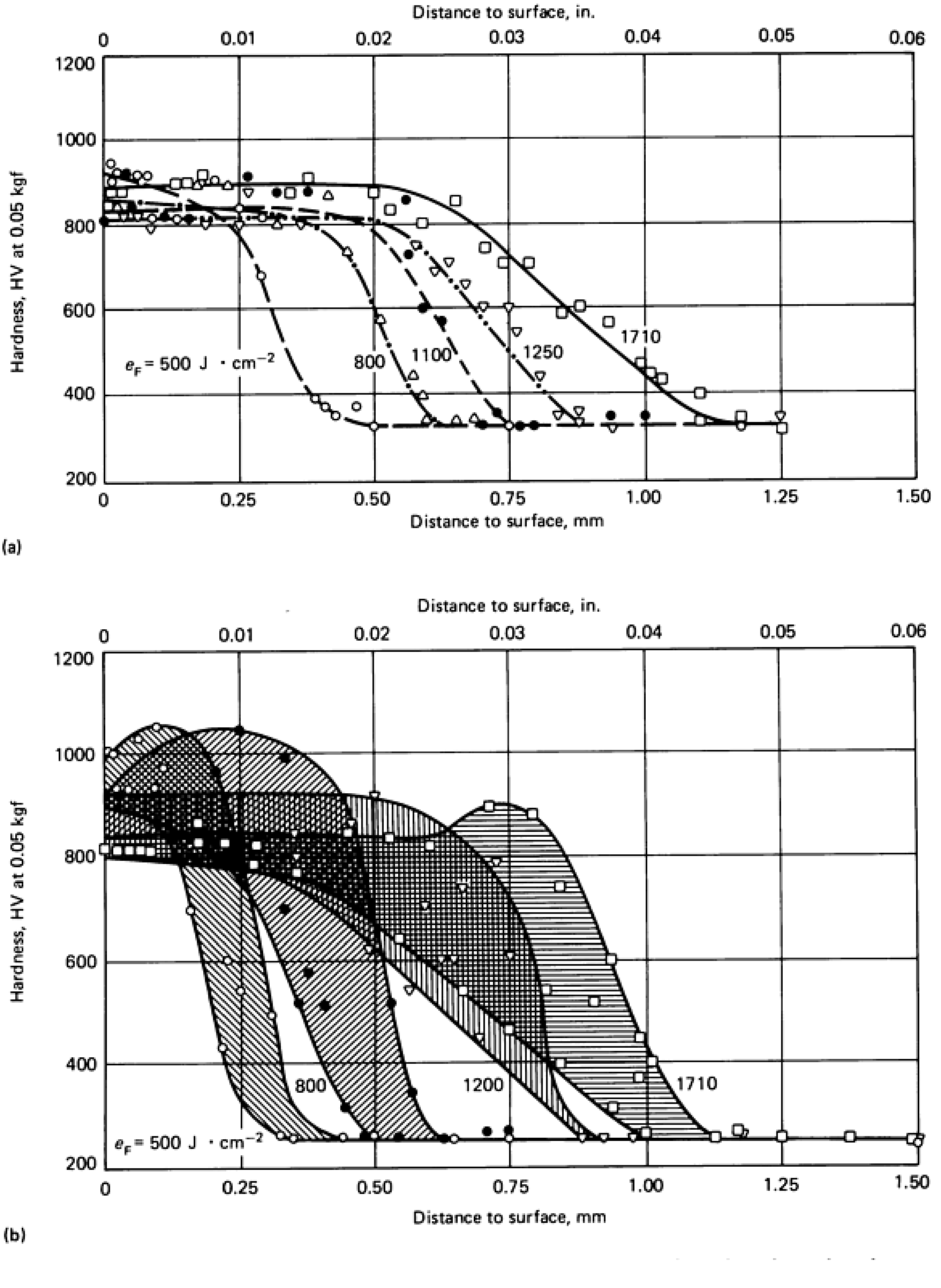
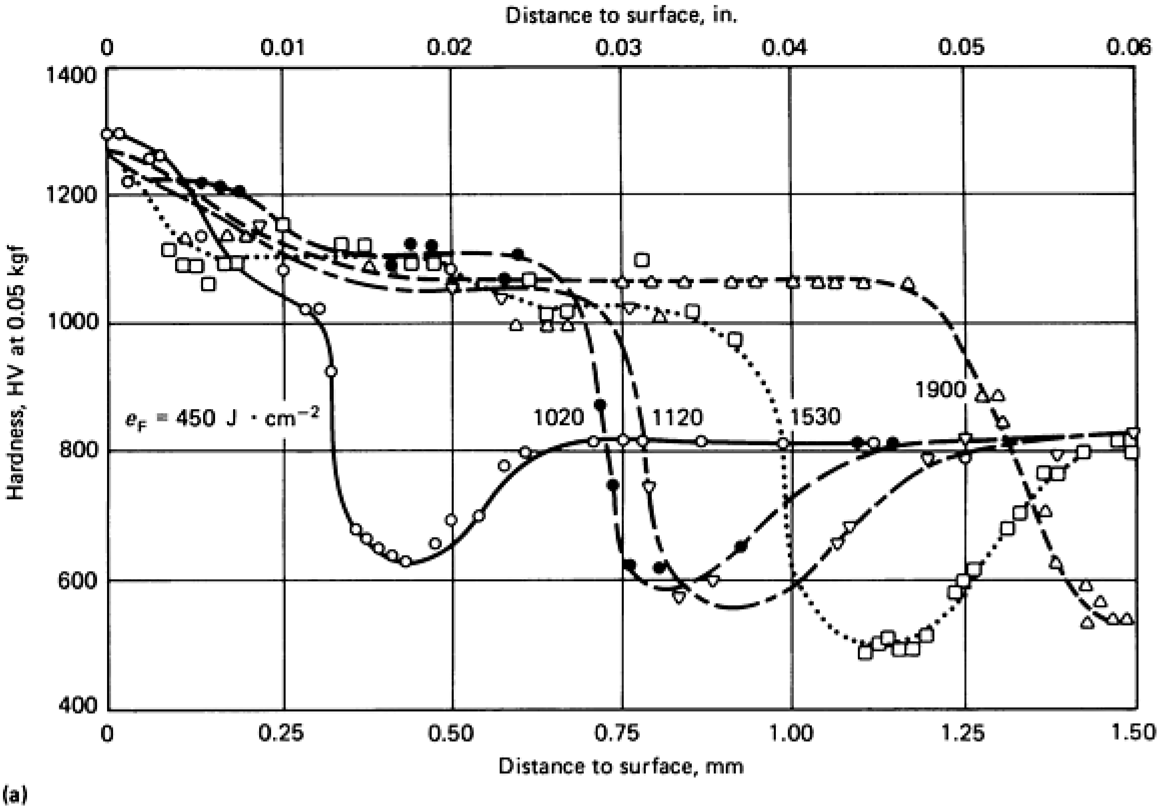


Fig. 13 Effect of preheating state on the hardening depth profile of C 45 steel at selected transferred energy densities, e_F. (a) Refined by heat treatment. (b) Normalized. Source: Ref 11

Figure 14 shows the hardening profiles obtained with 100 Cr 6 hypereutectoid steel both in the hardened and tempered state (Fig. 14a) and in the soft initial state (Fig. 14b). Similar to the data in Fig. 13 for C 45 steel, pronounced differences are obtained for the various heat treatment states of 100 Cr 6 material. In addition, the plot in Fig. 14 introduces a distinct hardness minimum in the boundary region between the hardened layer and the base material for the hardened and tempered 100 Cr 6 material. The minimum hardness values become progressively lower as the hardening depth increases.

This is a consequence of the increased dwell times required as the tempering temperature is approached. However, the hardness values in this tempered layer (about 500 to 550 HV at a distance of 0.50 mm, or 0.02 in., below the surface) are much higher than the 250 HV hardness value obtained at a distance of 0.5 mm (0.02 in.) found in the soft-annealed material. Similar tempering zones also occur with quenched and/or tempered hardened materials as well as with the initial tempered states of other materials if the basic hardness exceeds 500 HV at a distance of 0.50 mm (0.02 in.) below the surface. As already evident from Fig. 11, a notably greater hardness penetration is obtained with the hardened and tempered base material compared to the soft-annealed material although the energy input is similar. When compared to normalized C 45 carbon steel, the hardness values measured for soft-annealed 100 Cr 6 steel exhibit much less scatter. Above all, the quenched and tempered or hardened and tempered initial states of both materials differ with respect to the slope of the hardness transition in the base material.



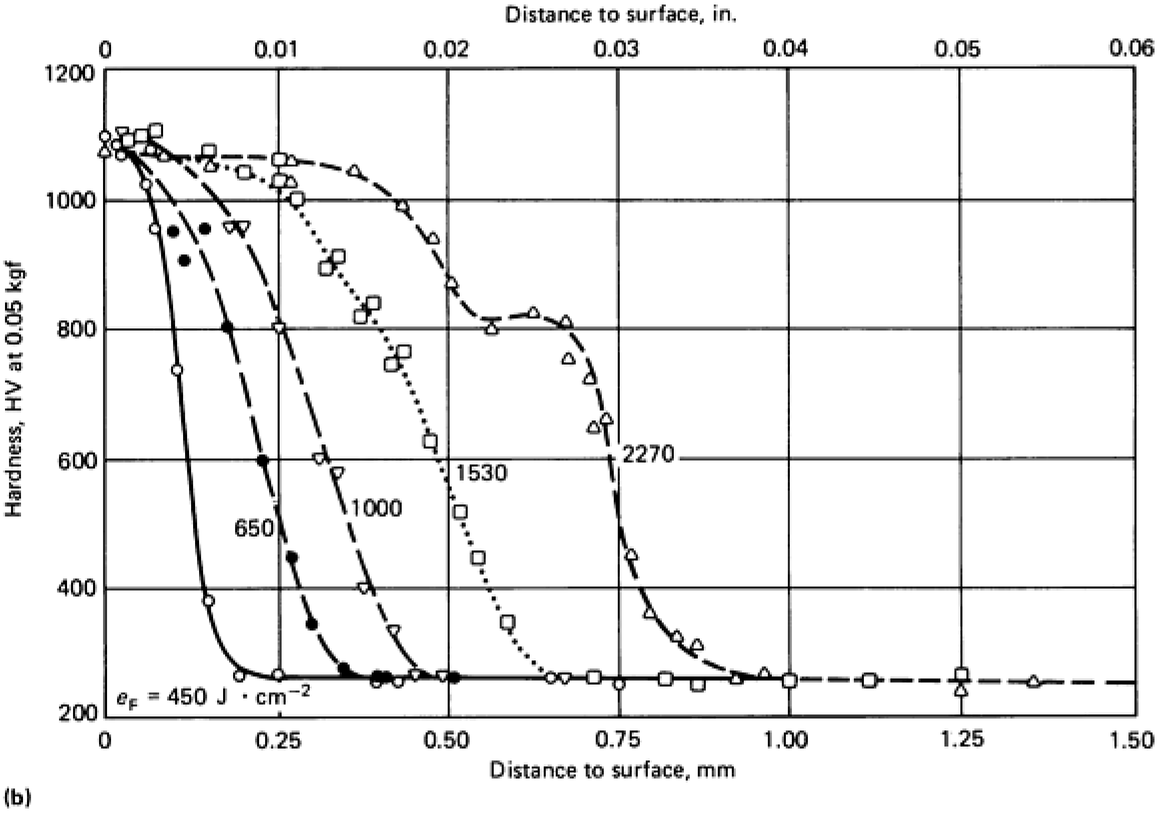


Fig. 14 Effect of preheating state on the hardening depth profile of 100 Cr 6 hypereutectoid steel at selected transferred energy densities, e_F. (a) Hardened and tempered. (b) Soft. Source: Ref 11

In the transition region of the base material, the hardness gradient is determined by the material-dependent transformation kinetics and the temperature gradient in this region. However, the temperature gradient can be directly affected via the power density distribution selected for the energy transfer region. A relatively straight hardness transition curve is obtained at a constant power density distribution in the energy transfer region when compared to that obtained with an isothermal energy transfer (Ref 12). However, it should be noted that such a measure increases the thermal stress imposed on the workpiece if a layer thickness having maximum hardness is to be maintained.

Surface Roughness. The crystalline transformation processes linked to the temperature cycles also cause changes in the geometrical surface structure. For example, surfaces polished to an average surface roughness, *Rz*, of 0.05 μm (2 μin.) had a surface roughness of up to 1.5 μm (60 μin.) after the hardening process (Fig. 15). Depending on the material, the surface roughness increases with the surface temperature and the duration of the energy transfer.

Fig. 15 Surface relief of a normalized C 45 steel sample polished before hardening that had the isothermal energy transfer at approximately the melting temperature. Energy density transferred, 1250 J · cm^{-2}; surface roughness, R_z, is 1.2 μm (48 μin.). Source: Ref 9

Because temperatures close to the melting point provide a greater surface roughness and maximum surface temperatures, a reduction in roughness that is caused by a heat buildup and the incipient fusion of the surface peaks is observed.

Surface Deformation. The various specific volumes of the initial and transformation products cause a surface deformation in the region of the hardness track. The surface of the hardened track becomes elevated compared to its initial level. The graphs in Fig. 16 confirm that the surface deformation is a function of the energy density transferred and the composition of the material. In addition, a slight surface retraction may occur in the marginal zone of the hardened track. With hardening depths of approximately 1.5 mm (0.06 in.), surface elevations as high as 15 μm (600 μin.) were observed. Because no direct correlation has been established between material composition and the temperature cycle used, no general linear relation between hardening depth and surface deformation can be determined. However, it is evident that the surface deformation is more pronounced than the surface roughness.

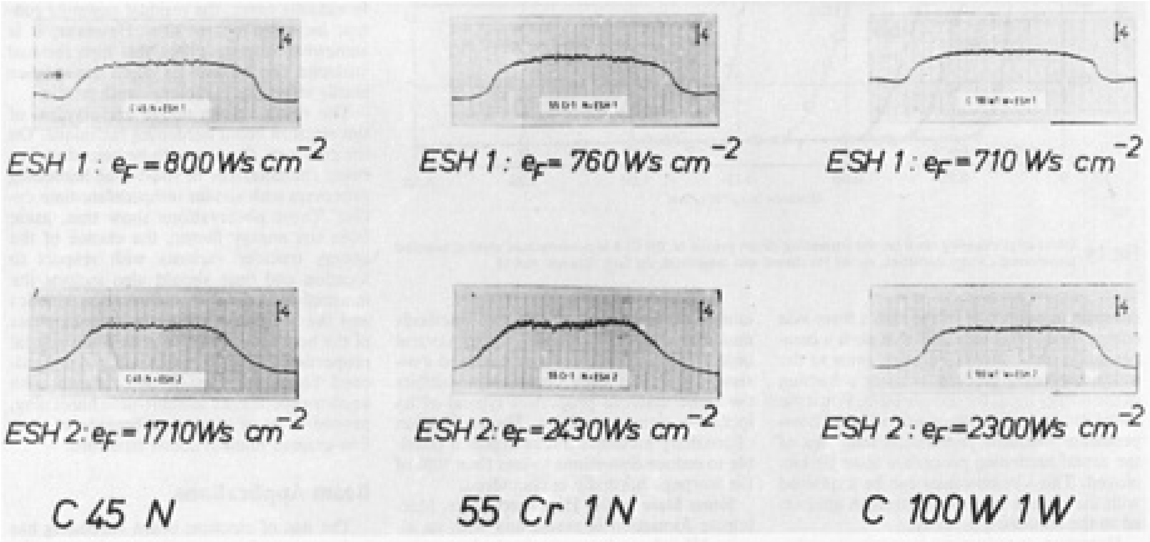


Fig. 16 Surface deformation in the region of the hardness track for C 45, 55 Cr 1, and C 100 W1 steels. N, normalized; W, soft. W · s = watt · second = J. Source: Ref 9

Workpiece Distortion. Although electron beam hardening is generally classified as a method that produces minimal distortion, the degree of distortion encountered cannot be neglected in all cases. Because workpiece distortion depends not only on factors such as component rigidity, hardening depth, location, and extension of the hardened surface but also on the material composition and its pretreatment state, it is difficult to set up general guidelines for workpiece distortion. Parts having a low areal moment of inertia (for example, ledges hardened on one side only) are especially sensitive to warpage.

Sample slabs of 90 Mn V 8 steel measuring 8 mm ($\frac{5}{16}$ in.) thick by 305 mm (12 in.) long have a distortion of more than 1 mm (0.04 in.) after being hardened to a depth of 0.8 mm (0.03 in.) over the total (35 mm, or $1\frac{3}{8}$ in.) width. In this case, the hardened plane developed a concave shape.

There are two possible methods of lowering the distortion during the hardening of the slabs:

- Prestressing in the direction opposite to warpage during the energy transfer
- Applying an ancillary hardness track at the rear side of the slab before the actual hardening process commences

Identical energy transfer conditions are used for front-side hardening as are used for rear-side hardening but at reduced beam current settings. Figure 17 shows the residual warpage following hardening to be a function of the energy input on the rear side of the slab. Note that an optimum compensation of the distortion obtained for the slab's rear-side energy input is approximately 50% of the value obtained for the subsequent hardening of the slab's front-side energy input. This indicates that such a compensation must always be made prior to the actual hardening process by using a fraction of the energy input for this purpose. When the timed sequence is transposed, a higher compensation hardness penetration than that of the actual hardening procedure must be employed. This circumstance can be explained with the change in material strength attributed to the hardening process.

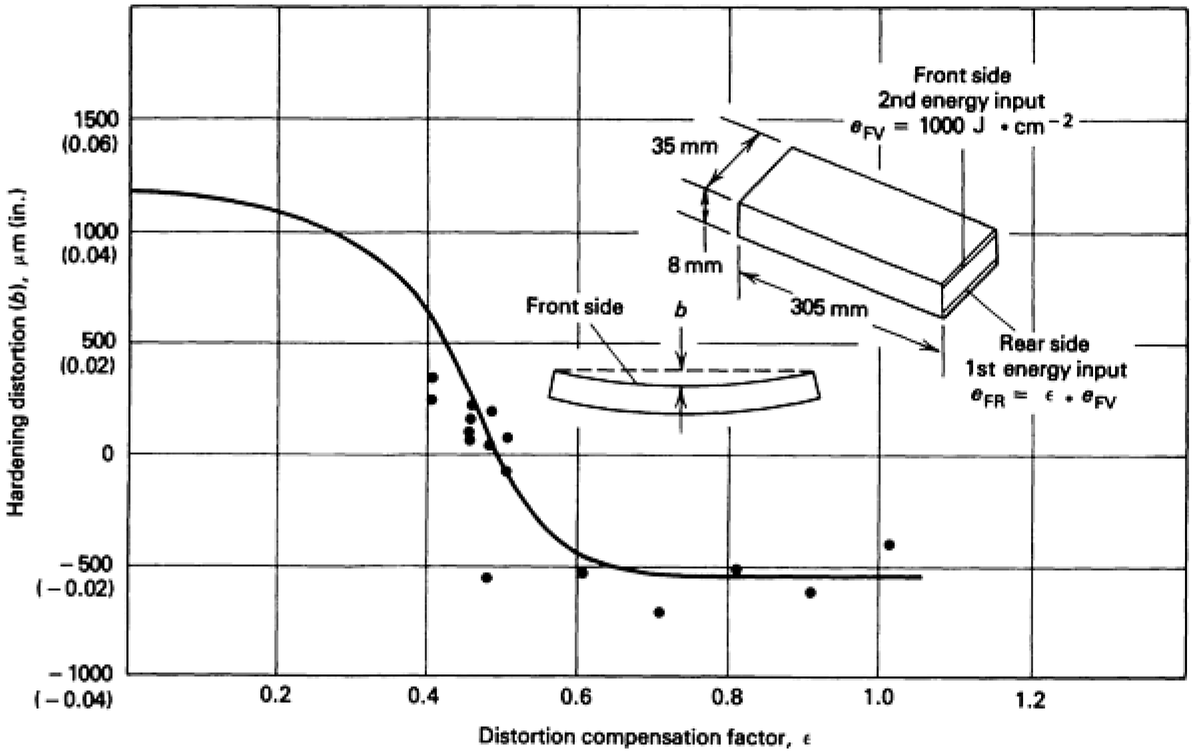


Fig. 17 Hardening distortion, *b*, as a function of the portion of the energy density, ε, transferred to the rear side during the preceding rear-side hardening process. Material is 90 MnV 8 steel having transferred energy density of 1000 J · cm^{-2}.

However, a reduction in workpiece distortion comparable to the reduction obtained through one of the two methods mentioned above (typically up to several orders of magnitude) can be obtained consistently only if each component exhibits the same material properties typical of its locked-in stress condition. The application of auxiliary hardness tracks makes it possible to reduce distortions to less than 10% of the warpage normally encountered.

Stress State in the Hardened Layer. Martensite formation is associated with an almost 1% volume increase. As the increasing cooling action diffuses from the inside core of the component to its surface and the martensite progressively forms in the same direction, residual compressive forces in the hardened layer are typically generated by the electron beam hardening technique. In the subsurface zones of a workpiece track hardened to a depth of 0.8 mm (0.03 in.), residual compressive forces of 300 MPa (45 ksi) were obtained in C 45 steel both in the longitudinal and transverse directions to the track (Ref 4).

Hardened Layer Microstructure. Because the material and crystalline reactions that occur during the hardening process are sensitive to the temperature-time cycle, relevant property gradients must be present in the hardened layer. Generally, the grain size in the hardened layer (especially pronounced in the case of hypoeutectoid steel grades) gradually decreases with increasing depth from the surface into the base material core. At hardening depths greater than 1 mm (0.04 in.), a rather coarse-grained structure is obtained near the surface whereas the deep-seated zones exhibit an extremely fine-grained structure as indicated in Fig. 18. At lower hardness penetrations, however, a fine-grained structure is also found on the surface. An incomplete dissolution structure is present in the transition region to the base material because it is only partially austenitized. As is the case with hypereutectoid steel grades, particularly those grades having a higher chromium content, carbides are dissolved only incompletely toward the surface. It is also typical of these steel grades that, other than martensite, a high residual austenite content is likely to be present in the hardened layer. With increasing hardness penetration, the residual austenite content also increases toward the surface. In extreme cases, the residual austenite content increases up to 30%. However, it is somewhat surprising that this high residual austenite content and its depth dependence hardly affect the hardening depth profile.

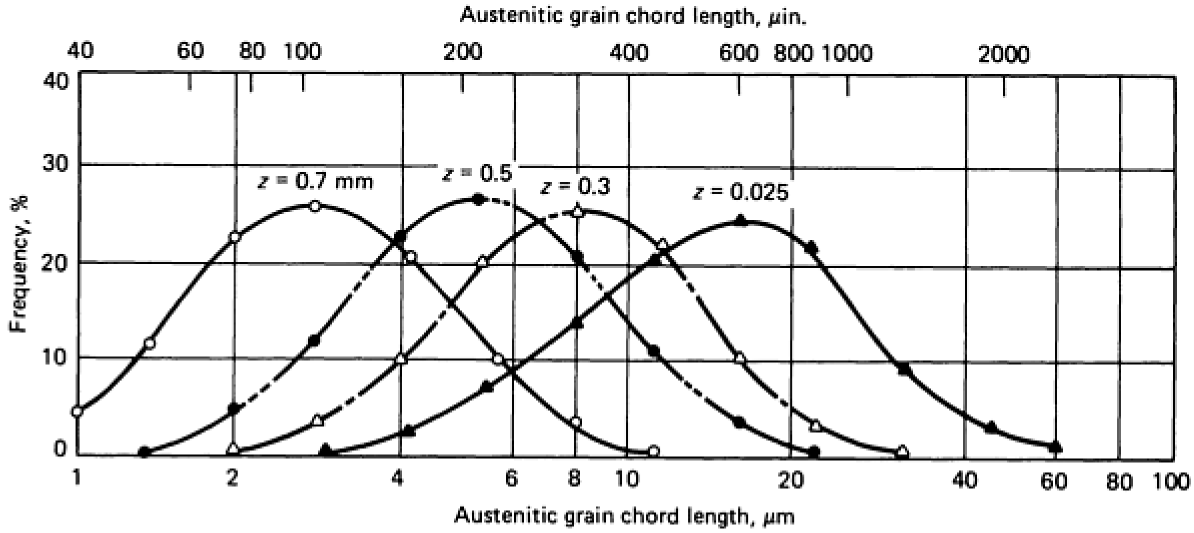


Fig. 18 Frequency distribution of austenitic grain chord lengths for various distances to the surface, *z*, obtained via thermal energy transfer at approximately the melting temperature. Data are for C 45 steel, refined by heat treatment to a hardening depth of 0.86 mm (0.034 in.). Source: Ref 9

The results given above are atypical of the electron beam hardening technique. On the contrary, they have to be considered as being characteristic of short-time hardening processes with similar temperature-time cycles. These observations show that, aside from the energy factor, the choice of the energy transfer variants with respect to location and time should also include the material-dependent transformation kinetics and the structural properties requirements of the hardened layer. In regard to material properties, quenched and tempered or hardened base materials, in accordance with known experiences in short-time hardening, proved to be of advantage because of their fine-grained homogeneous structure.

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Beam Applications

The use of electron beam hardening has to be assessed in compliance with material and technological requirements and, above all, economic criteria. The prevailing conditions in an industry may also be of critical importance. In the vast majority of applications, this technique can compete successfully with induction hardening and other conventional hardening techniques such as case hardening.

From an engineering aspect, practically all parts with surfaces that are accessible to the beam and with a thermal capacity that is sufficient for self-quenching can be considered candidates for electron beam surface hardening. In terms of material specifications, the workpiece thickness that is in direct thermal contact with the hardened layer should be at least five to ten times the hardening depth. Another material consideration is the minimum temperature required for martensite formation. A very straightforward process regime is obtained with throughgoing, interrupted plane, or cylindrically hardened surfaces. For example, the circumferential surfaces of bores are hardenable with diameter-to-depth ratios up to unity. The flank-profile hardening of gears and racks generally calls for specialized beam guidance techniques. Occasionally, crucial problems may arise when the hardening of irregular and spherically bent surfaces is attempted.

Technologically, this process is preferred for hardening depths in a range of 0.3 to 1 mm (0.01 to 0.04 in.). Depending on the material being used, however, it can also produce a maximum hardening depth of approximately 2 mm (0.08 in.). In some cases, the maximum hardening depth is also fixed by the coarse-grain growth and the bainite or pearlite formation caused by a low cooling rate. Hardness penetrations below 0.3 mm (0.01 in.) (minimums of 10 μm, or 400 μin., on the order of the electron range are possible) can be implemented without difficulty but are not yet demanded in practice. It is especially these thin hardened layers where the most outstanding materials properties (for example, extreme grain fineness and very high hardness values) can be attained.

Electron beam hardening offers the following technological benefits:

- Precise control and reproducibility of the energy input with respect to location and time
- Constant hardening depth for both areal and laterally patterned hardening up to a track width of 50 to 100 mm (2 to 4 in.)
- Low thermal stress is imposed on the workpiece to minimize warpage
- No scaling or oxidation of component surfaces
- No component-dependent means of energy transfer
- No preparation of surfaces to be hardened or of regions that have to be left untreated
- Computer numerical control (CNC) or computer-controlled processing similar to that used for machine tools, which are CAD/CAM (computer-aided design/computer-aided manufacturing) compatible and easy to integrate into mechanical flow lines
- Plant operation requires only electric power and low quantities of cooling water (usually in closed circulation systems) but neither transport media such as a working gas or an inert gas nor hardening salts or quenching oils are required
- High energy efficiency
- High process productivity with available beam power ranging from 20 to 50 kW
- No waste products generated
- Technological equipment suitable for several processes such as deep welding, hardening, and fusion treatment of surfaces

With an initial outlay of $500,000 to 1,200,000 required, the investment costs of electron beam facilities are relatively high and, therefore, usually limit the profitable use of this technique to high-volume production. As is the case with other machine tools and production equipment, the facility is most cost-effective when it is designed to match the requirements of a given application. In terms of the lot sizes containing identical parts, the programmability of the process makes no particular demands provided they do not arise from such secondary considerations such as the change of component loading and handling devices.

Experience has shown that the quality improvements obtained can be expressed as a direct gain only conditionally. Above all, economic estimates should also be based on the technological benefits of electron beam hardening. In general, substantial sections of component technology must often be altered because of limited materials selection in order to utilize the advantages of the process to the maximum. Frequently, the most important sources of economic gain are time savings gained at final machining or grinding, the omission of production processes, and a reduction in transport and energy expenditures.

Aside from these general economic considerations, it is the presence of equipment already installed in a facility that determines whether or not the addition of an electron beam hardening operation is feasible. An electron beam welding installation can be modified to convert the equipment for electron beam hardening operations. This conversion allows the

gradual introduction of electron beam hardening into the plant, thus providing multiple utilization of the plant equipment while minimizing the financial risks inherent in the introduction of innovative technology.

Example 1: Electron Beam Hardening of a Milling Machine Quill.

Figure 19 shows the quill of a milling machine that has been electron beam hardened. The entire surface of the cylindrical portion of the workpiece is hardened to a depth of 0.7 mm (0.03 in.). Hardening is achieved via isothermal energy transfer using a helical track to provide complete coverage of the surface to be hardened (Ref 4). Because the energy transfer data can be easily programmed into a computer, it is easy to isolate areas not to be hardened (that is, toothing and various plane faces). The hardened surface makes up 76% of the circumferential surface and totals 2100 cm^2 (325 $in.^2$) in area. The processing time required to harden one quill amounts to 8 min. This comparatively long time is fixed solely by the power of the electron beam used and in this case is restricted to 5 kW. The processing time could be lowered to 2 min if the beam generated 20 kW of power. Even for processing times of 8 min, however, electron beam hardening is still a cost-effective method for heat treating quills used in milling machines. Electron beam hardening is cost effective because of reduced expenditures for (Ref 13):

- Grinding operations
- Production steps and auxiliary procedures, including in-plant transport
- Energy used for heat treatment operations when compared to conventional techniques

Processing times, energy consumption data, and grinding allowances for milling machine quills hardened by several methods are compared in Fig. 20. This example is typical of the economic advantages that result partly by a mere substitution of one hardening process by another. The most significant savings, however, result from an overall streamlined flow of engineering processes. In addition to electron beam hardening of the quill, the same firm now heat treats approximately 60 other components having plane and cylindrical surfaces.

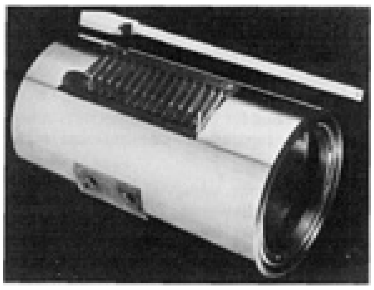

Fig. 19 Milling machine quill that was surface-hardened to a depth of 0.7 mm (0.03 in.) by electron beam hardening. Toothed region and plane surfaces of the quill were not hardened.

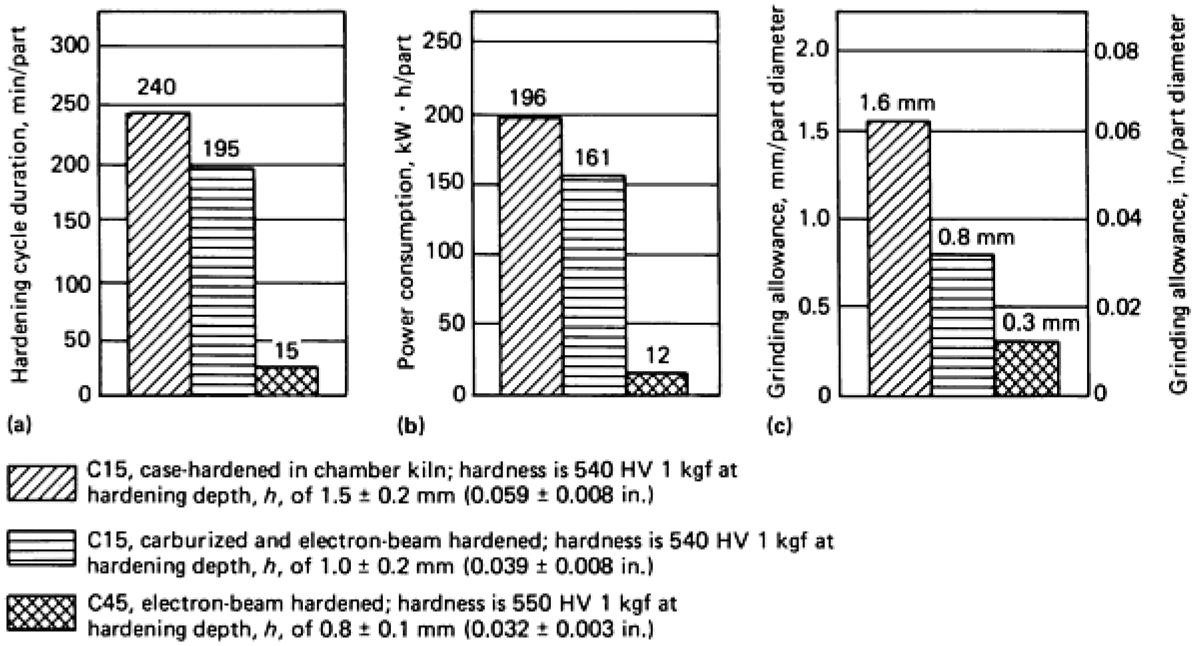

Fig. 20 Comparison of electron beam hardened and conventional case hardened milling machine quills shown in Fig. 19 to show electron beam hardening is a cost-effective option when heat treating C 15 and C 45 steels when the following factors are considered: (a) processing times, (b) electrical energy consumption, and (c) grinding allowance

Example 2: Partial Electron Beam Hardening of Shaft to a Depth of 0.3 to 0.7 mm (0.012 to 0.028 in.).

A variety of low-volume production components can be partially surface hardened with an electron beam (Ref 3). Shafts made of quenched and tempered steel (for example, 50 CrV 4, C 45, 42 Cr Mo 4, and 42 Mn V 7) can be hardened on the bearing and running surfaces of seal rings in order to reduce wear and tear (Fig. 21). The hardness penetration ranges from 0.3 to 0.7 mm (0.012 to 0.028 in.). Electron beam hardening had to prove it could be competitive against conventional methods such as flame or induction hardening and case- or nitrogen-hardening. In this application, electron beam hardening has the following economic advantages over conventional hardening techniques:

- Lower reject rates (for example, avoidance of quench cracks sometimes found with flame hardening)
- Reduced grinding expenditure because of almost warpage-free hardening
- Streamlining of the process flow, including a reduction in transportation steps

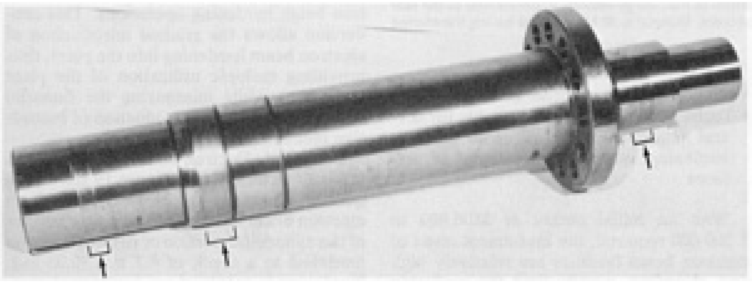

Fig. 21 Partially surface-hardened shaft that was hardened to reduce wear on bearing surfaces (indicated by arrows)

Narrow Tempering Zone Anomaly. An anomaly from Examples 1 and 2 and similar applications is the existence of a narrow tempering zone in the boundary region of the applied helical or ring-shaped hardness tracks. This tempering zone whose hardness ranges from 500 to 550 HV is approximately one to two times the hardening depth. In many cases, these temper zones can be avoided by extending the energy transfer field over an adequately large contact angle of 20 to 90° depending on the material composition. Thus, the boundary line between the previously heated track and the energy transfer field will be passed prior to martensite precipitation.

Example 3: Cutting Edges of a Ck 67 Steel Harvester Mower Blade Hardened in a Line-Shaped Pattern.

Figure 22 shows a typical component having preferred wear-resistant properties imparted via the use of an electron beam hardened layer. The cutting region of the harvester mower blade can be electron beam hardened either in the areal mode or, as shown in Fig. 22, in a line-shaped pattern. Compared to conventionally hardened blades; these electron beam hardened mower blades provide a much longer service life. The blade hardening time is about 0.6 s.

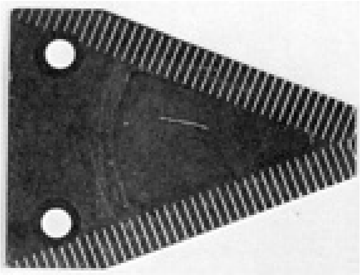

Fig. 22 Austempered Ck 67 steel harvester mower blade with cutting edges hardened in a line-shaped pattern

Additional Electron Beam Hardened Components. Other examples of typical components that can be electron beam hardened on a cost-effective basis are shown in Fig. 23.

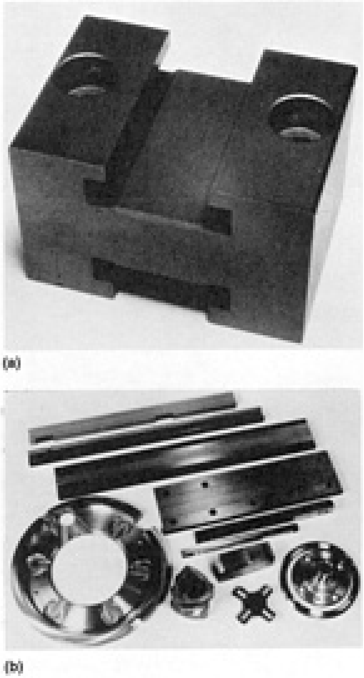

Fig. 23 Typical components heat treated with electron beam hardening method. (a) Roller-bearing element support. (b) Selected components used for both linear and rotary motion applications. Courtesy of Chemnitzer

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Electron Guns and Auxiliary Equipment Required for EB Hardening

One significant additional component in the beam guidance system of an electron beam hardening system distinguishes this device from a typical electron beam welding system. Figure 24 is a schematic of the electron-optical setup of an electron gun used for hardening operations. A three-electrode system, with a tungsten bolt cathode that is heated by electron bombardment, is used to generate the beam. The rotationally symmetrical accelerated stream of electrons enters the beam guidance system via the anode bore as a beam that is focused onto the work plane by means of a magnetic focusing lens. The electron gun used for welding lacks the additional complex electron-optical package that is present in the magnetic field lens system of the electron gun used for hardening applications. This lens system consists of a dedicated deflection unit, a dynamic lens, and a magnetic octupole. The nearly distortion-free deflection unit is, with the exception of its field winding, of a nonmetallic composition that has low inductance properties. When connected with a matching power supply unit, it allows for linear time beam deflections at frequencies exceeding 100 kHz. When used in conjunction with the dynamic focusing lens, the magnetic octupole is suitable for elliptic focal spot shaping at an axial ratio of 10:1.

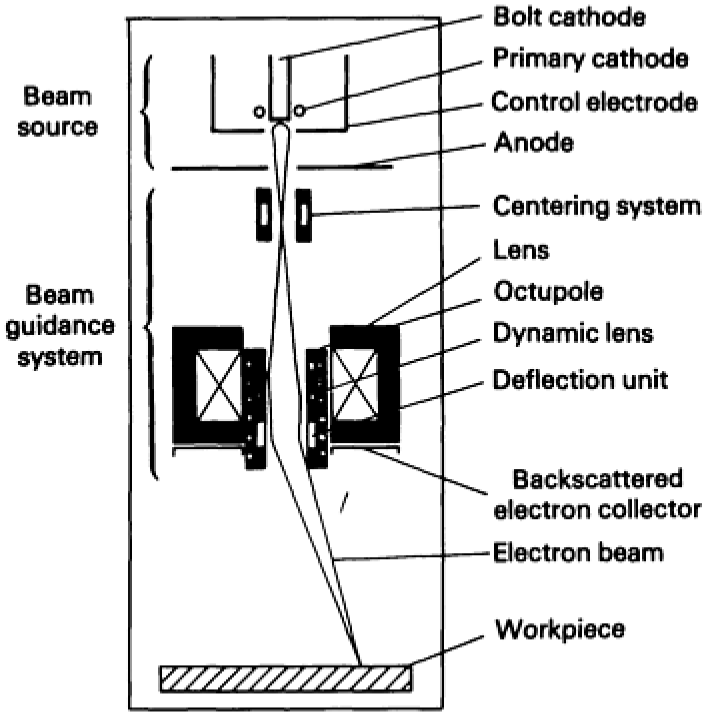

Fig. 24 Schematic of the beam generating system and the optical focusing system of a cutting, treatment, and welding (CTW) electron gun

Figure 25 is a photograph of a typical electron gun. The exit side of the beam contains an electron collector to provide process control for the hardening operations (Ref 10). The gun operates with an acceleration voltage of 60 kV and generates a beam power of up to 5, 10, or 20 kW, depending on the specific version used. In addition to welding and

hardening applications, the electron gun can be used for other thermal surface modifications. The electron gun can easily be programmed to function in numerous applications without any modification or dismantling of the setup shown in Fig. 24.

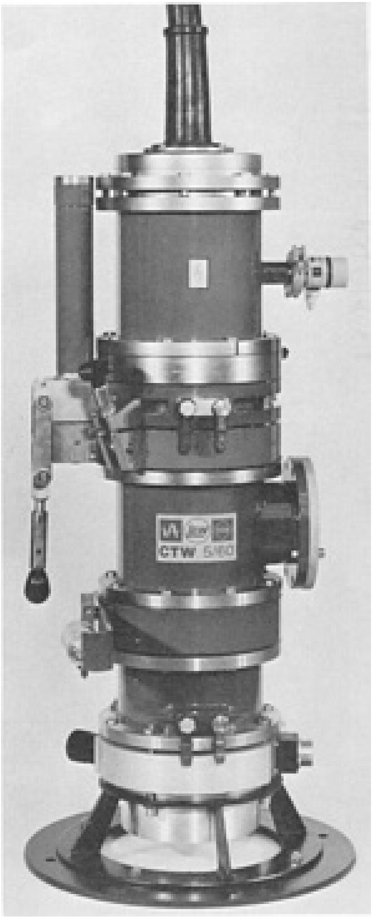

Fig. 25 An electron gun with acceleration voltage, U_B, of 60 kV and beam power, *P,* of 10 kW

Electron beam hardening facilities can be designed either as part of a flexible manufacturing (FMS) system (see the article "Multiple-Operation Machining" in Volume 16 of *ASM Handbook,* formerly 9th Edition *Metals Handbook*) or as stand-alone installations.

Figure 26 shows a system solution used to manufacture suppport elements for roller bearings. The flexible manufacturing system consists of two CNC-controlled milling machines for the complete machining of the workpieces (see Fig. 26) that are subsequently heat treated in the CNC-controlled electron beam hardening machine (see Fig. 27). The raceway for the guiding rollers is hardened similar to the slot flanks shown in Fig. 23(a). The electron beam hardening machine is equipped with a vertically adjustable electron gun that emits a horizontal beam at the rear of the process chamber.

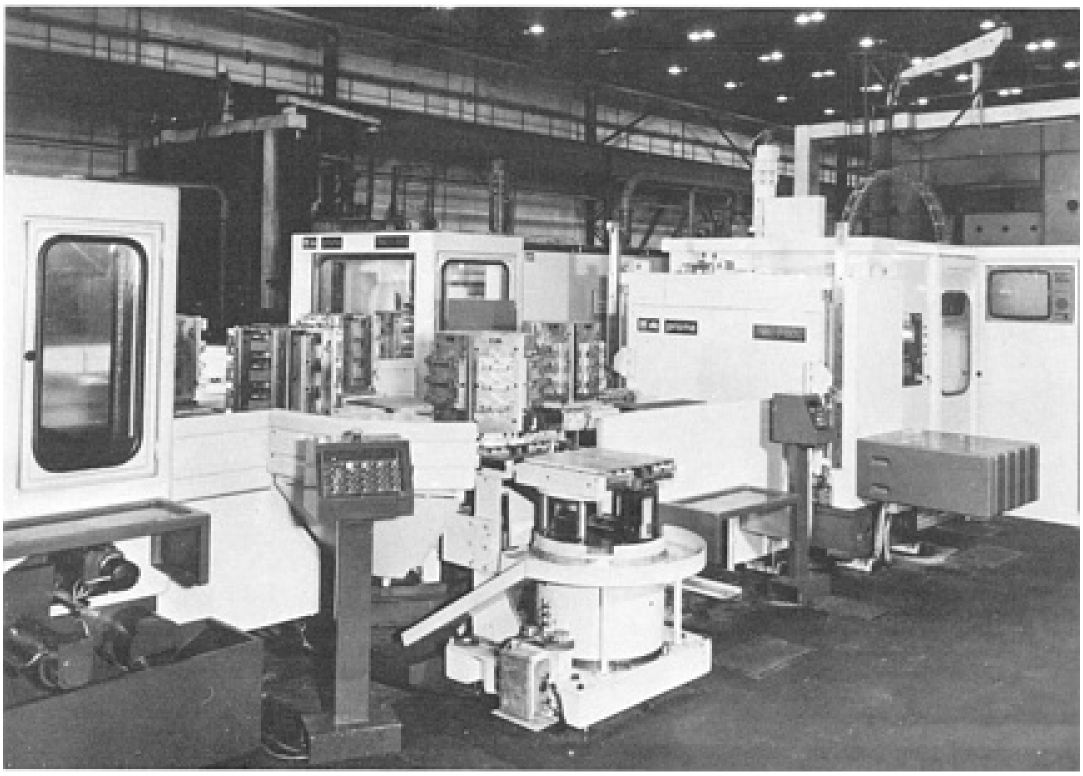

Fig. 26 Integration of electron beam hardening equipment (right-hand side of the photograph) into a flexible manufacturing system to provide complete machining and electron beam hardening of bearing components in a centralized location in a plant and to ensure a continuous flow of parts. Courtesy of Chemnitzer Werkzeugmaschinen GmbH

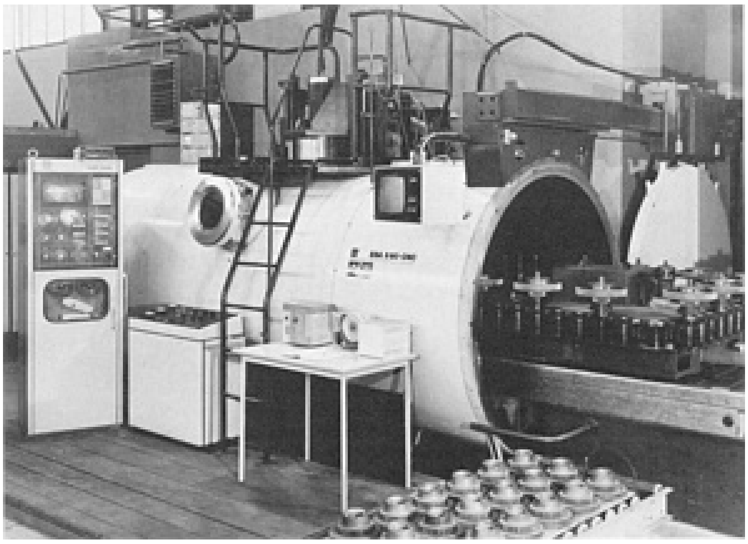

Fig. 27 A computer numerical control (CNC) electron beam installation used for either electron beam welding applications or thermal surface modification applications. Courtesy of Sächsische Elektronenstrahl GmbH

The integration of the hardening process with the machining process made possible by heat efficient operations such as electron beam hardening has resulted in increased productivity and a more cost-effective product. In general, electron beam hardening facilities require pumps capable of providing a vacuum in the work chamber of the machine that ranges from 0.01 to 1 Pa (75 μtorr to 7.5 mtorr).

Electron Beam Hardening versus Laser Beam Hardening. In recent years, heat-treating engineers have focused their efforts on pinpointing the properties that differentiate electron beam hardening from laser beam hardening. The qualitative results of both hardening techniques are almost identical. However, differences do arise from the varying properties of both beam types and the entirely different methods that generate the beams. Comparing electron beam hardening and laser beam hardening to each other and to conventional hardening methods is the most accurate gage of their performance. Both techniques have common advantages and drawbacks compared to conventional hardening techniques as well as specific positive and negative qualities with respect to each other.

Both beam techniques overshadow conventional hardening methods because of the following primary factors:

- Locally well-defined and reproducible energy transfer to the workpiece regions
- Low thermal stress imposed on the component

Secondary benefits include the capability to adapt to a CNC-control process similar to that used in mechanical processing lines and the omission of cooling media for quenching. However, the rather high capital investment costs of high-energy beam hardening facilities may be prohibitive to some customers.

Laser beam hardening has the advantage over electron beam hardening whenever the following factors are significant:

- Relatively large distance between beam source (laser oscillator) and process site
- Beam guidance aided by mirrors (that is, in robot levers and multistation machining)
- Comparatively low costs with low beam power setting (2 to 3 kW) sufficient for hardening
- Parts whose bulk and configuration prevent them from being placed in a vacuum and therefore processing at atmospheric pressure

The following factors favor electron beam hardening as a viable option:

- Inert environment characteristic of a low-or high-vacuum atmosphere is required
- No working or protective gases are required
- Energy absorption properties of the component surface are independent of the optical surface properties (no application of absorption layers for energy coupling)
- High overall energy efficiency of the installation increases with the beam power
- Easy generation of limited energy transfer fields to a maximum of >10 cm^2 (>1.6 $in.^2$) and of any desired power density distribution via cyclic rf beam deflection programs (usability of the energy absorption layer as heat accumulator)
- High-volume productivity at beam powers of 10 kW and above

This discussion indicates that the variables that favor either electron beam hardening or laser beam hardening are clearly delineated. Conditions that must exist for the advantages provided by both hardening methods to overlap and actually compete against each other are very narrow and limited. Therefore, electron beam hardening and laser beam hardening cannot be classified as true competitors within the heat-treating industry.

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Gas Carburizing of Steels

C.A. Stickels, Ford Motor Company, Manufacturing Development Center

Introduction

CARBURIZING is a case-hardening process in which carbon is dissolved in the surface layers of a low-carbon steel part at a temperature sufficient to render the steel austenitic, followed by quenching and tempering to form a martensitic microstructure. The resulting gradient in carbon content below the surface of the part causes a gradient in hardness, producing a strong, wear-resistant surface layer on a material, usually low-carbon steel, which is readily fabricated into parts. In gas carburizing, commercially the most important variant of carburizing, the source of carbon is a carbon-rich furnace atmosphere produced either from gaseous hydrocarbons, for example, methane (CH_4), propane (C_3H_3), and butane (C_4H_{10}), or from vaporized hydro-carbon liquids.

Acknowledgements

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Carbon Sources

Low-carbon steel parts exposed to carbon-rich atmospheres derived from a wide variety of sources will carburize at temperatures of 850 °C (1560 °F) and above. In the most primitive form of this process, the carbon source is so rich that the solubility limit of carbon in austenite is reached at the surface of the steel and some carbides may form at the surface. (In earlier editions of *Metals Handbook,* the carbon gradient produced by maintaining saturated austenite at the surface of the steel is referred to as the normal carbon gradient.) Such atmospheres will also deposit soot on surfaces within the furnace, including the parts. While this mode of carburizing is still practiced in parts of the world in which resources are limited, the goal of current practice in modern manufacturing plants is to control the carbon content of furnace atmospheres so that:

- The final carbon concentration at the surface of the parts is below the solubility limit in austenite
- Sooting of the furnace atmosphere is minimized

Controlled carburizing atmospheres are produced by blending a carrier gas with an enriching gas, which serves as the source of carbon. The usual carrier, endothermic gas, is not merely a diluent, but plays a role, described below, in accelerating the carburizing reaction at the surface of the parts. The amount of enriching gas required by the process depends primarily on the carbon demand, that is, the rate at which carbon is absorbed by the work load.

Endothermic gas (Endogas) is a blend of carbon monoxide, hydrogen, and nitrogen (with smaller amounts of carbon dioxide, water vapor, and methane) produced by reacting a hydrocarbon gas such as natural gas (primarily methane), propane, or butane with air. Endogas is usually produced in a separately fired retort furnace (Endogas generator) using an air-to-hydrocarbon feed ratio that will produce an oxygen-to-carbon atom ratio of about 1.05 in the Endogas. For Endogas produced from pure methane, the air-to-methane ratio is about 2.5; for Endogas produced from pure propane, the air-to-propane ratio is about 7.5. These ratios will change depending on the composition of the hydrocarbon feed gases and the water vapor content of the ambient air. Table 1 lists typical compositions of natural gas. Propane for atmosphere generation should contain less than 5% propylene ($CH_3CH{=}CH_2$) and less than 2.5% butane or heavier hydrocarbons, satisfying the requirements in ASTM D 1835 for so-called special-duty propane or the Gas Producers Association specification 2140, grade HD 5.

Table 1 Specific gravity and composition of natural gas in selected regions of the United States

State	Specific gravity	Composition, vol %

		CH_4	CH_3CH_3	N_2	CO_2
New York	0.58-0.59	94.1-96.3	1.8-2.0	0.3-1.8	0.83-0.96
Illinois	0.57-0.61	89-97.5	1.6-4.4	0.31-5.7	0.39-0.75
California	0.60-0.63	92-98.8	3.9-5	1.2-1.24	0.76-3.0

CH_4, methane; CH_3CH_3, ethane: N_2, nitrogen.

Source: American Gas Association

A carrier gas similar in composition to Endogas produced from methane can be formed from a nitrogen-methanol blend. The proportions of nitrogen and methanol (CH_3OH) are usually chosen to give the same nitrogen-to-oxygen ratio as that of air, that is, about 1.9 volumes of nitrogen for each volume of gaseous methanol. Upon entering the furnace, each volume of gaseous methanol cracks to form approximately one volume of carbon monoxide and two volumes of hydrogen.

A carrier gas can be generated *in situ* by the direct addition of air and a hydrocarbon gas to the carburizing furnace (Ref 1). Special precautions (low flow rates, high temperatures, and good mixing) must be taken in setting up and controlling such a process to ensure a thorough reaction of the feed gases and uniformity of carburizing. Similar precautions are needed if carrier gases high in either carbon dioxide or water vapor content (such as exothermic gas) are used.

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Carburizing Equipment

Gas carburizing furnaces vary widely in physical construction, but they can be divided into two major categories, batch and continuous furnaces. In a batch-type furnace, the work load is charged and discharged as a single unit or batch. In a continuous furnace, the work enters and leaves the furnace in a continuous stream. Continuous furnaces are favored for the high-volume production of similar parts with total case depth requirements of less than 2 mm (0.08 in.).

Batch Furnaces. The most common types of batch furnaces are pit furnaces and horizontal batch furnaces. Pit furnaces are usually placed in a pit with the cover or lid located just above floor level and are often loaded and unloaded with the aid of an overhead crane (Fig. 1). Pit furnaces are frequently used for large parts requiring long processing times. If the work is to be direct quenched, the load must be moved through air before quenching. As a result, parts will be covered by an adherent black scale, which, depending on the needs of the application, may have to be removed by shot blasting or acid pickling.

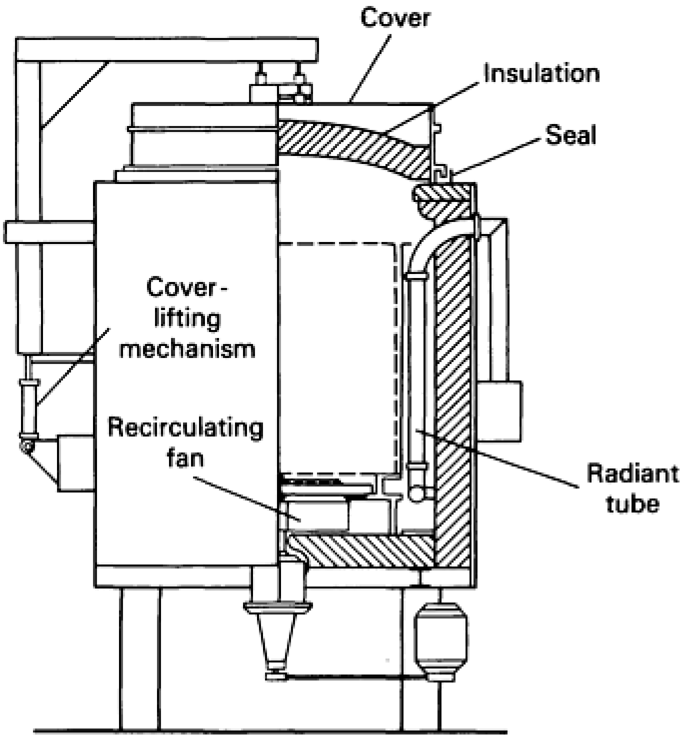

Fig. 1 A pit batch carburizing furnace. Dashed lines location of workload.

Horizontal batch furnaces are frequently used for carburizing and direct quenching. Many of these furnaces are so-called sealed quench, or integral quench, furnaces; that is, parts are discharged from the furnace into a vestibule that covers an oil quench tank (Fig. 2). Because the furnace atmosphere also flows through the vestibule, parts can be kept free of oxidation prior to quenching. Sealed-quench batch furnaces are capable of processing many different types of loads with widely varying case depth requirements. Like pit furnaces, they can be made quite gas tight, with the result that positive furnace pressures are easily achieved.

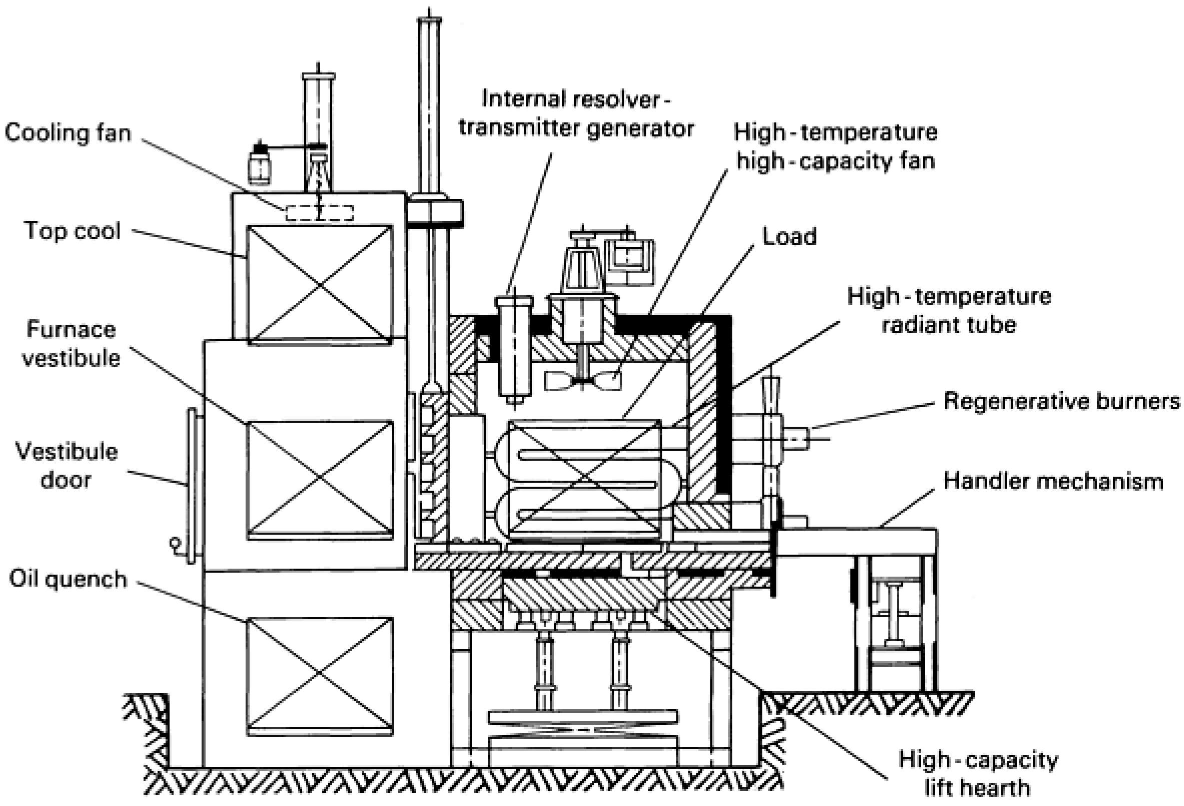

Fig. 2 **A high-productivity gas-fired integral quench furnace**

Continuous Furnaces. Types of continuous furnaces used for carburizing include mesh belt, shaker hearth, rotary retort, rotary hearth, roller hearth, and pusher designs. Many of these furnaces can be built with sealed oil quenching so that oxide-free parts can be produced. Most of these furnaces can be sealed well enough that positive furnace pressures can be maintained. Some continuous mesh belt furnaces, on the other hand, are open to the air at either end. Because air cannot be positively excluded, carburizing in these furnaces is often difficult to control.

Furnace Atmosphere Parameters. Certain principles of operation apply to all controlled-atmosphere furnaces regardless of design. First, in order to ensure the uniformity of carburizing, the furnaces must be equipped with internal fans so that the atmosphere is well circulated through the work load. In addition, the individual parts within the work load must be well spaced to allow the atmosphere to penetrate the load. Critical parts, such as gears, are usually placed on fixtures to control not only their spacing, but also their orientation entering the quenchant. At times the weight of trays and fixtures in pusher furnaces is two to three times the weight of the parts processed.

Second, the furnace should be operated at a positive pressure so that if the furnace has small leaks, air does not enter the furnace. Pressures of 12 to 37 Pa (0.09 to 0.28 torr, or 0.05 to 0.15 in. water column) are usually satisfactory for carburizing furnaces. The furnace pressure can be controlled by adjusting the orifice size in atmosphere vent lines and the carrier gas flow rate.

Because the hot gases inside a furnace are low in density, the pressure differential (furnace pressure minus ambient pressure, measured at the same height) will have its smallest value at the lowest point in the furnace. The minimum furnace pressure needed (at any height) to maintain a positive differential at all heights (P_{min}) can be computed from the relation:

$$P_{min} = H(D_A - D_F) \quad \textbf{(Eq 1)}$$

where H is the internal height of the furnace chamber, D_A is the density of ambient air outside the furnace, and D_F is the density of the atmosphere inside the furnace. Because $D_A >> D_F$, a suitable minimum value for the furnace pressure in pascals is:

$$P_{min} = H(0.117) \quad \textbf{(Eq 2)}$$

where H is in centimeters and it is assumed that the ambient air is at 1 kPa (1 atm) pressure and 20 °C (70 °F). Even though the furnace pressure is nominally positive, air can still enter the furnace through small openings if there are local fluctuations in the ambient pressure. A large cooling fan blowing at the furnace might raise the ambient pressure locally by as much as 25 Pa (0.19 torr, or 0.1 in. water column).

Third, the rate at which the furnace atmosphere responds to changes in inlet gas composition depends on the mean residence time of the atmosphere gases in the furnace. The mean residence time (t_{res}) is approximately:

$$t_{res} = \frac{(V.T_A)}{F.T_F} \quad \textbf{(Eq 3)}$$

where V is the furnace volume; F is the carrier gas flow rate measured at T_A, the absolute ambient temperature; and T_F is the absolute furnace temperature. Residence times in carburizing furnaces vary from about 2 to 15 min. If the inlet gas composition is changed, it takes about three residence times for 95% of the effect of the change to be felt in the furnace. Therefore, batch furnaces, in which the atmosphere composition must be changed during the course of a processing cycle, are usually operated with shorter residence times than are continuous furnaces. It is often considered an advantage to use high flow rates of carrier gas to speed the purging of air that enters the furnace when parts are charged. However, the same result can usually be achieved more economically by using an automatic control system to regulate the flow of the hydrocarbon enriching gas.

Preparation of Parts for Carburizing

Parts, trays, and fixtures should be thoroughly cleaned before they are charged into a carburizing furnace. Often they are washed in a hot alkaline solution. Some users heat washed parts, trays, and fixtures in an oxidizing atmosphere at 400 °C (750 °F) before carburizing to remove traces of organic contaminants (Ref 2).

Very thin oxide layers on parts (such as those produced by oxidation below 500 °C, or 900 °F) are reduced by the carburizing atmosphere. Heavy oxide layers, such as forging scale, will be reduced to iron flakes, which are not adherent to the part.

Residues from alkaline washer solutions deposited on parts, particularly those with silicates, can cause spotty carburizing, as well as give the parts a blotchy appearance. In addition, alkaline residues can adversely affect the life of heat-resistant furnace alloys. Quenching salts remaining on trays and fixtures can also damage furnace hardware (for example, silicon carbide rails in pusher furnaces). Chlorine- or sulfur-containing residues on parts will release gases that can react with brickwork, the protective oxide films on heat-resistant alloy fixtures, or the work load.

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Carburizing Process Variables

The successful operation of the gas carburizing process depends on the control of three principal variables:

- Temperature
- Time

- Atmosphere composition

Other variables that affect the amount of carbon transferred to parts include the degree of atmosphere circulation and the alloy content of the parts.

Temperature. The maximum rate at which carbon can be added to steel is limited by the rate of diffusion of carbon in austenite. This diffusion rate increases greatly with increasing temperature; the rate of carbon addition at 925 °C (1700 °F) is about 40% greater than at 870 °C (1600 °F).

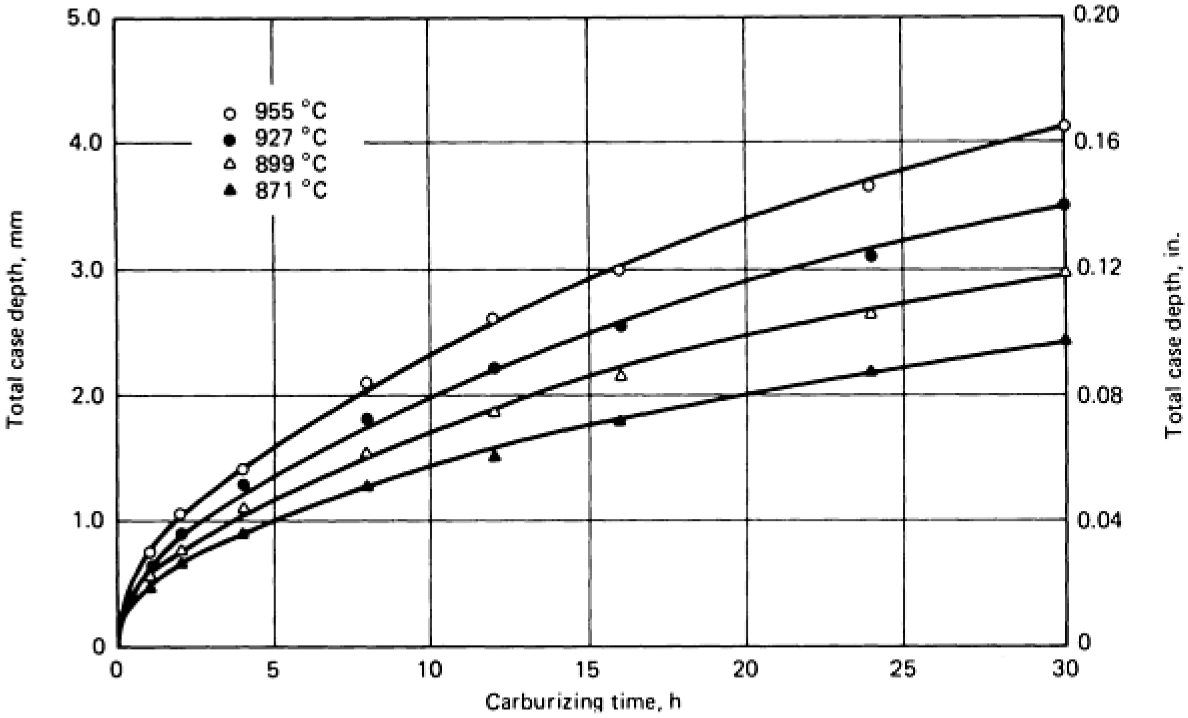
The temperature most commonly used for carburizing is 925 °C (1700 °F). This temperature permits a reasonably rapid carburizing rate without excessively rapid deterioration of furnace equipment, particularly the alloy trays and fixtures. The carburizing temperature is sometimes raised to 955 °C (1750 °F) or 980 °C (1800 °F) to shorten the time of carburizing for parts requiring deep cases. Conversely, shallow case carburizing is frequently done at lower temperatures because case depth can be controlled more accurately with the slower rate of carburizing obtained at lower temperatures.

For consistent results in carburizing, the temperature must be uniform throughout the work load. Temperature gradients through the work load will persist for a substantial period of time while the work is being heated to the carburizing temperature. Because parts at the exterior of the load reach the furnace temperature first, they will begin carburizing well before parts at the interior of the load. The consequence is variability in case depth from part to part and within a single part. In addition, soot can be deposited on cold parts exposed to a carburizing atmosphere. Therefore, for best results, the work load should be heated to the carburizing temperature in a near-neutral furnace atmosphere. In batch furnaces, parts can be heated in Endogas until they reach the furnace temperature; then carburizing can commence with the addition of the enriching gas. Many new continuous furnaces are being built with separate preheat chambers to ensure that the load is at a uniform temperature before entering the carburizing zone. In continuous furnaces that lack positive separation between heating and carburizing stages, the best that can be done is to:

- Add only Endogas to the front of the furnace
- Establish a front-to-back internal flow of atmosphere gases by adjusting flow rates and orifice size in the effluent lines at either end of the furnace

In batch furnaces, the thermocouple used for temperature control is usually positioned so that it reaches the set-point temperature before the work load does. In continuous furnaces that are not positively separated into zones, the thermocouple in the first zone (used for heating) should be placed near the end of that zone. This prevents overheating of the work load. The control thermocouple is usually positioned near the center of the carburizing zone. If the last zone is at a lower temperature than the carburizing zone, the control thermocouple is usually placed near the discharge end of the zone. However, the features of individual furnaces, such as the location of radiant tubes, must be considered when positioning control thermocouples.

Time. The effect of time and temperature on total case depth is shown in Fig. 3. The data given, originally published by Harris (Ref 3) in 1944, are computed assuming saturated austenite at the surface of the workpieces. When the surface carbon content is controlled so that it is less than the saturation value, case depths will be less than they otherwise would be. Figure 4 shows how the carburizing time decreases with increasing carburizing temperature for a case depth of 1.5 mm (0.06 in.). In addition to the time at the carburizing temperature, several hours may be required to bring large workpieces or heavy loads of smaller parts to operating temperature. For work quenched directly from the carburizing furnace, the cycle may be lengthened further by allowing time for the work to cool from the carburizing temperature to about 843 °C (1550 °F) prior to quenching. If the workload is exposed to the carburizing atmosphere during heating, some carburizing will occur before the nominal start of carburizing. Similarly, additional diffusion and interchange of carbon with the atmosphere will occur during cooling prior to quenching. Thus, the actual case depth achieved may differ significantly from the values listed in the table in Fig. 3. More complex mathematical models that allow for variations in temperature and atmosphere carbon potential with time can be constructed to allow a better prediction of case depth.



Time, h	871 °C (1600 °F)		899 °C (1650 °F)		927 °C (1700 °F)		955 °C (1750 °F)	
	mm	in.	mm	in.	mm	in.	mm	in.
1	0.46	0.018	0.53	0.021	0.64	0.025	0.74	0.029
2	0.64	0.025	0.76	0.030	0.89	0.035	1.04	0.041
4	0.89	0.035	1.07	0.042	1.27	0.050	1.30	0.051
8	1.27	0.050	1.52	0.060	1.80	0.071	2.11	0.083
12	1.55	0.061	1.85	0.073	2.21	0.087	2.59	0.102
16	1.80	0.071	2.13	0.084	2.54	0.100	2.97	0.117
24	2.18	0.086	2.62	0.103	3.10	0.122	3.66	0.144

Fig. 3 Plot of total case depth versus carburizing time at four selected temperatures. Graph based on data in

table

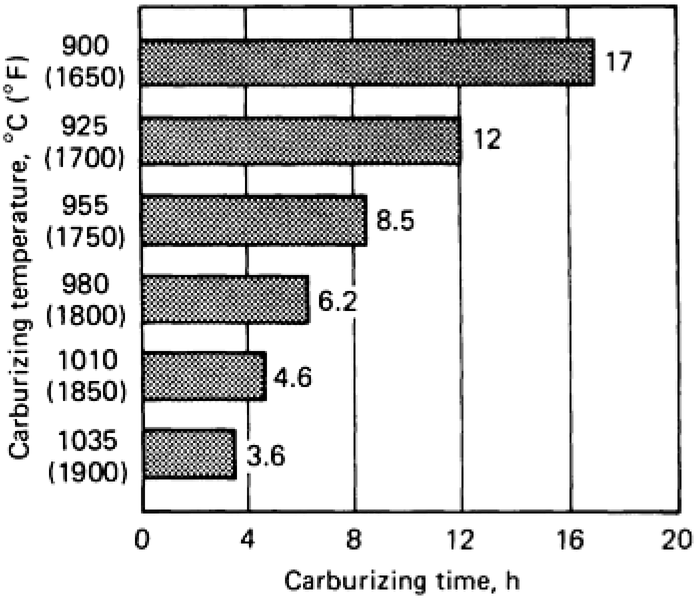


Fig. 4 Reducing effect of increased process temperature on carburizing time for 8620 steel. Case depth: 1.5 mm (0.060 in.). Source: Ref 4

Carbon Potential. The carbon potential of a furnace atmosphere at a specified temperature is defined as the carbon content of pure iron that is in thermodynamic equilibrium with the atmosphere. The carbon potential of the furnace atmosphere must be greater than the carbon potential of the surface of the workpieces in order for carburizing to occur. It is the difference in carbon potential that provides the driving force for carbon transfer to the parts.

Carbon Diffusion. The combined effects of time, temperature, and carbon concentration on the diffusion of carbon in austenite can be expressed by Fick's laws of diffusion. Fick's first law states that the flux of the diffusing substance perpendicular to a plane of unit cross-sectional area is proportional to the local carbon gradient perpendicular to the plane. The constant of proportionality is the diffusion coefficient *D,* which has the units $(\text{distance})^2/\text{time}$. Fick's second law is a material balance within an elemental volume of the system; the flux of carbon into an elemental volume of iron minus the flux of carbon out of the elemental volume equals the rate of accumulation of carbon within the volume. Combining the two laws leads to a partial differential equation that describes the diffusion process. Reference 5 provides solutions to the diffusion equation for a variety of boundary conditions and part configurations, for example, plate, rod, sphere, and so on. With these solutions and values of the diffusion coefficient, it is possible to predict the carbon gradient and depth of penetration occurring for any combination of time, temperature, and surface carbon concentration.

The diffusion coefficient for carbon in austenite is a function of carbon content and temperature. The following expression, proposed by Tibbetts (Ref 6) summarizes the experimental data:

$$D = 0.47 \exp[-1.6\,C - (37000 - 6600\,C)/RT] \qquad \textbf{(Eq 4)}$$

where D is in cm^2/s, C is the weight percent carbon, T is temperature in degrees Kelvin, and R is the gas constant. Exact solutions to the diffusion equation when the diffusion coefficient depends on composition are available for steady-state diffusion (Ref 5), but for time-dependent solutions, numerical methods must be used. Figure 5 lists a BASIC computer program for finding the carbon concentration gradient below a flat surface using the expression above for the diffusion coefficient. In this program, the surface boundary condition is:

$$\text{Carbon flux} = \beta\sigma(CP - C_0) \qquad \textbf{(Eq 5)}$$

where carbon flux is in g/s · cm^2, β is an effective reaction rate constant in s^{-1}, σ, is the density in g/cm^3, *CP* is the atmosphere carbon potential, and C_0 is the surface carbon content. The value of β may vary depending on the degree of atmosphere circulation within the furnace. Taking β equal to 0.00002 s^{-1} seems to produce results that are in reasonable agreement with experience. However, values of β that are as much as a factor of two larger or smaller may be needed to model carburizing behavior in specific furnaces.

```
1Ø 'Diffusion of Carbon in Austenite
12 'Tibbetts' Expression for the Diffusion Constant of Carbon
15 DEF FNDFC(T,WC) = .47*EXP(-1.6*WC - (37ØØØ! - 66ØØ*WC)/(1.987*T))
2Ø INPUT "Temperature in Degrees C  ",TC
3Ø INPUT "Time in Hours  ",TH
4Ø INPUT "Carbon Potential, wt. pct.  ",CP
5Ø INPUT "Surface Reaction Rate Constant  ",BETA
6Ø INPUT "Initial Carbon Content of Steel  ",CØ
7Ø T = TC + 273.15  :  TSEC = TH*36ØØ
8Ø DT = 15  :  DX = .Ø1
9Ø DIM C(31), CL(31)
1ØØ L1 = 2*DT/DX  :  L2 = DT/DX^2
11Ø NN% = INT(TSEC/DT)  :  V% = Ø
12Ø FOR I% = Ø TO 31
13Ø   CL(I%) = CØ
14Ø NEXT I%
15Ø FOR J% = 1 TO NN%
16Ø   WC = (CL(Ø) + CL(1))/2
17Ø   DB = FNDFC(T,WC)
18Ø   ETA = .75*CL(Ø) + .25*CL(1) + L1*(BETA*(CP - CL(Ø))
            + DB*(CL(1) - CL(Ø))/DX)
19Ø   FOR I% = 1 TO 3Ø
2ØØ     IF (V% = Ø) THEN GOTO 22Ø
21Ø     C(I%) = CØ  :  GOTO 27Ø
22Ø     DA = DB
23Ø     WC = (CL(I%) + CL(I%+1))/2
24Ø     DB = FNDFC(T,WC)
25Ø     C(I%) = CL(I%) + L2*(DB*CL(I%+1) - (DA+DB)*CL(I%)
                + DA*CL(I%-1))
26Ø     IF (ABS(C(I%) - CØ) < .ØØØØ5) THEN V% = 1
27Ø   NEXT I%
28Ø   C(Ø) = 4*(ETA - .25*C(1))/3  :  V% = Ø
29Ø   FOR I% = Ø TO 31
3ØØ     CL(I%) = C(I%)
31Ø NEXT I%,J%
32Ø PRINT "Depth, mm","Wt. Pct. C","Depth, mm.","Wt. Pct. C"
33Ø FOR I% = Ø TO 15
34Ø   PRINT USING "#.####        ";DX*I%*1Ø,C(I%),DX*(I%+15)*1Ø,C(I%+15)
35Ø NEXT I%
36Ø END
```

Fig. 5 Finite-difference computation of the diffusion of carbon in austenite using BASIC computer program

Alloy Effects. The various alloying elements found in carburizing steels have an influence on the activity of carbon dissolved in austenite. A definition of carbon activity (a_C) is:

$$a_C = (\text{wt\% } C)\ \Gamma \qquad \textbf{(Eq 6)}$$

where Γ, the activity coefficient, is chosen so that a_C = 1 for an amount of carbon in solution that is in equilibrium with graphite. Chromium tends to decrease the activity coefficient, and nickel tends to raise it. As a consequence, foils of a chromium-bearing steel equilibrated with a specific furnace atmosphere will take on more carbon than pure iron, and nickel-bearing steels will take on less carbon. It is also true that carbides are produced at lower carbon potentials in chromium-bearing steels than in carbon steels. The primary effect of alloying elements on the diffusion of carbon is due to their effect on the driving force for the surface reaction (Eq 5). To obtain the true driving force, the surface carbon content in an alloy must be converted into the equivalent carbon content in pure iron. Methods of correcting the activity coefficient of carbon for alloy content are available (Ref 7). However, the quantity of experimental data upon which such

correlations are based is rather limited. Therefore, predictions should be verified by experiments, particularly when an alloy contains substantial amounts of more than one alloying element.

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5. J. Crank, *The Mathematics of Diffusion,* 2nd ed., Oxford University Press, 1975
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Gas Carburizing Atmospheres

In the discussion of carburizing atmospheres in this section, it will be assumed that the atmosphere consists of an endothermic carrier gas (produced from methane) that is enriched by a methane addition, which serves as the source of the carbon being transported to the work load. The main constituents of the atmosphere are CO, N_2, H_2, CO_2, H_2O, and CH_4. Of these constituents, N_2 is inert, acting only as a diluent. The amounts of CO, CO_2, H_2, and H_2O present are very nearly the proportions expected at equilibrium from the reversible reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \textbf{(Eq 7)}$$

given the particular ratios of carbon, oxygen, and hydrogen in the atmosphere. Methane is invariably present in amounts well in excess of the amount that would be expected if all the gaseous constituents were in equilibrium.

Although the sequence of reactions involved in carburizing is not known in detail, it is known that carbon can be added or removed rapidly from steel by the overall reversible reactions:

$$2CO \leftrightarrow C \text{ (in Fe)} + CO_2 \qquad \textbf{(Eq 8)}$$

and

$$CO + H_2 \leftrightarrow C \text{ (in Fe)} + H_2O \qquad \textbf{(Eq 9)}$$

A carburization process based solely on the decomposition of CO would require large flow rates of atmosphere gas to produce appreciable carburizing. As an example, the loss of just 0.47 g C from a cubic meter of endothermic gas at 927 °C (1700 °F) is sufficient to reduce the CO-to-CO_2 ratio from 249 to 132 and the carbon potential from 1.25 to 0.8%. The loss of 0.47 g C represents about the same amount present in a steel part of 100 cm^2 (15.5 $in.^2$) surface area carburized to a depth of 1 mm (0.040 in.).

The methane enrichment of endothermic gas provides carbon for the process by slow reactions such as:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \textbf{(Eq 10)}$$

and

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \textbf{(Eq 11)}$$

which reduce the concentrations of CO_2 and H_2O, respectively. These reactions regenerate CO and H_2, thereby directing the reactions of Eq 8 and 9 to the right. Because the methane content of carburizing atmospheres is usually far above the

content that is expected at equilibrium, given the CO_2 and H_2O contents present, it is evident that the reactions in Eq 10 and 11 do not approach equilibrium. The sum of the reactions in Eq 8 and 10 and in Eq 9 and 11 is reduced to:

$$CH_4 \rightarrow C \text{ (in Fe)} + 2H_2 \qquad \textbf{(Eq 12)}$$

Thus, with constant CO_2 content and constant dew point, the net atmosphere composition change during carburizing is a reduction in methane content and an increase in the hydrogen content. In most commercial operations, atmosphere flow rates are high enough and the rate of methane decomposition is low enough to prevent a large buildup of hydrogen during a carburizing cycle. However, with carburizing loads having high surface area, there is a drop in the CO content of 1 to 3% at the beginning of the cycle when the carbon demand is greatest. This is caused by the dilution of the furnace atmosphere with hydrogen.

Carbon potential control during carburizing is achieved by varying the flow rate of the hydrocarbon-enriching gas, while maintaining a steady flow of endothermic carrier gas. As a basis for regulating the enrichment gas flow, the concentration of some constituent of the furnace atmosphere is monitored:

- Water vapor content by dew point measurement
- Carbon dioxide content by infrared gas analysis
- Oxygen potential using a zirconia oxygen sensor

The first two quantities provide measures of carbon potential according to the reactions of Eq 8 and 9. Oxygen potential is related to carbon potential by the reaction:

$$C \text{ (in Fe)} + \tfrac{1}{2}O_2 \leftrightarrow CO \qquad \textbf{(Eq 13)}$$

When the carbon monoxide content of the atmosphere remains relatively constant, both the carbon dioxide and the oxygen potential provide good measures of the carbon potential. For the dew point to be a valid measure of carbon potential, the product of the hydrogen and carbon monoxide contents must be stable. If the hydrogen content of the furnace atmosphere rises, as a result of either carburizing or sooting, the relationships between CO_2 content, oxygen potential, dew point, and the carbon potential will be altered. For this reason, some process control systems include infrared analysis of CO and the measurement of CO_2 or oxygen potential so that a true carbon potential may be computed for all operating conditions.

Calculation of Equilibrium Compositions. Gas carburizing is a nonequilibrium process; that is, the gaseous constituents of the atmosphere are not fully in equilibrium with one another, and the atmosphere is not in equilibrium with the steel being carburized. Nevertheless, several important reactions, for example, reactions in Eq 7, 8, and 9, approach equilibrium rapidly enough to permit predictions of the rate of carburizing from the atmosphere composition. Thus, the same case carbon gradient can be expected from different furnaces with different atmosphere gas flow rates when certain factors are held constant:

- Carbon potential, as inferred from CO_2, H_2O, or oxygen potential measurements
- Carburizing time
- Carburizing temperature

To compute the equilibrium gas composition resulting from the reaction of a blend of a hydrocarbon gas and air:

- Six gaseous species are assumed to be present in the reacted gas: CO, CO_2, H_2, H_2O, CH_4, and N_2. The partial pressures of five of these are unknowns to be determined; the sixth can be found by computing the difference after the others are known
- The carbon-to-hydrogen and oxygen-to-nitrogen ratios are fixed by the nature of the hydrocarbon and the composition of air. With the air-to-hydrocarbon ratio fixed, three equations can be found that relate the five unknown partial pressures

- Two equilibrium relationships, for example, the reactions in Eq 7 and 10, provide two additional equations; thus, all the partial pressures are determined

Because explicit expressions for the unknowns cannot be written, trial-and-error computation methods must be used with the aid of a computer (Ref 8). After the equilibrium composition of the gas is known, its carbon potential is found by writing the equilibrium relationship for Eq 8:

$$K_8 = (a_C \cdot P_{CO_2})/(P_{CO})^2 \qquad \textbf{(Eq 14)}$$

where P_{CO} and P_{CO_2} are partial pressures of CO and CO_2, respectively; a_C is the activity of carbon (a_C = 1 when the atmosphere is in equilibrium with graphite); and K_8 is the equilibrium constant for the reaction in Eq 8.

The constant K_8 can be computed from the Gibbs free energy of formation of CO and CO_2 at the temperature of interest (free energy values are tabulated in Ref 9):

$$\Delta F^\circ_{CO_2} - 2\Delta F^\circ_{CO} = -R\,T \cdot \ln K_8 \qquad \textbf{(Eq 15)}$$

where ΔF°_{CO} and $\Delta F^\circ_{CO_2}$ are free energies of CO and CO_2, respectively; T is the absolute temperature; and R is the gas constant.

The carbon activity is related to the carbon content of austenite by the expression (Ref 10):

$$\ln a_C = \ln y_C + (9167\, y_C + 5093)/T - 1.867 \qquad \textbf{(Eq 16)}$$
$$\text{where } y_C = (4.65\, w)/(100 - w)$$

where T is the temperature in degrees Kelvin, w is the weight percent carbon in austenite, and y_C is the atom ratio of carbon to iron. Combining Eq 14 and 16 gives a relation between carbon potential (that is, the equilibrium carbon content in austenite) and the carbon dioxide and carbon monoxide contents. As long as the assumptions of the calculation are satisfied, measuring just the CO_2 content suffices to define the carbon potential. However, when carbon is removed from the atmosphere by carburizing, there is a reduction in the carbon-to-hydrogen ratio characterizing the atmosphere. When the carbon-to-hydrogen ratio may vary, it is necessary to measure two constituents of the atmosphere, CO and CO_2 content, to define the carbon potential accurately. However, unless the changes in the atmosphere are large, it is seldom worth measuring both CO and CO_2 because of the effect of the added measuring error on the uncertainty of the computed carbon potential.

Endothermic gas derived from propane has a carbon monoxide content of about 23%, whereas that derived from methane has a carbon monoxide content of about 20%. Therefore, the carbon dioxide contents corresponding to a given carbon potential are higher for atmospheres derived from propane than for those derived from methane. Figures 6 and 7 show the relationship between carbon dioxide content and carbon potential for endothermic gas atmospheres derived from methane and propane, respectively.

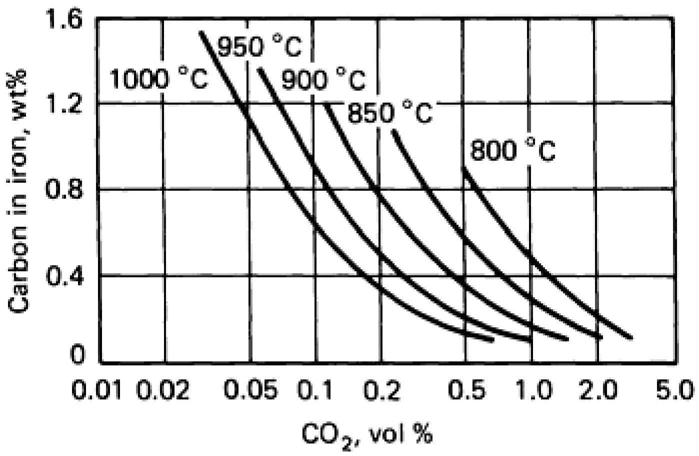

Fig. 6 Relationship between CO_2 content and carbon potential for endothermic gas from methane

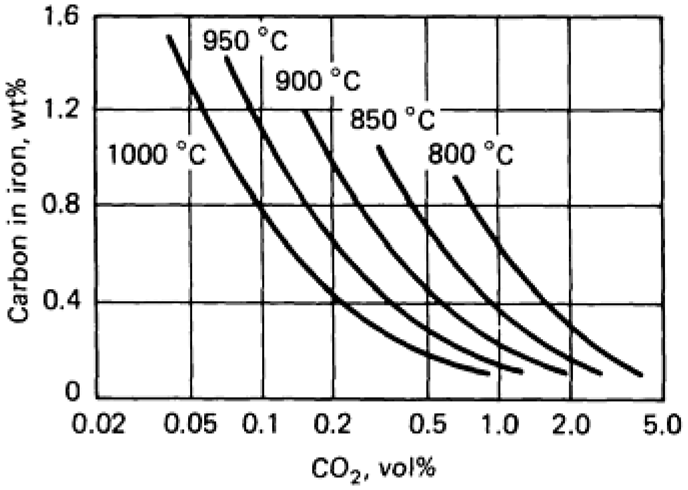

Fig. 7 Relationship between CO_2 content and carbon potential for endothermic gas from propane

The oxygen potential (or oxygen partial pressure), as measured by a zirconia oxygen sensor, is related to the carbon activity by the equilibrium equation for the reaction given in Eq 13:

$$a_c = \frac{P_{CO}}{K_{13} P_{O_2}} \quad \textbf{(Eq 17)}$$

where $P\ O_2$ is the oxygen partial pressure and K_{13} is the equilibrium constant. In carburizing atmospheres, the oxygen partial pressure is approximately 10^{-14} to 10^{-20} Pa (10^{-19} to 10^{-25} atm).

The voltage output of a zirconia oxygen sensor, with air as a reference gas, is a function of the absolute temperature (T) and the oxygen partial pressure ($P\ O_2$) according to the expression:

$$emf = 0.000049593 T \log_{10}\left(\frac{P_{O_2}}{0.209}\right) \quad \textbf{(Eq 18)}$$

where emf is in volts. Combining Eq 16, 17, and 18 yields a relation between carbon potential and emf. Because this relation also depends on the carbon monoxide content of the atmosphere (Eq 18), emf measurements corresponding to a

certain carbon potential for endothermic gas atmospheres derived from methane (Fig. 8) differ from those for atmospheres derived from propane (Fig. 9).

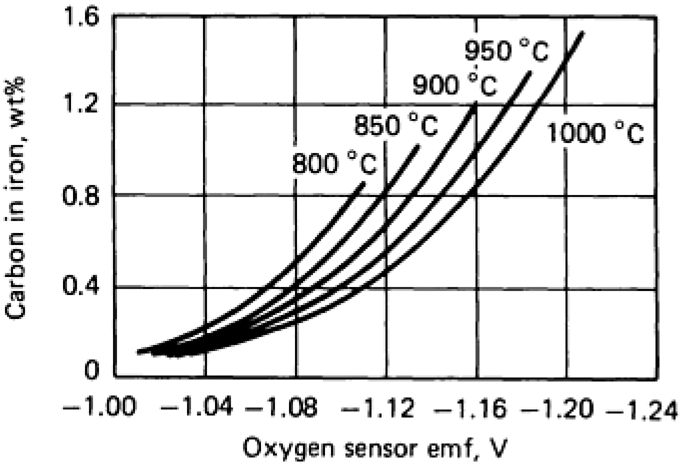

Fig. 8 Measurements of the emf of endothermic gas from methane

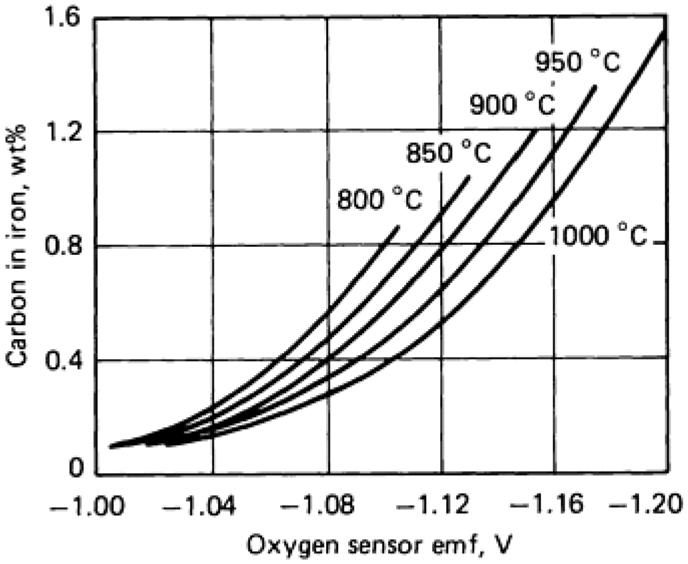

Fig. 9 Measurements of the emf of endothermic gas from propane

The water vapor content of the atmosphere is related to the carbon potential by the reaction in Eq 11. The equilibrium relation is:

$$a_c = \frac{K_{11} P_{CO} P_{H_2}}{P_{H_2O}} \qquad \textbf{(Eq 19)}$$

where K_{11} is the equilibrium constant.

For atmospheres derived from a particular hydrocarbon, the product of the carbon monoxide and hydrogen contents varies little for large changes in water vapor content. The water vapor content of the atmosphere is usually measured by determining its dew point. An equation relating dew point in degrees Celsius and P_{H_2O} in atmospheres is:

$$Dew\ \text{point} = \frac{5422.18}{14.73316 - \ln P_{H_2O}} - 273.16 \quad \textbf{(Eq 20)}$$

Equations 16, 19, and 20 can be combined to produce the relations between dew point and carbon potential plotted in Fig. 10 and 11 for endothermic gas atmospheres derived from methane and propane, respectively.

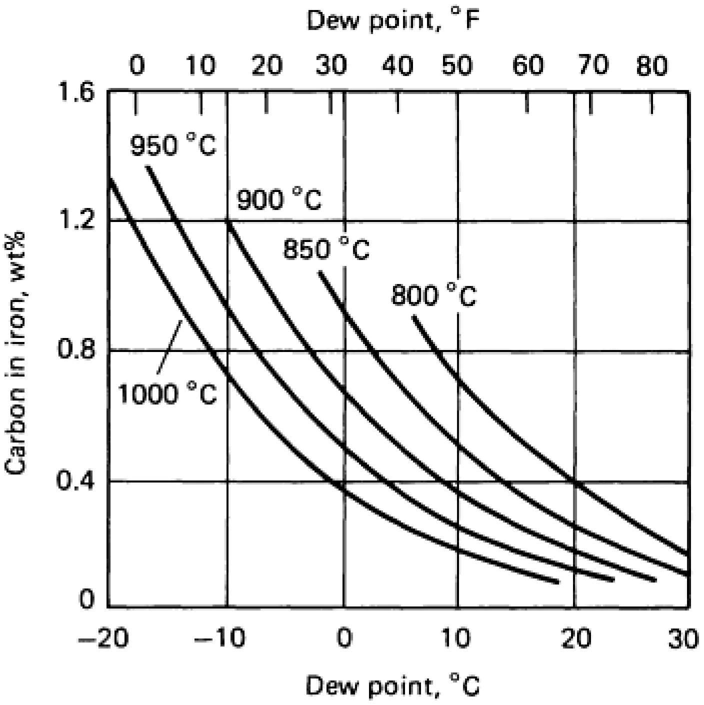

Fig. 10 Relationship between dew point and carbon potential for endothermic gas derived from methane

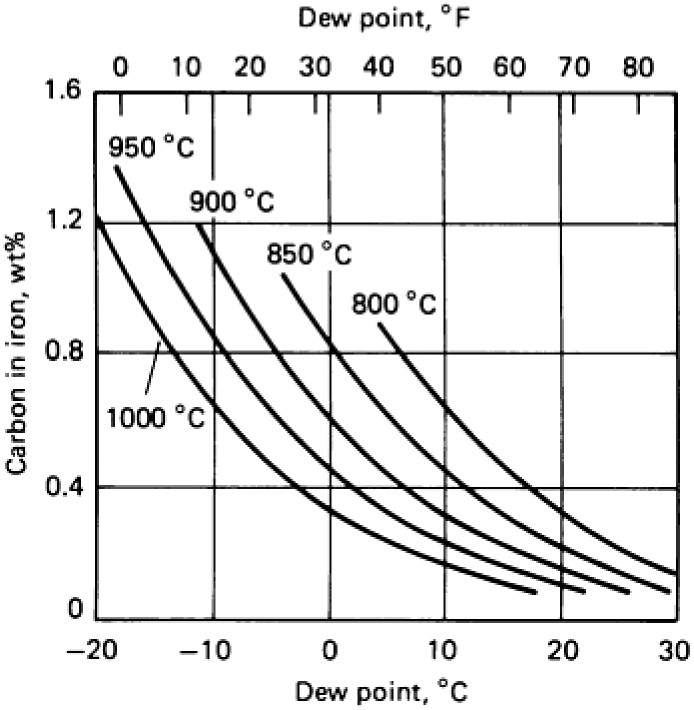

Fig. 11 Relationship between dew point and carbon potential for endothermic gas derived from propane

Sooting. If the carbon potential of a furnace atmosphere is allowed to become very high, sooting will occur. As carbon is lost from the atmosphere, hydrogen is produced. One symptom of a sooting condition is a pronounced drop in the CO content due to hydrogen dilution. When a furnace becomes sooted, it is found that the carbon potential of the furnace atmosphere is no longer controllable; that is, changes to the flow of enriching gas no longer produce the expected changes in atmosphere composition and carbon potential. The only practical solution is to empty the furnace of parts, introduce air, and burn out the soot.

Some care is necessary in burning out accumulated soot to prevent local overheating in the furnace. Typically, the furnace temperature will be set at about 815 °C (1500 °F) for burnout, and air will be admitted to the furnace, by either opening doors or introducing a flow of air. The rise in temperature due to the combustion of soot should be monitored. The air supply can be reduced if the temperature rise is excessive.

Modern automatic atmosphere control systems minimize sooting by maintaining a constant atmosphere composition, thereby matching carbon supply to carbon demand. However, even with the best system, a furnace can be sooted up if the control carbon potential is set too high.

Furnace Conditioning. When a carburizing atmosphere is introduced into an empty furnace that has been idle for some time or that has just been burned out to remove soot, it is found that the amount of enriching gas needed to maintain a given carbon potential is much higher than would be expected. As time passes (typically, 12 to 24 h), the amount of enriching gas needed to maintain the carbon potential decreases to a steady-state value. This process is called conditioning a furnace.

During the time in which conditioning is occurring, carbon is deposited in the crevices of the brickwork and at other locations where the temperature is low. This occurs because the carbon potential of a carburizing atmosphere increases as the temperature falls. An atmosphere with a carbon potential of 1% at 927 °C (1700 °F) is capable, thermodynamically, of depositing soot at or below 843 °C (1550 °F). Eventually, the crevices will be filled with carbon, and the exposed carbon will be at a high enough temperature that further carbon deposition cannot occur. However, there will be some locations, such as sight ports and gas sample lines, where soot will continue to be deposited as the furnace is used. Soot may also form in unheated furnace vestibules as the furnace atmosphere gas cools upon entering the vestibule.

Process Controllers. A process controller compares the output of a sensor with a set point and generates a control signal intended to reduce the difference between these two values. The sensor can be a thermocouple, if the temperature is to be controlled, or an oxygen sensor or infrared gas analyzer, if the atmosphere composition is to be controlled. In the case of atmosphere control, the device being controlled is usually a valve on the enriching gas line. Valves are of two types:

- Those in which the flow through the valve is proportional to the motion, linear or angular, of the valve stem
- Those simply used to switch the flow on and off

In the first case, the control signal is translated into the position of the valve stem. In the second case, time proportioning is used: The fraction of the time that the valve is open is proportional to the control signal.

Most controllers used with furnaces employ proportional, integral, and derivative (PID) modes of feedback control (Ref 11). The controller converts an error signal (E) (the difference between the actual output of the sensor and the desired output) into a control signal (M) using the logic:

$$M = K\left(E + \frac{1}{T_1}\int E.dt + T_d.dE/dt\right) \qquad \textbf{(Eq 21)}$$

where K is the proportional gain, T_I is the integral time constant, and T_d is the derivative time constant. M can be thought of as the fraction of maximum possible flow through the valve. The quantity $100/K$ is often called the percent proportional band. The quantity $1/T_I$ is often called the reset rate. Derivative control is often called rate control. A process can be controlled using only proportional control (the control signal directly proportional to the error signal), but it will always stabilize at a nonzero value of E. For the process to stabilize at $E = 0$, both integral control and proportional

control are needed. The integral portion of the logic effectively generates an offset signal that allows the process to stabilize at E = 0. When the set point on the controller is changed, the integral logic must generate a new offset signal for the process to stabilize at E = 0. If T_I is too large, the rate of approach to E = 0 will be very sluggish; if T_I is too small, the process will overshoot the set point. Finding proper values for K, T_I, and T_d can be quite time consuming, but it is necessary to ensure a controlled process. Fortunately, controller manufacturers have recently introduced self-tuning controllers capable of sensing the response of the system and choosing appropriate values of K, T_I, and T_d.

Nitrogen-Methanol Atmospheres. The *in situ* generation of a carrier gas from a blend of nitrogen and methanol has become more common in recent years. The primary advantage of this approach is that separately fired endothermic gas generators are no longer required. The primary disadvantage is that operating costs are often higher, although this obviously depends on the local cost and availability of natural gas and propane.

Upon entering a heat-treating furnace, methanol cracks to form CO and H_2. The nitrogen-to-methanol ratio is usually chosen so that the nitrogen-to-oxygen ratio is the same as that for air.

$$CH_3OH + 1.89N_2 \rightarrow CO + 2H_2 + 1.89N_2 + CH_4 + 2.39\,(0,2095O_2 \overset{Air}{+} 0.7905N_2) \rightarrow CO + 2H_2 + 1.89N_2 \quad \textbf{(Eq 22)}$$

The material balances above show that when the nitrogen-to-methanol mole ratio is 1.89, the atom ratios of oxygen, hydrogen, carbon, and nitrogen will be the same as those produced from air-to-methane mole ratio of 2.39. Because Endogas is usually produced with an air-to-methane ratio of about 2.5, it is clear that a nitrogen-methanol carrier gas is richer than conventional Endogas. This poses no special problems when carburizing, but may lead to sooting if the nitrogen-methanol blend is run into an empty furnace for long periods of time. Air is often added to nitrogen-methanol to reduce its carbon potential for neutral hardening applications.

Heat is required to vaporize methanol and the cracking of methanol to CO and hydrogen is quite endothermic. Therefore, successful cracking is favored by higher furnace temperatures and lower rates of carrier gas usage. The presence of lower than expected CO contents in furnace atmospheres is symptomatic of incomplete cracking. However, low CO contents can also arise if the proportions of nitrogen and methanol change with changes in the carrier gas flow.

Because of the similarity in atmosphere composition, a 1.89 mole ratio nitrogen-methanol carrier gas enriched with methane can be controlled using the same control points (Fig. 6, 8, and 10) as an Endogas atmosphere produced from methane. The only additional complication is the need for maintaining a constant mole ratio for the carrier gas, particularly when changing the carrier gas flow rate. Rather than invest in sophisticated flow metering, some users have chosen to control their processes by measuring two atmospheric constituents (CO and oxygen potential, for example), rather than just one, to determine carbon potential.

Nitrogen of high purity (about 10 ppm residual CO_2 and water vapor) is produced by liquifying air and then using the differences in boiling points of the various constituents to effect the separation of nitrogen. In most instances, liquid nitrogen is shipped from an air separation plant to the heat-treating plant and stored in vacuum-insulated vessels. Nitrogen of lesser purity can be produced on site by a variety of means:

- *Combustion processes.* Air is burned with natural gas, and the CO_2 and H_2O are stripped from the gas by absorption and condensation
- *Pressure swing absorption, vacuum swing absorption.* Air separation using zeolite molecular sieves
- *Membrane air separation.* Differences in molecular diffusion rates through thin-walled fibrous tubes are used to separate oxygen and nitrogen

Low-purity less expensive nitrogen can be used with methanol to form satisfactory furnace atmospheres. However, because the oxygen content of the nitrogen should be kept relatively constant, the nitrogen generation process must be designed with this requirement in mind.

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Process Planning

Designers usually specify the case hardness, case depth, and core hardness required to meet the service loads they anticipate for a particular part. It is the task of the process engineer to develop the carburizing treatment that will produce the properties desired. Some of the considerations involved in setting up processes include:

- Case microstructure
- Residual stress
- Alloy selection
- Operating schedules
- Quenchants
- Reheating for quenching
- Tempering
- Selective carburizing

Case Microstructure. A carburized case is usually a mixture of tempered martensite and retained austenite. Other microconstituents, such as primary carbides, bainite, and pearlite, are generally avoided. For a particular alloy, the amount of retained austenite in the case increases as the case carbon content increases. An appreciable decrease in case hardness is usually found when the amount of retained austenite exceeds about 15%, but for applications involving contact loading, such as rolling element bearings, the best service life is found when the retained austenite content is quite high, for example, 30 to 40%. In other applications, especially when dimensional stability is critical, the retained austenite content should be low.

Figure 12 shows the dependence of retained austenite content on carbon content for iron-carbon alloys (Ref 12). For a given carbon content, more retained austenite is usually present in alloy steels. Therefore, by controlling the case carbon content, the amount of retained austenite can be regulated. Tempering above 260 °C (500 °F) will also eliminate retained austenite, but at the expense of case hardness.

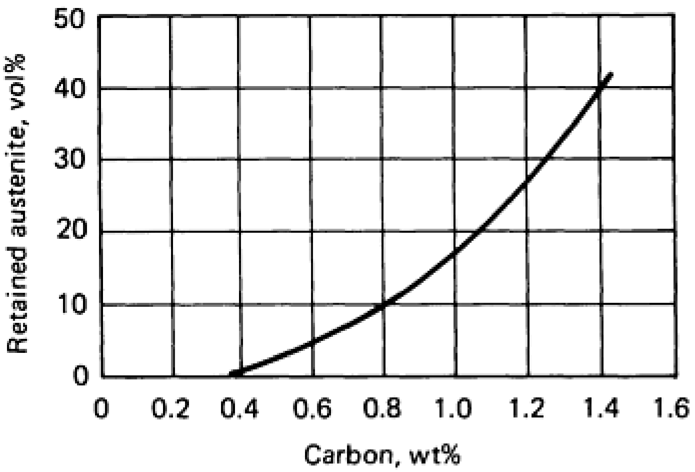

Fig. 12 Effect of retained austenite content on carbon content for iron-carbon alloys

Residual Stress. Carburized parts have a compressive residual stress in the case that is balanced by a tensile residual stress in the core. The presence of this stress distribution is an advantage for applications in which maximum tensile

stresses are experienced at the surface of the part, for example, bending or torsional loading. When other factors are the same, the magnitude of the compressive residual stress at the surface depends on the ratio of case and core thicknesses. When the core is much thicker than the case, compressive stresses at the surface will be high. When the reverse is true, surface compressive stress will be low and core tensile residual stress will be high. Because retained austenite is more dense than is martensite, the former will tend to reduce the magnitude of the compressive residual stress in the surface.

Alloy Selection. Frequently used carburizing steels are listed in Table 2. Carburizing steels are usually selected on the basis of case and core hardenability; comparative hardenability data for these alloys can be found in the SAE specifications J1268 and J1868 (*SAE Handbook,* Volume 1 or the article "Hardenability Curves" in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook*). As a rule, carburized plain carbon steels with less than 1% Mn must be water quenched to form a martensitic case. If an oil quench must be used, adequate case hardenability can usually be obtained by carbonitriding a coarse-grained steel.

Table 2 Composition of carburizing steels

Steel	Composition, %					
	C	Mn	Ni	Cr	Mo	Other
Carbon steels						
1010	0.08-0.13	0.30-0.60	. . .	. . .	. . .	[a], [b]
1018	0.15-0.20	0.60-0.90	. . .	. . .	. . .	[a], [b]
1019	0.15-0.20	0.70-1.00	. . .	. . .	. . .	[a], [b]
1020	0.18-0.23	0.30-0.60	. . .	. . .	. . .	[a], [b]
1021	0.18-0.23	0.60-0.90	. . .	. . .	. . .	[a], [b]
1022	0.18-0.23	0.70-1.00	. . .	. . .	. . .	[a], [b]
1524	0.19-0.25	1.35-1.65	. . .	. . .	. . .	[a], [b]
1527	0.22-0.29	1.20-1.50	. . .	. . .	. . .	[a], [b]
Resulfurized steels						
1117	0.14-0.20	1.00-1.30	. . .	. . .	. . .	0.08-0.13 S
Alloy steels						
3310	0.08-0.13	0.45-0.60	3.25-3.75	1.40-1.75	. . .	[b], [c]

4023	0.20-0.25	0.70-0.90	. . .	. . .	0.20-0.30	[b], [c]
4027	0.25-0.30	0.70-0.90	. . .	. . .	0.20-0.30	[b], [c]
4118	0.18-0.23	0.70-0.90	. . .	0.40-0.60	0.08-0.15	[b], [c]
4320	0.17-0.22	0.45-0.65	1.65-2.00	0.40-0.60	0.20-0.30	[b], [c]
4620	0.17-0.22	0.45-0.65	1.65-2.00	. . .	0.20-0.30	[b], [c]
4815	0.13-0.18	0.40-0.60	3.25-3.75	. . .	0.20-0.30	[b], [c]
4820	0.18-0.23	0.50-0.70	3.25-3.75	. . .	0.20-0.30	[b], [c]
5120	0.17-0.22	0.70-0.90	. . .	0.70-0.90	. . .	[b], [c]
5130	0.28-0.33	0.70-0.90	. . .	0.80-1.10	. . .	[b], [c]
8617	0.15-0.20	0.70-0.90	0.40-0.70	0.40-0.60	0.15-0.25	[b], [c]
8620	0.18-0.23	0.70-0.90	0.40-0.70	0.40-0.60	0.15-0.25	[b], [c]
8720	0.18-0.23	0.70-0.90	0.40-0.70	0.40-0.60	0.20-0.30	[b], [c]
8822	0.20-0.25	0.75-1.00	0.40-0.70	0.40-0.60	0.30-0.40	[b], [c]
9310	0.08-0.13	0.45-0.65	3.00-3.50	1.00-1.40	0.08-0.15	[b], [c]
Special alloys						
CBS-600	0.16-0.22	0.40-0.70	. . .	1.25-1.65	0.90-1.10	0.90-1.25 Si
CBS-1000M	0.10-0.16	0.40-0.60	2.75-3.25	0.90-1.20	4.00-5.00	0.40-0.60 Si 0.15-0.25 V
Alloy 53	0.10	0.35	2.00	1.00	3.25	1.00 Si, 2.00 Cu, 0.10 V

(a) 0.04 P max, 0.05 S max.

(b) 0.15-0.35 Si.

(c) 0.035 P max, 0.04 S max

Alloy steels are used for most heavily loaded parts, not only because of their increased hardenability, but also because the standards of steel cleanliness are more restrictive. Many of the alloy steels are similar in hardenability but differ in other important respects. For example, nickel-molybdenum alloys provide the most trouble-free processing because the principal alloying elements are neither strong oxide nor strong carbide formers. However, economic considerations often dictate the use of less expensive steels, such as chromium-manganese alloys, which are prone to alloy depletion (and loss of hardenability) because of the formation of grain-boundary oxides near the surface during carburizing. Chromium-nickel-molybdenum steels, such as SAE 8620 and 8720, provide a balance between cost, hardenability, and ease of processing that leads to their being specified for many parts. More expensive steels, such as SAE 9310 and 3310, are used for critical gearing applications. Some special carburizing alloys, CBS 1000M, for example, have secondary hardening characteristics that provide resistance to softening for temperatures up to about 550 °C (1025 °F).

Operating Schedules. To minimize the total amount of time required for carburizing to a given case depth, most processes are set up in a boost-diffuse mode. The boost step is at a relatively high temperature and high carbon potential to facilitate the rapid development of a deep case; the diffuse step is at a lower carbon potential, allowing the case carbon content to decrease to the level desired. Mathematical models for diffusion, described above, are very helpful in choosing the times and temperatures required for each step.

In practical situations, many considerations, in addition to minimizing processing time, enter into the choice of processing parameters. In continuous furnaces that cannot be separated into distinct zones by means of internal doors, there is a limit to the magnitude of the differences in temperature and carbon potential that can be sustained over the length of the furnace. Similarly, in batch furnaces, the rate at which the temperature can be lowered depends on the thermal inertia of the furnace and load and the magnitude of the heat losses; the rate at which the atmosphere gas composition can be changed depends on the mean residence time of the gas in the furnace. In the absence of a detailed mathematical model incorporating furnace operating characteristics, some trial-and-error experimentation may be required to find the operating set points that produce the desired results. The maximum operating temperature can be limited by the accelerated degradation of fixtures experienced at higher temperatures. Lower processing temperatures are generally favored when the distortion of parts must be minimized.

Thin-cased parts (0.5 mm, or 0.02 in., effective case or less) tend to be processed at 870 °C (1600 °F) or below simply because the processing time at higher temperatures is so short that it is difficult to control the results. For the same reason, thin-cased parts are carburized using a constant carbon potential rather than a boost-diffuse process. Sometimes the available equipment, for example, a continuous pusher furnace, is larger than the process requires. In this situation the furnace may be run at a lower-than-customary temperature to avoid the frequent door openings, which tend to upset the furnace atmosphere, that would be necessary at higher temperatures.

Quenchants. Carburized parts can be quenched in brine or caustic solutions, water-based polymer quenchants, oils, or molten salt. The more rapid the quench, the lower the requirements for hardenability, but the greater the likelihood of distortion. If a part is used as-heat treated (no finishing operations to control dimensions), marquenching into molten salt or hot oil may be used. Rings and shafts are often press quenched, that is, clamped in a fixture while hot and sprayed with oil, to reduce distortion. The choice of alloy and quenchant and the manufacturing-process design are interrelated and must be compatible.

Reheating for Quenching. It has been the practice in some industries to carburize parts at a relatively high temperature (927 °C, or 1700 °F, or above), cool slowly to ambient temperature, then reheat to a lower temperature (843 °C, or 1550 °F, for example), and quench. The advantages of this approach are:

- The final austenite grain size, which controls the size of the martensite plates and laths, is smaller, and therefore the microstructure is more refined
- The low reheat temperature places an upper limit on the amount of carbon dissolved in austenite, thereby limiting the amount of retained austenite present in the case

The main disadvantage of this processing, aside from added cost, is increased distortion of the parts. As better controls have become available for regulating furnace atmospheres and as the use of fine-grain steels has become the norm, the need for this practice has diminished.

Tempering. As high-carbon martensite is tempered, carbides precipitate, increasing the density and reducing the hardness of this constituent. The retained austenite, which accompanies the high-carbon martensite, transforms in the temperature range of 220 to 260 °C (425 to 500 °F), reducing the density and increasing the hardness of this constituent. Thus, the response of case hardness to tempering can be complex, affected by the fraction of retained austenite present initially.

Density changes during tempering affect the relief of residual stresses produced by carburizing. Figure 13 (Ref 13) shows the effect on stress relief of tempering for 1 h at various temperatures. Stress relief occurs at lower tempering temperatures, as the amount of carbon dissolved in austenite increases. The dependence of stress relief on tempering temperature in carburized parts is qualitatively similar to these results, although more complex behavior can be expected in steels with high levels of retained austenite.

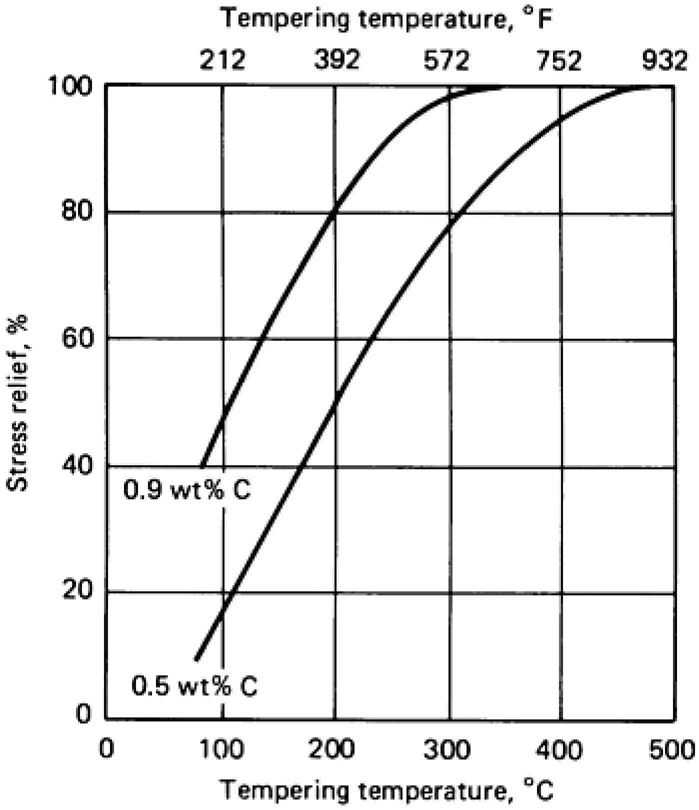

Fig. 13 Plot of stress relief versus tempering temperatures held for 1 h for two carbon concentrations in austenite. Source: Ref 13

The decrease in hardness with tempering is shown in Fig. 14 for four carburized steels. The HRC hardness values shown were converted from Rockwell A for surface hardness and from Vickers microhardness for the subsurface values. It should be noted that the hardness changes very little for tempering temperatures up to 205 °C (400 °F). However, a substantial degree of stress relief will have been experienced as indicated in Fig. 13.

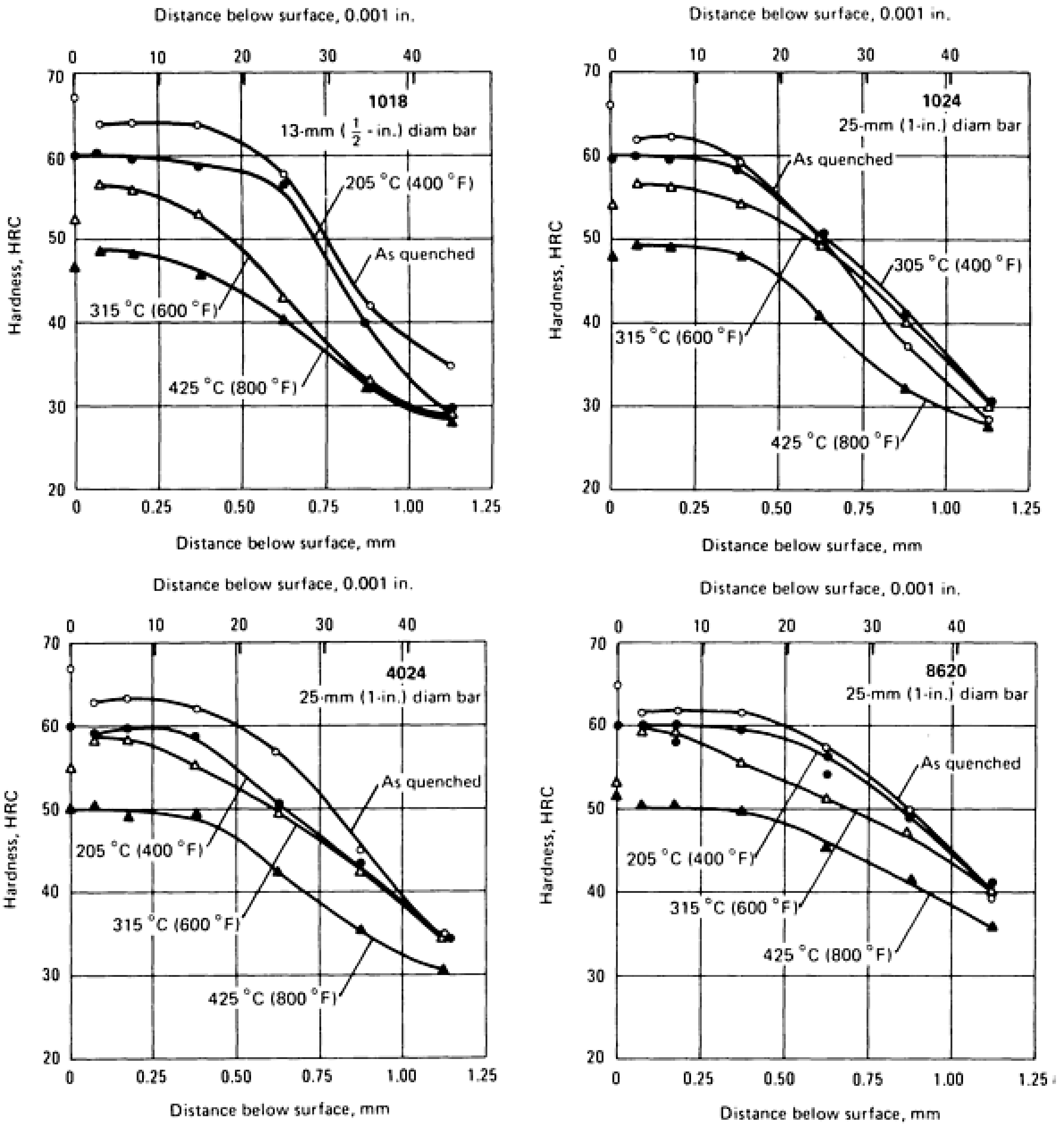

Fig. 14 Effect of tempering on hardness in carburized cases for selected steels. Samples were carburized at 925 °C (1700 °F) for 4.5 h, then oil quenched and tempered.

Parts that are to be ground after heat treatment should always be tempered. The tempering temperature should be greater than the surface temperature experienced during grinding. If it is not, grinding will produce surface tensile residual stresses. Tempering in the range of 150 to 205 °C (300 to 400 °F) improves subsequent dimensional stability. If the best possible stability is required, as in some instrument bearings, the treatment should also be designed to eliminate retained austenite. On the other hand, because tempering reduces the compressive residual surface stresses, resistance to bending and torsional fatigue may be best if the parts are not tempered at all. Tempering is omitted on many thin-cased parts (0.5 mm, or 0.02 in., case depth or less) that are not finished after heat treatment.

Selective Carburizing. To function properly, some parts must be selectively carburized, that is, carburized only on certain surfaces. Some gears are carburized only on teeth, splines, and bearing surfaces. In addition to satisfying the performance requirements of a part, selective carburizing may facilitate the machining or welding of noncarburized surfaces in the hardened condition.

Surfaces that are not to be carburized must be protected by a coating or shield that is impervious to the carburizing atmosphere. Various means are employed to protect or stop off selected surfaces from the atmosphere.

Copper plating to a minimum thickness of 13 μm (0.5 mil) is widely used for this purpose because it is relatively easy to apply, is machinable, and does not contaminate furnace atmospheres. Prior to carburizing a large, 915 mm (36 in.) diam, 4620 steel ring gear, for example, the gear is copper plated on the inside diameter flange area only to permit finish machining, after hardening, of the bore and bolt holes located in the flange. Surfaces that are not to be copper plated can be coated with a chemical-resistant lacquer, which is removed prior to carburizing. Alter carburizing, the copper can be chemically stripped from the part or removed in subsequent machining operations.

Ceramic coatings in the form of paint can also protect selected surfaces from carburizing. Surfaces must be thoroughly cleaned before ceramic paint is applied, and the first coat is allowed to dry before a second coat is applied. Ceramic paint coatings must adhere tightly in order to be impervious to the carburizing atmosphere. The application of ceramic paint to the bushing and button recesses of a rock bit cutter, for example, has been used in production.

Stopoffs. Blind holes can be stopped off by inserting copper plugs or by filling them with clay. If air is entrapped by the plug, a means of venting must be provided to relieve the pressure buildup during heating. Through holes may be plugged at either end to limit access by the atmosphere, thereby minimizing carburization. Internal threads can be protected by the insertion of a copper screw; external threads by capping with a copper nut. If a steel screw or nut is used, the threads should be coated with a stopoff material to facilitate removal. The success of all stopoff methods depends largely on the care used in their applications. Seldom are mechanical stopoffs completely effective in production.

If parts are cooled slowly after carburizing, they will be soft enough to permit the removal of the case in selected areas by machining. After subsequent reheating and quenching, these areas will remain lower in carbon and relatively soft. Operations can also be planned so that the case on a hardened part can be removed selectively by grinding. This practice is usually confined to small areas and generally to cases less than 1.3 mm (0.05 in.) in depth.

A part that has been carburized may be locally softened by induction heating. The heat may just temper the part, or, for steels with low hardenability, may actually normalize the area to be softened. This practice is used to soften threads on carburized shafts in the automotive industry.

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Dimensional Control

Parts should be as near to final dimensions as possible before carburization so that heat treating times may be kept short. Nevertheless, some growth and distortion will be encountered in all carburized parts. Part size and shape strongly influence distortion, but a host of other factors can play a role as well, such as:

- Residual stresses existing in parts prior to heat treatment
- Shape changes induced by heating too rapidly
- Method of stacking or fixturing parts during carburizing and quenching
- Increasing growth as the case depth increases
- Severity of quenching (including variations caused by changing quench temperatures)
- Hardenability, as influenced by variations in steel composition

A variety of methods, to be described, are used to minimize distortion. All of them add to heat treating cost, but they may be cost effective when total production costs are considered.

In the high-volume production of precision components, such as automotive transmission gears, a general objective is to hold constant all of the processing variables affecting growth and distortion and then to compensate for the changes that do take place by adjusting the shape of the green machined (unhardened) part. For example, the lead angle of a helical

gear becomes smaller after it has been carburized because the gear becomes longer. Once the change has been documented, the machining operation prior to heat treatment can be adjusted to compensate for the growth. Trial lots of parts are processed using the intended production process and then measured to determine shape changes. After production has begun, parts may be checked periodically to ensure that processing conditions that affect distortion have not changed.

Fixturing can be used to separate parts, allowing more uniform heating and access to the carburizing atmosphere, and to orient parts so that each part enters the quench bath the same way. Fixturing adds labor cost (fixtures are often loaded and unloaded by hand) and adds operating cost because the fixtures may weigh as much as, or more than, the work load. However, proper fixturing is often effective in reducing variations in growth and lessening distortion, thereby allowing compensation for the changes in the shape of the green part.

Marquenching, or martempering, involves quenching in molten salt or in hot oil; the quenchant temperature is above the M_s temperature (the temperature at which martensite starts to form from austenite upon cooling) of the case, but below the M_s temperature of the core. Consequently, the core transforms, while parts are in the quenchant, to a mixed microstructure of martensite, bainite, and ferrite. The case transforms to martensite while the parts are cooling in air after leaving the quenchant. Distortion is reduced because the transformation strains in the core are reduced, and because thermal gradients are much lower during transformation in the case and core.

Press quenching and other means of quenching in fixtures, such as plug or cold die, are effective for reducing distortion. While quench presses may have automated loading systems, they are often loaded manually, one part at a time. Quenching in fixtures adds significantly to the cost of heat treating, but there may be no practical alternative for limiting distortion of certain parts, for example, thin-walled rings and slender shafts.

Straightening is employed to reduce the distortion of heat-treated shafts. Most straightening is done by flexing the part. There is always a risk of cracking the case when straightening carburized parts, so it is the usual practice to straighten after tempering. Some manufacturers find it best to straighten while parts are still hot from the tempering furnace. In one instance, shafts which cracked upon straightening after tempering could be straightened without cracking immediately after quenching. Many straighteners are equipped with acoustic emission sensors to detect cracking. Selective peening has also been used as a method for straightening parts.

Case Depth Measurement

Case depth is usually specified as the depth below the surface at which a defined value of some property occurs. A case depth to a hardness of 50 HRC and a case depth to a carbon content of 0.4 wt% are examples of specifications for an effective case depth. Also used is the term total case depth, which is too vague for general use as a specification because of the gradual transition between case and core properties in most carburized parts. However, some carbonitrided parts and induction case hardened parts will have a sharp transition in microstructure clearly separating case and core. Only in these instances is total case depth defined well enough to be useful as a specification. Methods of measuring case depth are described in detail in SAE Recommended Practice J423.

Many parts, such as gears, consist of some surfaces that are convex, some that are relatively flat, and some that are concave. It is usually found that the case depth will be least at the concave surface (the root) and greatest at the convex surface (the tooth tip). The effect of surface curvature on effective case depth is shown in Fig. 15. These data are computed for a particular case:

- Surface carbon, 1%
- Core carbon, 0.2%
- Diffusion time/temperature sufficient to produce a case depth to 0.4% of 1 mm (0.04 in.) beneath the flat surface of a slab of infinite thickness

From Fig. 15, the same treatment that will produce a case depth of 1 mm (0.04 in.) in a plane slab of 3 mm (0.12 in.) half-thickness will produce a case depth of 1.13 mm (0.0445 in.) in a rod of 3 mm (0.12 in.) radius, a case depth of 1.28 mm (0.0504 in.) in a sphere of 3 mm (0.12 in.) radius, and a case depth of 0.93 mm (0.037 in.) in a circular hole of 3 mm (0.12 in.) radius. The effect of surface curvature is quite pronounced if the radius of curvature of the surface is less than about five times the effective case depth beneath a flat surface. The effect of curvature is small when the radius of curvature of

the surface is more than ten times the effective case depth. Surface curvature also affects cooling so that in parts with marginal hardenability there may be a greater difference between convex and concave surfaces when effective case depth is defined in terms of depth to a specified hardness than when it is defined as depth to a specified carbon content. These facts must be kept in mind when comparing case depth at various locations on a part and when comparing case depths on parts with case depths on testpieces.

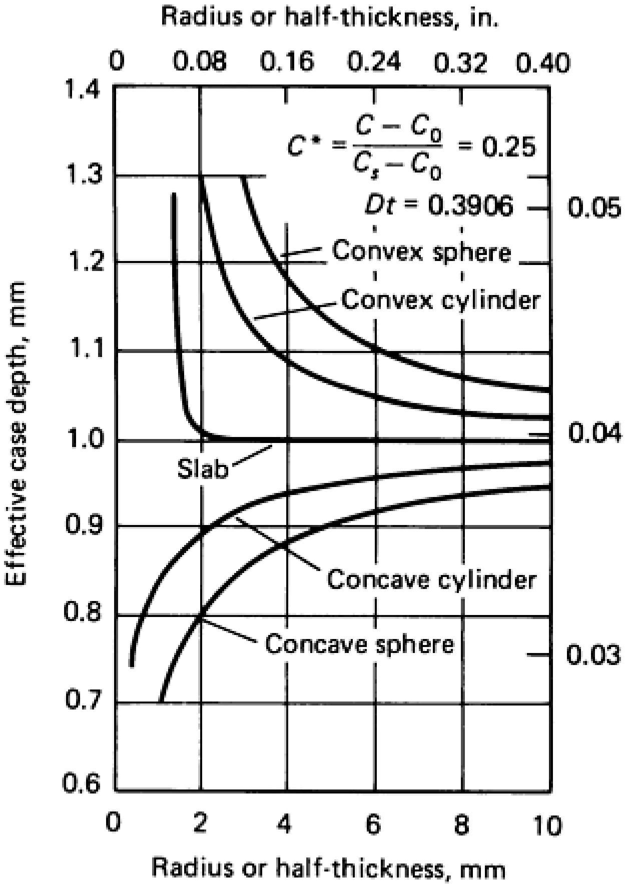

Fig. 15 Influence of surface curvature on case depth. *C**, **normalized carbon content; *C*, concentration of diffusing substance; C_0, base carbon content of the alloy; C_s, surface carbon content (often taken to be the maximum dissolved carbon content in austenite at the carburizing temperature); *D*, diffusion constant, having units (distance)^2/time; *t*, time**

Effective case depth to a specified hardness value is best measured by means of a microhardness traverse on a polished metallographic section cut normal to the surface. Vickers (diamond pyramid hardness) or Knoop or Rockwell microficial indenters may be used with loads of 0.5 to 2 kg. Specifications can be written in terms of a microhardness value or in terms of HRC hardness, where it is understood that microhardness (HV, HK, or HRMF) is converted to HRC using standard tables (50 HRC = 513 HV = 542 HK = 870 HRMF). Surface hardness, which is often a part of carburizing specifications, can be obtained by extrapolating subsurface microhardness values to the surface. Alternatively, the microhardness at a depth of 0.1 mm (0.004 in.) beneath the surface can be defined as the surface hardness. It is difficult to get reliable microhardness readings closer than 0.1 mm (0.004 in.) to the edge of a polished section because of edge rounding, which occurs during polishing.

Effective case depth to a specified carbon content is most frequently measured on testpieces of the same alloy and shape as the workpieces and processed simultaneously with the work load. Typically, a ground bar about 25 mm (1 in.) in diameter is used. If it is quenched with the work load, it must be tempered at about 650 to 700 °C (1200 to 1300 °F) prior to machining. Bars are cut dry, at very slow speeds to avoid burning, and washed between cuts with Freon. Turnings are collected on clean paper, rewashed, and analyzed for carbon. To detect the effect of the final atmosphere exposure on the near surface carbon gradient, three or four initial cuts of 0.025 mm (0.001 in.) thickness should be made. Thereafter, cuts of 0.075 to 0.125 mm (0.003 to 0.005 in.) thickness can be made through the case. The accuracy of the method depends

on good machining practice in addition to well-standardized analytical procedures. One user reports repeatability of 0 to 0.03% C at depths greater than 0.075 mm (0.003 in.) and 0 to 0.05% C for samples taken closer to the surface.

As a plant floor test, test bars about 10 to 12.5 mm (0.4 to 0.5 in.) can be processed with the work load, quenched, and fractured. The depth of the case, evident on the fracture surface, can be read with a 10× Brinell glass. Even workpieces can be fractured if their shape (and cost) allow easy fracture. A variant of this test involves reheating a test bar to 780 °C (1440 °F) and then quenching and fracturing. In plain carbon steels, only material with a carbon content of 0.4 wt% or greater will become austenitic at this temperature. Therefore, the line of demarcation between case and core on the fracture surface should occur at a carbon content of 0.4 wt%.

Another test for case depth makes use of the principle that the M_s temperature depends primarily on the dissolved carbon content of austenite. A carburized testpiece or part is austenitized, quenched in a bath at precisely controlled temperature, held for a few minutes to allow tempering of the martensite formed, and then quenched to room temperature. A polished, etched section will show a line of demarcation between the martensite tempered in the salt bath (dark) and the untempered martensite formed during the final quench (white). The location of the line of demarcation corresponds to a specific carbon content. The appropriate quenching bath temperature can be found from a correlation between M_s temperature (in degrees Fahrenheit) and composition (Ref 14):

$$M_s = 930 - 600(\%C) - 60(\%Mn) - 50(\%Cr) - 30(\%Ni) - 20(\%Si + \%Mo + \%W) \quad \textbf{(Eq 23)}$$

If the quenching bath temperature is chosen to be the M_s temperature for 0.4 wt% C in a given alloy, then the austenitizing temperature must be high enough to dissolve at least this much carbon in austenite, typically 830 °C (1525 °F).

Surface hardness is often measured on the plant floor on workpieces using a superficial hardness test, Rockwell 15N, for example. Because of the rather light load, the necessity for supporting pieces well, and the importance of a smooth surface, values tend to be unreliable. However, such checks of surface hardness is often necessary to detect the presence of a shallow, decarburized layer such as might occur if parts experience a delay when transferred from the carburizing furnace to the quench bath.

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Safety Precautions

Gas carburizing atmospheres are highly toxic and highly inflammable and form explosive gas mixtures when mixed with air. A safety program emphasizing furnace operator training and preventative maintenance should be established and adhered to for all heat-treating operations using controlled atmospheres. The installation of alarms and other safety devices cannot substitute for a properly trained operator.

Recommended procedures for safe furnace operation are provided by furnace manufacturers; this information should form the basis for operator training. Safety standards for furnaces and related equipment are also published by the National Fire Prevention Association. Because procedures differ somewhat for furnaces of different design, the discussion in this section focuses on the principles of safe operation, that is, the goal of operating procedures. The three factors of prime consideration are discussed below.

First, all atmosphere gas discharged from the furnace to the operating environment must be burned to ensure that poisonous carbon monoxide is converted to carbon dioxide. Pilot flames should be maintained on atmosphere vent lines at all times, and there must be a flame curtain that ignites automatically whenever a furnace door opens. There should be a thermocouple inserted into each pilot flame and connected to an alarm system to verify that each pilot is ignited. Air-Endogas mixtures that are too lean to support combustion can still contain enough carbon monoxide to be hazardous. The threshold limit value for long-term exposure to carbon monoxide, set by the American Conference of Governmental Industrial Hygienists, is 50 ppm. The short-term exposure limit is 400 ppm. A concentration of 50,000 ppm CO is quickly fatal.

Second, air and Endogas will self-ignite if mixed at a temperature of 760 °C (1400 °F) or above. That is, Endogas may be introduced into an air-filled furnace heated to 760 °C (1400 °F) or above without risk of explosion; the Endogas will simply burn until the oxygen in the furnace is consumed. At temperatures below 760 °C (1400 °F) there is the risk that Endogas will not ignite spontaneously upon entering an air-filled furnace and that the furnace will then fill with an air-Endogas mixture, which may then ignite explosively. Table 3 lists autoignition temperatures and composition limits within which combustion can occur for mixtures of several gases and air.

Table 3 Properties of air-combustible gas mixtures

Gas	**Autoignition temperature**		**Flammable limits in air, vol %**
	°C	**°F**	
Methane	540	1005	5.4-15
Propane	466	870	2.4-9.5
Hydrogen	400	750	4.0-75
Carbon monoxide	609	1130	12.5-74
Methanol	385	725	6.7-36

Third, it is very convenient to have available at each furnace a source of inert gas, such as nitrogen, that is available for purging the furnace in the event of power failure or other emergencies. Many operations use cylinders of compressed nitrogen to provide automatic purging whenever the furnace temperature falls below 760 °C (1400 °F) or whenever the pressure in the Endogas line falls below a critical value. Purging with nitrogen can also be used routinely prior to introducing Endogas into a furnace or when removing the atmosphere from a furnace prior to shutdown. As a rule of thumb, the volume of gas required for effective purging is at least five times the volume of the furnace chamber.

Special precautions are needed to introduce combustible atmospheres safely into furnaces equipped with unheated vestibules. The usual procedure is to raise the furnace temperature above 760 °C (1400 °F), close the furnace door, open the vestibule door, and introduce the atmosphere gas into the furnace while maintaining a pilot flame at the furnace door to ignite gas entering the vestibule. Once a gas flame has been established at the furnace door (one that will continue burning after the pilot flame has been removed), the vestibule door can be closed and pilot flames ignited at the point that gas exits the vestibule. The flame burning at the furnace door will consume oxygen in the vestibule, reducing it to the point at which combustion can no longer be supported. Vestibule explosions can occur during start-up if the flame at the furnace door blows out before sufficient oxygen is consumed in the vestibule. Start-up is simplified if nitrogen is available; thorough purging of the furnace and the vestibule with nitrogen prior to the introduction of the atmosphere gas will eliminate any risk of explosion.

Whenever a furnace must be operated with a flammable atmosphere below 760 °C (1400 °F), the usual practice is to raise the furnace temperature above 760 °C (1400 °F), introduce the furnace atmosphere, and decrease to the operating temperature. Other safe practices have been developed that make use of nitrogen gas for purging air from the furnace before combustible gases are introduced.

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Pack Carburizing of Steels

Revised by Robert W. Foreman, Consultant

Introduction

PACK CARBURIZING is a process in which carbon monoxide derived from a solid compound decomposes at the metal surface into nascent carbon and carbon dioxide. The nascent carbon is absorbed into the metal, and the carbon dioxide immediately reacts with carbonaceous material present in the solid carburizing compound to produce fresh carbon monoxide. The formation of carbon monoxide is enhanced by energizers or catalysts, such as barium carbonate ($BaCO_3$), calcium carbonate ($CaCO_3$), potassium carbonate (K_2CO_3), and sodium carbonate (Na_2CO_3), that are present in the carburizing compound. These energizers facilitate the reduction of carbon dioxide with carbon to form carbon monoxide. Thus, in a closed system, the amount of energizer does not change. Carburizing continues as long as enough carbon is present to react with the excess carbon dioxide.

Pack carburizing is no longer a major commercial process. This has been mainly due to replacement by more controllable and less labor-intensive gas and liquid carburizing processes. However, any labor cost advantage gas carburizing or liquid carburizing may have over pack carburizing can be negated should workpieces require additional steps such as cleaning and the application of protective coatings in carburizing stopoff operations. Environmental concerns have also led to reduced use of pack carburizing. It still has application to some specialized uses, however.

Advantages. Among the principal advantages of pack carburizing are:

- It can make use of a wide variety of furnaces because it produces its own contained environment
- It is ideally suited for slow cooling of work from the carburizing temperature, a procedure that may be advantageous for parts that are to be finish machined after carburizing and before hardening
- Compared to gas carburizing, it offers a wider selection of stop-off techniques for selective carburizing

Disadvantages. By its nature, pack carburizing is less clean and less convenient than other carburizing processes. Other disadvantages generally associated with pack carburizing include:

- It is not well suited to production of shallow case depths where strict case-depth tolerances are required
- It cannot provide the degree of flexibility and accuracy of control over surface carbon content and carbon gradient that can be obtained in gas carburizing
- It is not well suited for direct quenching or quenching in dies; thus, extra handling and processing are required for the hardening operation
- More processing time is required for pack carburizing than for gas or liquid carburizing because of the necessity of heating and cooling the extra thermal mass associated with the compound and the container
- It is labor intensive

Carburizing Compounds

The common commercial carburizing compounds are reusable and contain 10 to 20% alkali or alkaline earth metal carbonates bound to hardwood charcoal or to coke by oil, tar, or molasses. Barium carbonate is the principal energizer, usually comprising about 50 to 70% of the total carbonate content. The remainder of the energizer usually is made up of calcium carbonate, although sodium carbonate and potassium carbonate also may be used. It should be noted that barium carbonate, now designated by government regulations as a health hazard due to its toxicity and the disposal problems it presents, is gradually being phased out by U.S. manufacturers as a catalyst in pack-carburizing operations.

Hardwood charcoal is more reactive than coke as a source of carbon for pack carburizing Nevertheless, coke offers certain advantages, such as minimum shrinkage, good hot strength, and good thermal conductivity. More active carburizing compounds therefore contain both charcoal and coke, with typical compounds containing a greater percentage of coke.

Addition Rate. Because of losses associated with the use of pack-carburizing compounds, new compound usually is added to the used compound before it is returned to service. The loss in energizer normally is somewhat higher than loss of the rest of the compound. Therefore, somewhat larger percentages of new compound are used to ensure that the energizer level does not drop below approximately 5 to 8%. When direct quenching or severe mechanical handling methods are used, the addition rate may be as high as one part new compound to two parts used compound. When furnace cooling and careful handling methods are used, the addition rate may be one part new compound to three to five parts used compound.

Used compound often is screened to remove fines. The compound is then thoroughly mixed with the make-up material. Because many compounds, particularly those of the coated-charcoal type, are extremely friable, they require careful handling to minimize losses due to formation of dust or fines.

Process Control

In pack carburizing, as in other carburization processes, the carbon-concentration gradient obtained is a function of carbon potential, carburizing temperature and time, and the chemical composition of the steel. Two process-control attributes peculiar to pack carburizing are:

- There may be a variation in case depth within a given furnace load due to dissimilar thermal histories within the carburizing containers
- Distortion of parts during carburizing may be reduced because the compound can be used to support the parts

Carbon Potential. The carbon potential of the atmosphere generated by the carburizing compound, as well as the carbon content obtained at the surface of the work, increases directly with an increase in the ratio of carbon monoxide to carbon dioxide. Thus, more carbon is made available at the work surface by the use of energizers and carburizing materials that promote formation of carbon monoxide.

In pack carburizing, the rate of evolution of carbonaceous gas is fixed and is almost always in excess of the rate required to supply the necessary carbon for a saturated surface layer.

Temperature. Pack carburizing normally is performed at temperatures from 815 to 955 °C (1500 to 1750 °F). In recent years, the upper limits have been steadily raised, and carburizing temperatures as high as 1095 °C (2000 °F) have been used. Steelmaking processes have improved to the extent that fine grain size is maintained at temperatures approaching or exceeding 1040 °C (1900 °F). Above this temperature, the coarsening effect occurs only after prolonged periods of time, allowing high-temperature treatment without excessive grain coarsening.

The rate at which the carburized case is formed increases rapidly with temperature. If a factor of 1.0 is representative of 815 °C (1500 °F), the factor increases to 1.5 at 870 °C (1600 °F) and to more than 2.0 at 925 °C (1700 °F). Improved containers, fine-grain steels, and other improvements now permit the use of a wide variety of temperatures.

The surface carbon content is approximately that of the saturation limit for carbon in austenite. At operating temperature, the desired average carbon level throughout the case is directly dependent upon the carburizing temperature. When eutectoid cases are desired, the carburizing temperature is normally about 815 °C (1500 °F). AS more carbon is required in the case, the temperature is increased.

Time. The rate of change in case depth at a particular carburizing temperature is proportional to the square root of time. The rate of carburization is thus highest at the beginning of the cycle and gradually diminishes as the cycle is extended (see Fig. 1).

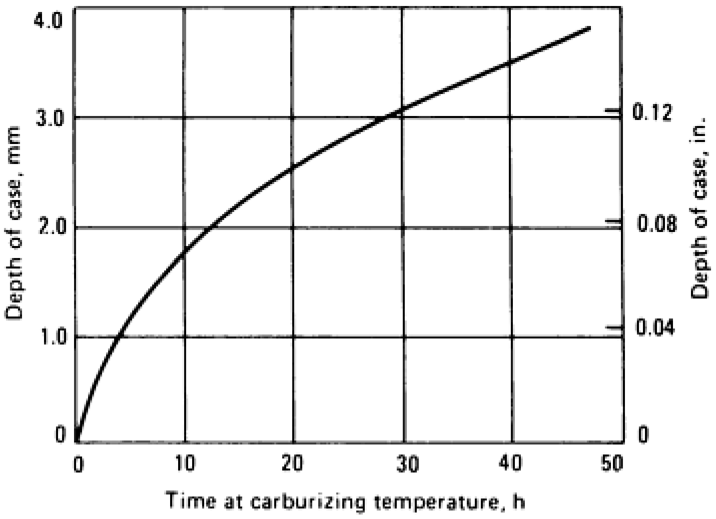

Fig. 1 Effect of time on case depth at 925 °C (1700 °F)

Steel Composition. Any carburizing grade of carbon or alloy steel is suitable for pack carburizing. It is generally agreed that the diffusion rate of carbon in steel is not markedly influenced by the chemical composition of the steel. Chemical composition does have an effect on the activity of carbon and thus can affect the carbon level at saturation for a particular temperature.

Depth of Case. Even with good process control, it is difficult to obtain parts with total case-depth variation of less than 0.25 mm (0.010 in.) from maximum to minimum in a given furnace load, assuming a carburizing temperature of 925 °C (1700 °F). Commercial tolerances for case depths obtained in pack carburizing begin at ±0.25 mm (±0.010 in.), and, for deeper case depths, increase to ±0.8 mm (±0.03 in.). Lower carburizing temperatures provide some reduction in case-depth variation because variation in the time required for all parts of the load to reach carburizing temperature becomes a smaller percentage of total furnace time. Because of the inherent variation in case depth and the cost of packing materials, pack carburizing normally is not used on work requiring a case depth of less than 0.8 mm (0.03 in.). Typical pack-carburizing temperatures selected to produce different case depths on a variety of production parts are given in Table 1.

Table 1 Typical applications of pack carburizing

Part	Dimensions[a]				Weight		Steel	Carburizing			
	OD		OA					Case depth to 50 HRC		Temperature	
	mm	in.	mm	in.	kg	lb		mm	in.	°C	°F
Mine-loader bevel gear	102	4.0	76	3.0	1.4	3.1	2317	0.6	0.024	925	1700
Flying-shear timing gear	216	8.5	92	3.6	23.6	52.0	2317	0.9	0.036	900	1650
Crane-cable drum	603	23.7	2565	101.0	1792	3950	1020	1.2	0.048	955	1750
High-misalignment coupling gear	305	12.0	152	6.0	38.5	84.9	4617	1.2	0.048	925	1700

Continuous-miner drive pinion	127	5.0	127	5.0	5.4	11.9	2317	1.8	0.072	925	1700
Heavy-duty industrial gear	618	24.3	102	4.0	150	331	1022	1.8	0.072	940	1725
Motor-brake wheel	457	18.0	225	8.9	104	229	1020	3.0	0.120	925	1700
High-performance crane wheel	660	26.0	152	6.0	335	739	1035	3.8	0.150	940	1725
Calender bull gear	2159	85.0	610	24.0	5885	12,975	1025	4.0	0.160	955	1750
Kiln-trunnion roller	762	30.0	406	16.0	1035	2280	1030	4.0	0.160	940	1725
Leveler roll	95	3.7	794	31.3	36.7	80.9	3115	4.0	0.160	925	1700
Blooming-mill screw	381	15.0	3327	131.0	2950	6505	3115	5.0	0.200	925	1700
Heavy-duty rolling-mill gear	914	36.0	4038	159.0	11,800	26,015	2325	5.6	0.220	955	1750
Processor pinch roll	229	9.0	5385	212.0	1700	3750	8620	6.9	0.270	1050	1925

(a) OD, outside diameter; OA, overall (axial) dimension

Distortion normally becomes more pronounced as processing temperature is increased. In some instances, carburizing temperature is selected on the basis of the maximum amount of distortion that can be tolerated. In any case, following proper container packing procedures will help minimize distortion.

Furnaces for Pack Carburizing

The suitability of a furnace for pack carburizing depends on its ability, at reasonable cost, to: provide adequate thermal capacity and temperature uniformity (furnaces must be controllable to within ±5 °C, or ±9 °F, and must be capable of uniform through heating to within ±8 to ±14 °C, or ±14 to ±25 °F); and provide adequate support for containers and workpieces at the required temperatures.

Modern heating systems and furnace construction provide ample heating capacity and temperature uniformity over a wide range of temperatures. A variation of ±8 °C (± 14 °F) throughout the entire working section of a large furnace can be easily maintained. Many furnaces incorporate automatic compensation for heat losses at doors or other connection points. Combustion systems that maintain constant pressure or constant flow permit close temperature control on variable loads. Zoning is also a major contributor to control. To maintain good uniformity, it is necessary to load the furnace as uniformly as possible and to allow adequate space between containers--50 to 100 mm (2 to 4 in.) or more--to permit circulation of the heating gases.

The three types of furnaces most commonly used for pack carburizing are the box, car-bottom, and pit types. Box furnaces are loaded by mechanical devices or by in-plant transportation equipment. Car-bottom furnaces provide for convenient loading of heavy units. A car-bottom furnace with a car at each end allows a second car to be loaded while the furnace is in use, which minimizes the heat loss and downtime between batches. Pit furnaces are general-purpose furnaces that may be used for carburizing and other heat-treating operations that require minimum floor space.

Adequate support of containers and workpieces does much to minimize distortion. It also helps maintain the shape and extend the life of carburizing containers. Three or more points of support should be used in car-bottom furnaces. The container should be blocked above the hearth to allow circulation around, and proper shimming of, the container. In box-type furnaces, silicon carbide and certain other hearth materials, provide excellent wear resistance to maintain the shape of the hearth. Their high thermal conductivity helps promote temperature uniformity.

Furnaces for pack carburizing have a minimum number of parts that are subject to high wear or that require frequent maintenance. Very few alloy parts inside the furnace are subjected to thermal fatigue, and a minimum of auxiliary equipment is needed. The personnel who operate these furnaces do not need extensive technical training. (For more information on equipment, see the next Section, "Heat-Treating Equipment," in this Volume.)

Carburizing Containers

Materials. Carburizing containers are made of carbon steel, of aluminum-coated carbon steel, or of iron-nickel-chromium heat-resisting alloys. Although uncoated carbon steel boxes scale severely during carburizing and have short lives, they often are the most economical for processing odd lots and unusual shapes.

Aluminum coating can significantly extend the life of a carbon steel container, making this material potentially the lowest in cost per hour per unit weight carburized.

In the long run, heat-resisting alloys are the most economical container materials for carburizing large numbers of moderate-size parts. However, because heat-resisting alloys are considerably higher in initial cost than plain or aluminum-coated carbon steel, they must be used continuously if they are to approach the lowest possible prorated cost.

Design and Construction. For containers of all three materials, the trend has been toward lighter construction from sheet or plate, rather than the heavier cast construction. These lighter containers require ribbing, corrugating, or other bracing methods to make them rigid enough to withstand long periods at high temperature. Containers often are equipped with braced lifting eyes or hooks, special lid-receiving sections, and test-pin openings.

A carburizing container should be no larger than necessary. If possible, it should be narrow in at least one dimension to promote uniform heating of the contents. A properly designed box will provide a cooling rate high enough to minimize formation of a carbide network in the case, but low enough to avoid distortion or excessive hardening.

Lid Construction. Lids for carburizing containers vary from simple sheet-metal plates to built-up lids of metal and refractory material. The lid may add rigidity to the container. It must be tight enough to prevent air from entering and burning the compound, yet not so tight as to prevent easy expulsion of excess gas generated within the container. Lids must be capable of venting the container, and the venting means must be able to withstand the intense heat liberated by combustion of flammable gas. Lids that fit too loosely can be partly sealed with clay-base cements.

Conditioning. Before new alloy carburizing containers are placed in service, they may be conditioned by "precarburizing" without a work load. This pretreatment eliminates the possibility of the container, rather than the work load, being carburized during the first production carburizing cycle.

Packing

Intimate contact between compound and workpiece is not necessary; however, when properly packed, the compound will provide good support for the workpiece. The layer of compound surrounding the work must be heavy enough to allow for shrinkage and to maintain a high carbon potential during the entire cycle, but not so heavy as to unduly retard heating of the workpiece to carburizing temperature. If the container can be designed to conform to the shape of the workpiece, the compound will be of both uniform and minimum thickness.

Work-load density --that is, net weight (piece weight) divided by gross weight (weight of the carburizing container, compound, and workpieces)--is an important factor in the efficiency of pack carburizing, because it affects heating and cooling time. The smaller this percentage, the lower the relative efficiency of the process. Table 2 shows work-load densities for three different carburized parts.

Table 2 Work-load densities in pack carburizing

Part	Dimensions[(a)]				Weight per piece				Net weight, % of gross weight
	OD		OA		Net		Total[(b)]		
	mm	in.	mm	in.	kg	lb	kg	lb	
Roll	75	3	1220	48	37	82	72	159	51
Crane wheel	560	22	125	5	130	287	150	331	87
Gear	660	26	205	8	285	628	440	970	65

(a) OD, outside diameter; OA, overall (axial) dimension.

(b) Total weight of work plus packing material plus container, divided by number of pieces in pack

Procedure. Packing of the workpieces in a compound is a dusty and disagreeable operation (one of the reasons this process is losing favor in industry). For this reason, grouping of boxes, workpieces, and compound should be carefully planned so as to minimize handling of the compound. If possible, workpieces should come to the packer already stacked and sorted, preferably on open trays or in pans.

First, a layer of compound from 13 to 50 mm ($\frac{1}{2}$ to 2 in.) deep is placed in the empty box. The part or parts are then stacked in the container, and, if necessary, metal or ceramic supports or spacers are applied and internal container supports are inserted.

Whenever possible, workpieces should be packed with the longest dimension vertical to the base of the container. This is extremely important in processing long parts such as shafts and rolls because it minimizes the tendency of these parts to sag. Suspension of the work within the container or within the furnace is useful in minimizing distortion in relatively thin or delicate parts. For applications where small teeth or small holes are to be uniformly carburized, a 6- or 8-mesh material should be used to ensure good filling.

After the compound is sufficiently tamped, a final layer is placed on top of the parts. The thickness of the top layer varies according to the type of work, depth of case, type of container, and shrinkage rate of the compound, but it should be adequate to ensure that the work will be covered after shrinkage and other movements have occurred. A minimum depth of 50 mm (2 in.) is recommended. In the final step, the lid is put in place.

Process-Control Specimens. In order to control and evaluate the carburizing process, test pins or shims normally are included in the charge. To provide valid results, section sizes and locations of test specimens must closely approximate those of the workpieces. Placing a test pin close to a workpiece often will produce a thermal history identical to that of the workpiece.

For control purposes, many containers are equipped with a test-pin section that can be removed from the load during the carburizing cycle. After the pins have been quenched and fractured, case-depth readings made on them aid in evaluating whether satisfactory carburizing results are being obtained and in determining when the prescribed case depth has been attained.

Selective Carburizing

Stop-off techniques described in the article on gas carburizing in this Volume apply to selective carburization by pack carburizing. In addition, it may be possible to permit any portion of a part that is not to be carburized to protrude from the carburizing container. Alternatively, an inert or lightly oxidizing material may be packed around those areas of a part that are not to be carburized.

Liquid Carburizing and Cyaniding of Steels

Revised by Arthur D. Godding, Heatbath Corporation

Introduction

LIQUID CARBURIZING is a process used for case hardening steel or iron parts. The parts are held at a temperature above Ac_1 in a molten salt that will introduce carbon and nitrogen, or carbon alone, into the metal. Diffusion of the carbon from the surface toward the interior produces a case that can be hardened, usually by fast quenching from the bath. Carbon diffuses from the bath into the metal and produces a case comparable with one resulting from gas carburizing in an atmosphere containing some ammonia. However, because liquid carburizing involves faster heat-up (due to the superior heat-transfer characteristics of salt bath solutions), cycle times for liquid carburizing are shorter than those for gas carburizing.

Most liquid carburizing baths contain cyanide, which introduces both carbon and nitrogen into the case. One type of liquid carburizing bath, however, uses a special grade of carbon, rather than cyanide, as the source of carbon. This bath produces a case that contains only carbon as the hardening agent.

Liquid carburizing may be distinguished from cyaniding (which is performed in a bath containing a higher percentage of cyanide) by the character and composition of the case produced. Cases produced by liquid carburizing are lower in nitrogen and higher in carbon than cases produced by cyaniding. Cyanide cases are seldom applied to depths greater than 0.25 mm (0.010 in.); liquid carburizing can produce cases as deep as 6.35 mm (0.250 in.). For very thin cases, liquid carburizing in low-temperature baths may be employed in place of cyaniding.

Cyanide-Containing Liquid Carburizing Baths

Light case and deep case are arbitrary terms that have been associated with liquid carburizing in baths containing cyanide. There is necessarily some overlapping of bath compositions for the two types of case. In general, the two types are distinguished more by operating temperature or by cycle times than by bath composition. Therefore, the terms low temperature and high temperature are preferred.

Both low-temperature and high-temperature baths are supplied in different cyanide contents to satisfy individual requirements of carburizing activity (carbon potential) within the limitations of normal dragout and replenishment. In many instances, compatible companion compositions are available for starting the bath or for bath make-up, and for regeneration or maintenance of carburizing potential.

Low-temperature cyanide-type baths (light-case baths) are those usually operated in the temperature range from 845 to 900 °C (1550 to 1650 °F), although for certain specific effects this range is sometimes extended to 790 to 925 °C (1450 to 1700 °F). Low-temperature baths are best suited to formation of shallower cases. Low-temperature baths are generally of the accelerated cyanogen type containing various combinations and amounts of the constituents listed in Table 1 and differ from cyaniding baths in that the case produced by a low-temperature bath consists predominantly of carbon. Low-temperature baths are usually operated with a protective carbon cover; however, when the carbon cover on a low-temperature bath is thin, the nitrogen content of the carburized case will be relatively high. Cyaniding baths produce cases that are about 0.13 to 0.25 mm (0.005 to 0.010 in.) deep and that contain appreciable amounts of nitrogen.

Table 1 Operating compositions of liquid carburizing baths

Constituent	Composition of bath, %	
	Light case, low temperature	Deep case, high temperature

	845-900 °C (1550-1650 °F)	900-955 °C (1650-1750 °F)
Sodium cyanide	10-23	6-16
Barium chloride	. . .	30-55[(a)]
Salts of other alkaline earth metals[(b)]	0-10	0-10
Potassium chloride	0-25	0-20
Sodium chloride	20-40	0-20
Sodium carbonate	30 max	30 max
Accelerators other than those involving compounds of alkaline earth metals[(c)]	0-5	0-2
Sodium cyanate	1.0 max	0.5 max
Density of molten salt	1.76 g/cm^3 at 900 °C (0.0636 lb/in.^{3} at 1650 °F)	2.00 g/cm^3 at 925 °C (0.0723 lb/in.^{3} at 1700 °F)

(a) Proprietary barium chloride-free deep-case baths are available.

(b) Calcium and strontium chlorides have been employed. Calcium chloride is more effective, but its hygroscopic nature has limited its use.

(c) Among these accelerators are manganese dioxide, boron oxide, sodium fluoride, and sodium pyrophosphate.

In a low-temperature cyanide-type bath, several reactions occur simultaneously, depending on bath composition, to produce various end products and intermediates. These reaction products include the following: carbon (C), alkali carbonate (Na_2CO_3 or K_2CO_3), nitrogen (N_2 or 2N), carbon monoxide (CO), carbon dioxide (CO_2), cyanamide (Na_2CN_2 or $BaCN_2$), and cyanate (NaNCO).

Two of the major reactions believed to occur in the operating bath are the cyanamide shift and the formation of cyanate:

$$2NaCN \leftrightarrow Na_2CN_2 + C \qquad \textbf{(Eq 1)}$$

and either

$$2NaCN + O_2 \rightarrow 2NaNCO \qquad \textbf{(Eq 2)}$$

or

$$NaCN + CO_2 \leftrightarrow NaNCO + CO \quad \textbf{(Eq 3)}$$

Reactions that influence cyanate content proceed as follows:

$$NaNCO + C \rightarrow NaCN + CO \quad \textbf{(Eq 4)}$$

and either

$$4NaNCO + 2O_2 \rightarrow 2Na_2CO_3 + 2CO + 4N \quad \textbf{(Eq 5)}$$

or

$$4NaNCO + 4CO_2 \rightarrow 2Na_2CO_3 + 6CO + 4N \quad \textbf{(Eq 6)}$$

Equations 5 and 6 deplete the activity of the bath and lead to an eventual loss of carburizing effectiveness unless suitable replenishment practice is followed. Equations 1 and 3 are at least partly reversible. Reactions that produce either carbon monoxide or carbon are beneficial in producing the desired carburized case, as for example:

$$Fe + 2CO \rightarrow Fe[C] + CO_2 \quad \textbf{(Eq 7)}$$

and

$$Fe + C \rightarrow Fe[C] \quad \textbf{(Eq 8)}$$

Low-temperature (light-case) baths are usually operated at higher cyanide contents than high-temperature (deep-case baths). The preferred operating cyanide contents shown in Table 2 provide a case that is essentially eutectoidal (>0.80% C). If a hypoeutectoid (<0.80% C) case is desired, the bath is operated at the lower end of the temperature/cyanide range. Conversely, operation at the higher end of the suggested range favors formation of a hypereutectoid surface carbon content.

Table 2 Relation of operating temperature to sodium cyanide content in barium-activated liquid carburizing baths

Temperature		**NaCN, %**		
°C	**°F**	**min**	**Preferred**	**max[(a)]**
815	1500	14	18	23
845	1550	12	16	20
870	1600	11	14	18
900	1650	10	12	16

925	1700	8	10	14
955	1750	6	8	12

(a) The maximum limits are based on economy. If 30% NaCN is exceeded, there is danger that NaCN will break down, with production of carbon scum and attendant frothing. To correct such a condition, the bath temperature should be lowered and the NaCN content should be adjusted to the preferred value.

High-temperature cyanide-type baths (deep-case baths) are usually operated in the temperature range from 900 to 955 °C (1650 to 1750 °F). This range may be extended somewhat, but at lower temperatures the rate of carbon penetration decreases, and at temperatures higher than about 955 °C (1750 °F), deterioration of the bath and equipment is markedly accelerated. However, rapid carbon penetration can be obtained by operating at temperatures between 980 and 1040 °C (1800 and 1900 °F).

High-temperature baths are used for producing cases 0.5 to 3.0 mm (0.020 to 0.120 in.) deep. In some instances, even deeper cases are produced (up to about 6.35 mm, or 0.250 in.), but the most important use of these baths is for the rapid development of cases 1 to 2 mm (0.040 to 0.080 in.) deep. These baths consist of cyanide and a major proportion of barium chloride (Table 1), with or without supplemental acceleration from other salts of alkaline earth metals. Although the reactions shown for low-temperature liquid carburizing salts apply in some degree, the principal reaction is the so-called cyanamide shift. This reaction is reversible:

$$Ba(CN)_2 \leftrightarrow BaCN_2 + C \qquad \textbf{(Eq 9)}$$

In the presence of iron, the reaction is:

$$Ba(CN)_2 + Fe \rightarrow BaCN_2 + Fe[C] \qquad \textbf{(Eq 10)}$$

Cases produced in high-temperature liquid carburizing baths consist essentially of carbon dissolved in iron. However, sufficient nascent nitrogen is available to produce a superficial nitride-containing skin, which aids in resisting wear and which also resists softening during tempering and other heat treatments requiring higher than normal operating temperatures.

Combination Treatment. It is not uncommon for the carburizing cycle to be initiated in a high-temperature bath and then for the work load to be transferred to a low-temperature carburizing bath. Not only does this practice provide a maximum rate of carburizing, but quenching the work from the low-temperature bath reduces distortion and minimizes retained austenite.

Cyaniding (Liquid Carbonitriding)

Cyaniding, or salt-bath carbonitriding, is a heat-treating process that produces a file-hard, wear-resistant surface on ferrous parts. When steel is heated above Ac_1 in a suitable bath containing alkali cyanides and cyanates, the surface of the steel absorbs both carbon and nitrogen from the molten bath. When quenched in mineral oil, paraffin-base oil, water, or brine, the steel develops a hard surface layer, or case, that contains less carbon and more nitrogen than the case developed in activated liquid carburizing baths.

Because of greater efficiency and lower cost, sodium cyanide is used instead of the more expensive potassium cyanide. The active hardening agents of cyaniding baths--carbon monoxide and nitrogen--are not produced directly from sodium cyanide. Molten cyanide decomposes in the presence of air at the surface of the bath to produce sodium cyanate, which in turn decomposes in accordance with the following chemical reactions:

$$2NaCN + O_2 \rightarrow 2NaNCO \qquad \textbf{(Eq 11)}$$

$$4NaNCO \rightarrow Na_2CO_3 + 2NaCN + CO + 2N \quad \textbf{(Eq 12)}$$

$$2CO \rightarrow CO_2 + C \quad \textbf{(Eq 13)}$$

$$NaCN + CO_2 \rightarrow NaNCO + CO \quad \textbf{(Eq 14)}$$

The rate at which cyanate is formed and decomposes, liberating carbon and nitrogen at the surface of the steel, determines the carbonitriding activity of the bath. At operating temperatures, the higher the concentration of cyanate, the faster the rate of its decomposition. Because the rate of cyanate decomposition also increases with temperature, bath activity is greater at higher operating temperatures. A fresh cyaniding bath must be aged for about 12 h at a temperature above its melting point to provide a sufficient concentration of cyanate for efficient carbonitriding activity. For the aging cycle to be effective, any carbon scum formed on the surface must be removed. To eliminate scum, the cyanide content of the bath must be reduced to the 25 to 30% range by addition of inert salts (sodium chloride and sodium carbonate). At the bath aging temperature--usually about 700 °C (1290 °F)--the rate of its decomposition is low.

Bath Composition. A sodium cyanide mixture such as grade 30 in Table 3, containing 30% NaCN, 40% Na_2CO_3, and 30% NaCl, is generally used for cyaniding on a production basis. This mixture is preferable to any of the other compositions given in Table 3. The inert salts sodium chloride and sodium carbonate are added to cyanide to provide fluidity and to control the melting points of all mixtures. The 30% NaCN mixture, as well as the mixtures containing 45, 75, and 97% NaCN, may be added to the operating bath to maintain a desired cyanide concentration for a specific application.

Table 3 Compositions and properties of sodium cyanide mixtures

Mixture grade designation	Composition, wt%			Melting point		Specific gravity	
	NaCN	$NaCO_3$	NaCl	°C	°F	25 °C (75 °F)	860 °C (1580 °F)
96-98[(a)]	97	2.3	Trace	560	1040	1.50	1.10
75[(b)]	75	3.5	21.5	590	1095	1.60	1.25
45[(b)]	45.3	37.0	17.7	570	1060	1.80	1.40
30[(b)]	30.0	40.0	30.0	625	1155	2.09	1.54

(a) Appearance: white crystalline solid. This grade also contains 0.5% sodium cyanate (NaNCO) and 0.2% sodium hydroxide (NaOH); sodium sulfide (Na_2S) content, nil.

(b) Appearance: white granular mixture

The carbon content of the case developed in cyanide baths increases with an increase in the cyanide concentration of the bath, thus providing considerable versatility. A bath operating at 815 to 850 °C (1500 to 1560 °F) and containing 2 to 4% cyanide may be used to restore carbon to decarburized steels with a core carbon content of 0.30 to 0.40% C, while a 30% cyanide bath at the same temperature will yield a 0.13 mm (0.005 in.) case containing 0.65% C at the surface in 45 min. Sodium cyanide concentration also has some effect on case depth, as shown for 1020 steel in Table 4.

Table 4 Effect of sodium cyanide concentration on case depth in 1020 steel bars

Samples are 25.4 mm diam (1.0 in. diam) bars that were cyanided 30 min at 815 °C (1500 °F).

NaCN in bath, %	Depth of case	
	mm	in.
94.3	0.15	0.0060
76.0	0.18	0.0070
50.8	0.15	0.0060
43.0	0.15	0.0060
30.2	0.15	0.0060
20.8	0.14	0.0055
15.1	0.13	0.0050
10.8	0.10	0.0040

Noncyanide Liquid Carburizing

Liquid carburizing can be accomplished in a bath containing a special grade of carbon instead of cyanide as the source of carbon. In this bath, carbon particles are dispersed in the molten salt by mechanical agitation, which is achieved by means of one or more simple propeller stirrers that occupy a small fraction of the total volume of the bath. Agitation is also believed to introduce greater exposure and absorption of oxygen in the air.

The chemical reaction involved is not fully understood, but is thought to involve adsorption of carbon monoxide on carbon particles. The carbon monoxide is generated by reaction between the carbon and carbonates, which are major ingredients of the molten salt. The adsorbed carbon monoxide is presumed to react with steel surfaces much as in gas or pack carburizing.

Operating temperatures for this type of bath are generally higher than those for cyanide-type baths. A range of about 900 to 955 °C (1650 to 1750 °F) is most commonly employed. Temperatures below about 870 °C (1600 °F) are not recommended and may even lead to decarburization of the steel. The case depths and carbon gradients produced are in the same range as for high-temperature cyanide-type baths (see Fig. 1, 2, 3 for data on carbon and low-alloy steels), but there is no nitrogen in the case. The carbon content is slightly lower than that of standard carburizing baths that contain cyanide.

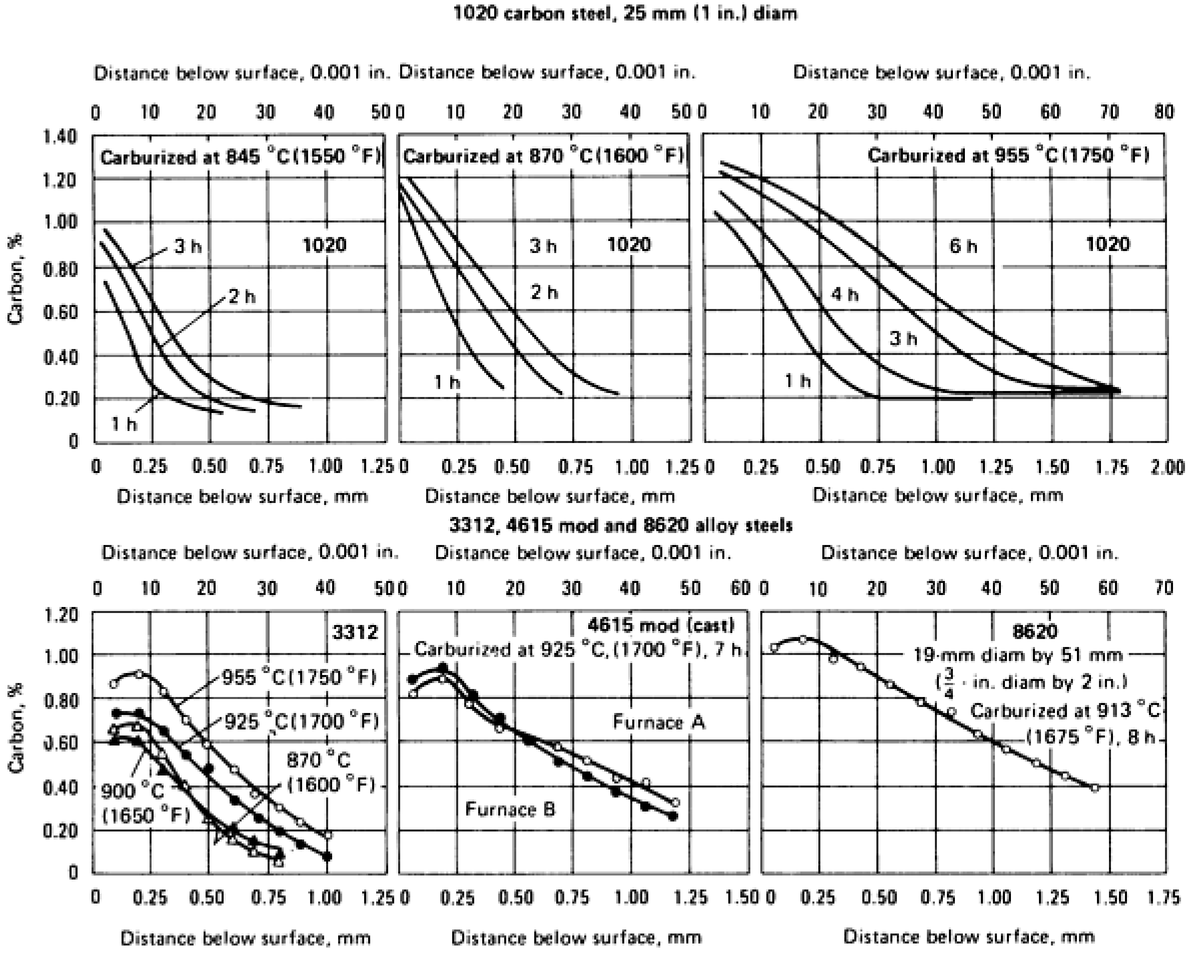

Fig. 1 Carbon gradients produced by liquid carburizing of carbon and alloy steels. Carbon gradients produced by liquid carburizing carbon and alloy steels in low-temperature and high-temperature baths. The 1020 carbon steel bars were carburized at 845, 870, and 955 °C (1550, 1600, and 1750 °F) for the periods shown. The data on 3312 alloy steel show the effect of four different carburizing temperatures on carbon gradient (time constant at 2 h). The data on modified 4615 steel castings indicate the slight differences in gradients obtained in two furnaces employing the same carburizing conditions (7 h at 925 °C, or 1700 °F). These data and the data on 8620 steel parts show a decrease in carbon content near the surface caused by diffusion of carbon during reheating to austenitizing temperature.

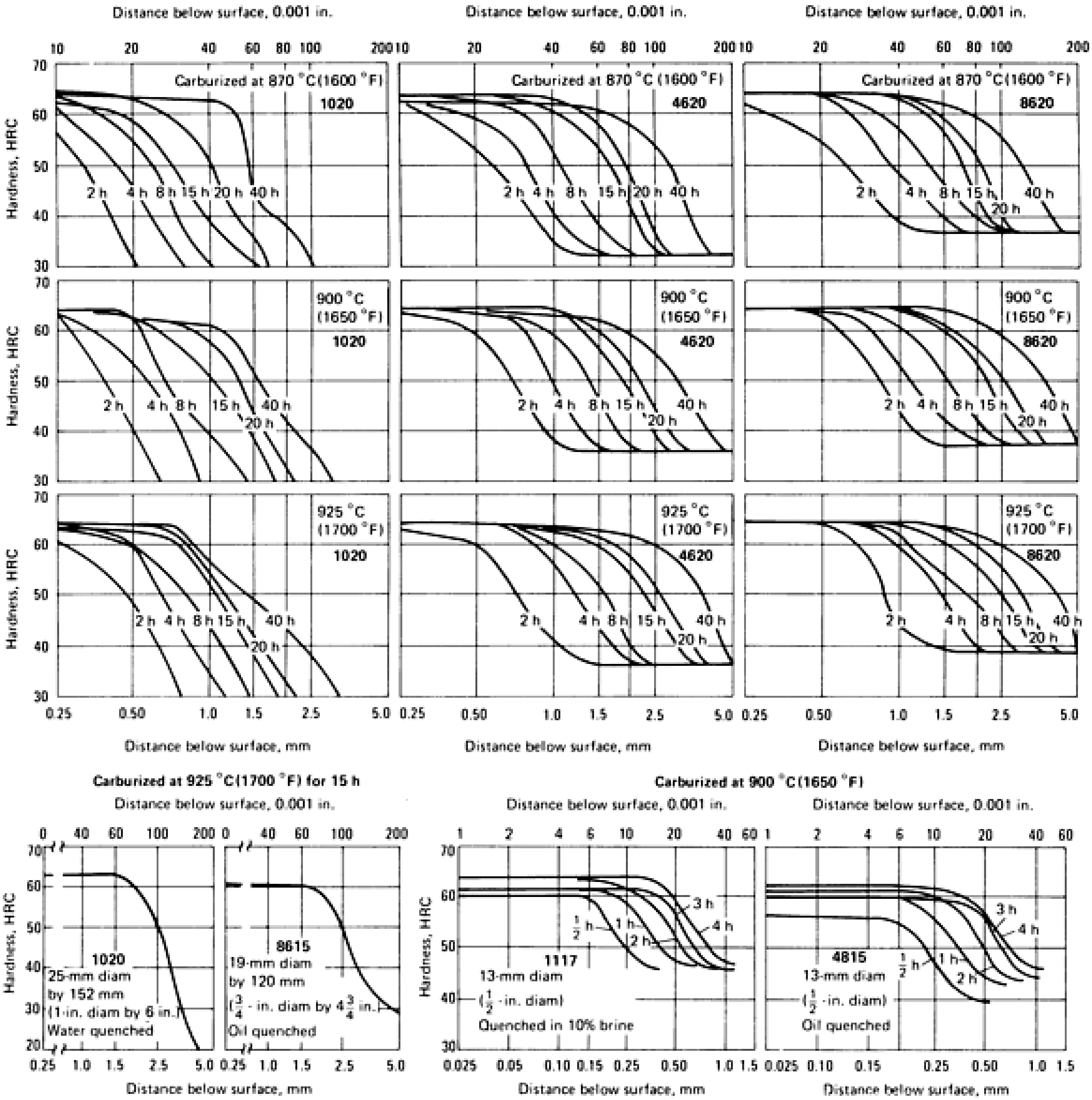

Fig. 2 Case-hardness gradients for two carbon steels and four low-alloy steels showing effects of carburizing temperature and time. Specimens measuring 19 mm diam by 51 mm ($\frac{3}{4}$ in. diam by 2 in.) were carburized, air cooled, reheated in neutral salt at 845 °C (1550 °F), and quenched in nitrate/nitrite salt at 180 °C (360 °F).

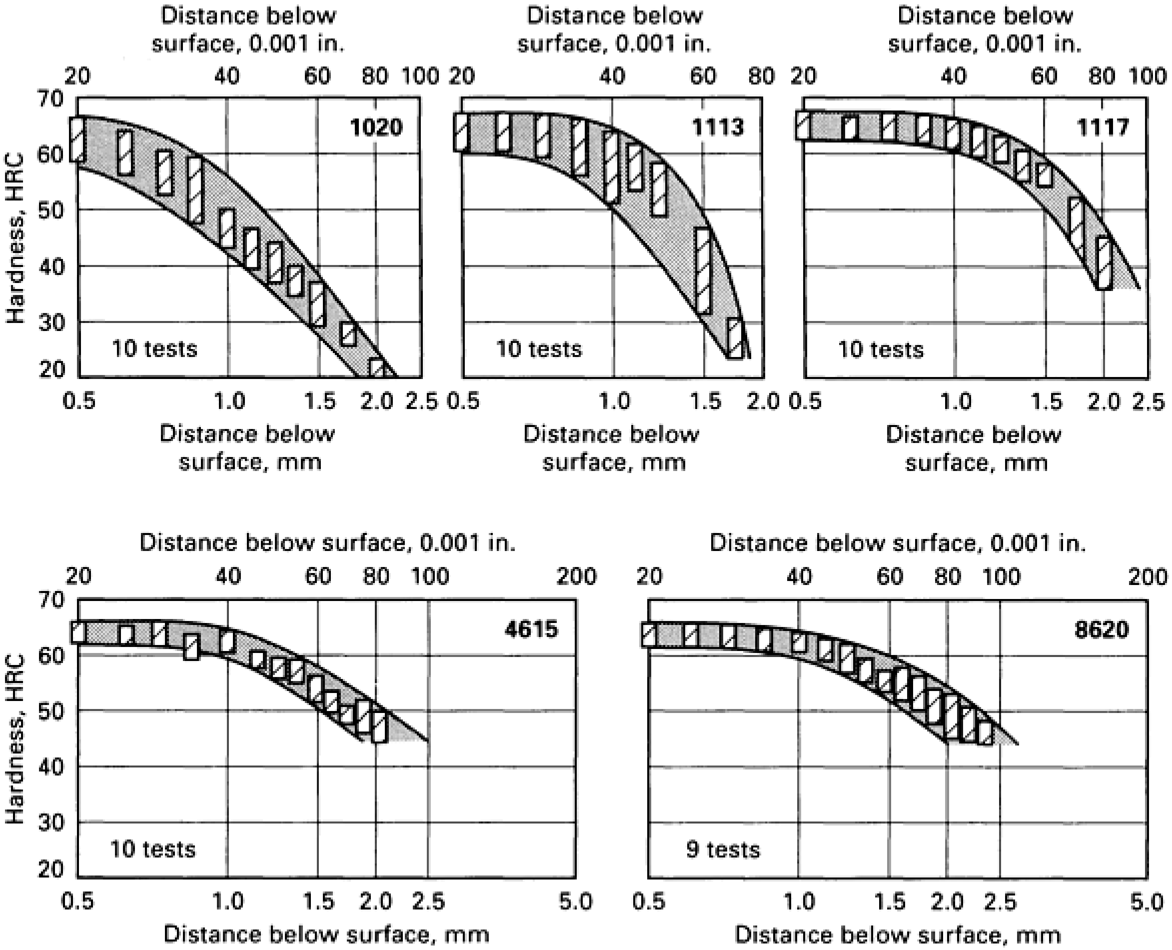

Fig. 3 Case-hardness gradients for selected steels showing scatter resulting from normal variations

Temperatures above 955 °C (1750 °F) produce more rapid carbon penetration and do not adversely affect noncyanide baths, because no cyanide is present to break down and cause carbon scum or frothing. Equipment deterioration is the chief factor that limits operating temperature.

Parts that are slowly cooled following noncyanide carburization are more easily machined than parts slowly cooled following cyanide carburization, because of the absence of nitrogen in noncyanide-carburized cases. For the same reason, parts that are quenched following noncyanide carburization contain less retained austenite than parts quenched following cyanide carburization.

Noncyanide Carburizing Process (Ref 1)

A noncyanide process for the liquid carburizing of steel that consists of a chloride mixture containing a small amount of specially selected carbon has recently been made commercially available. This carbon additive is a blend of selected graphite materials. The mixture should be held in a pot constructed of series 300 stainless steel, Inconel, or a ceramic material.

The chloride mixture laden with carbon is nontoxic and produces a classic carbon case that contains no nitrogen. Parts that have been carburized with this chloride-carbon material can be quenched directly into any nitrate/nitrite salt bath without the need for a neutral wash. Such a step is not recommended with cyanide carburizing salts, because of their incompatibility with strong oxidizers (for example, nitrates and nitrites).

This carbon-containing chloride mixture has the following properties:

Melting point, °C (°F)	663 (1225)
Working range, °C (°F)	954-982 (1750-1800)
Specific heat, J/kg · K (cal/g · °C)	
Solid	960 (0.23)
Liquid	1050 (0.23)
Heat of fusion, kJ/kg (Btu/lb)	414 (178)
Density at 954 °C (1750 °F), g/cm^3(lb/in.^{3})	1.44 (0.0520)

Initial Start-Up. A new bath is prepared by melting the chloride salt mixture and bringing it to an operating temperature of 954 °C (1750 °F). When the bath is molten and has stabilized at operating temperature, small amounts of carbon additive are introduced in the melt until a 13 to 25 mm (0.5 to 1.0 in.) thick cover remains on the surface.

Because the addition of carbon into the bath is necessary to achieve carburizing potential, the bath should be aged at heat for approximately 2 h before processing work through the bath. An adequate carbon cover should be maintained over the bath at all times while at operating temperature to ensure consistent results.

The bath level is maintained via additions of the chloride salt mixture; the carbon cover is maintained by additions of the graphite additive.

Control of Case Depth. Figure 4 shows typical effective case depths (to 50 HRC) obtainable in AISI 1117 carbon steel. Because variables such as surface condition and alloy content can affect the quality and depth of a carburized surface, test coupons should be prepared and examined in order to determine optimum operating parameters.

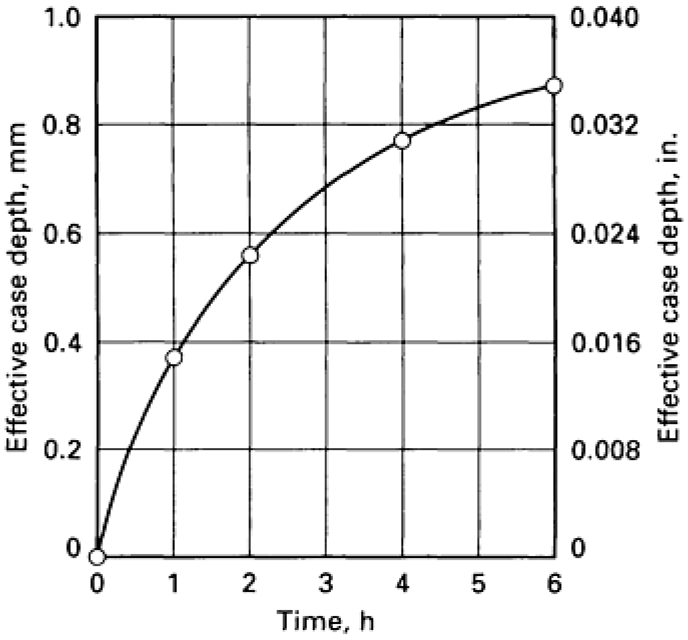

Fig. 4 Plot of carbon penetration versus holding time at 955 °C (1750 °F) for 1117 resulfurized carbon steel heat treated with Pure Case, a noncyanide carburizing process

Maximum carbon penetration can be achieved if parts are cleaned and descaled prior to the noncyanide carburizing Pure Case process. Most soils and oils can be removed with alkaline cleaner. Scale and heavy oxides may require mechanical cleaning (that, is sandblasting) or acid pickling prior to carburizing in the noncyanide mixture. It is vital that parts be completely dry before immersing the components in the molten bath.

Low-Toxicity Regenerable Carburizing and Carbonitriding Salt Bath Process (Ref 2, 3)

Extensive development work has been carried out in recent years to make salt bath processes ecologically attractive. The low-toxicity nitrocarburizing process Tufftride TF1 (see the article "Gaseous and Plasma Nitrocarburizing" in this Volume), which incorporates a nontoxic regenerator to produce the required composition within the working bath, was successfully developed in the mid-1970s (Ref 4, 5). It was apparent, therefore, that the objective of research on carburizing and carbonitriding should be directed at developing a cyanide-free regenerator to yield the required level of CN^- in the process bath. By using a base salt and a regenerator that are both cyanide-free, such a technique would avoid handling, storage, and transportation problems; eliminate the need to bail out the bath; and ease disposal requirements.

Early research to establish an ecologically acceptable process revealed that in order to maintain the high quality hitherto associated with salt bath carburizing, it was necessary to retain CN^- as the active carburizing constituent. Existing alternatives for the development of a new and ecologically safe carburizing process rapidly showed that the quality of the salt bath could only be maintained by using cyanide in the carburizing bath.

Experimental work with alternative active constituents, such as silicon carbide and suspended graphite, showed these approaches to be impracticable. Melts containing silicon carbide became viscous, generating large amounts of sludge, while graphite suspensions were difficult to control and distribute evenly throughout the molten bath. None of the options to CN^- allowed the desired reproducibility with respect to close control of carburized case depth and carbon content. The fundamental carburizing reactions taking place in a salt bath at a temperature on the order of 930 °C (1705 °F) involve the decomposition of cyanide by oxygen:

$$2CN^- + 2O_2 \rightarrow CO_3^{2-} + 2N + CO \quad \textbf{(Eq 15)}$$

followed by the subsequent diffusion of carbon into the surface of the component:

$$2CO \rightarrow C_{Fe} + CO_2 \quad \textbf{(Eq 16)}$$

A small amount of nitrogen also diffuses into the surface, depending on the temperature and composition of the bath. Experience has shown that salt baths completely free from cyanide do not yield reproducible results on a production scale. This not only applies to controlling the surface carbon content but also to the uniformity of carbon diffusion over the surface of the component.

Therefore, a cyanide-free regenerator had to be developed that would produce the required amount of cyanide in the bath. This aim was achieved by the use of an organic polymeric material which converts part of the carbonate present in the molten bath to CN^-. This regenerator is known as CeControl and the process is designated as Durofer (Ref 6, 7). The Durofer process is compared to conventional salt bath carburizing in Fig. 5.

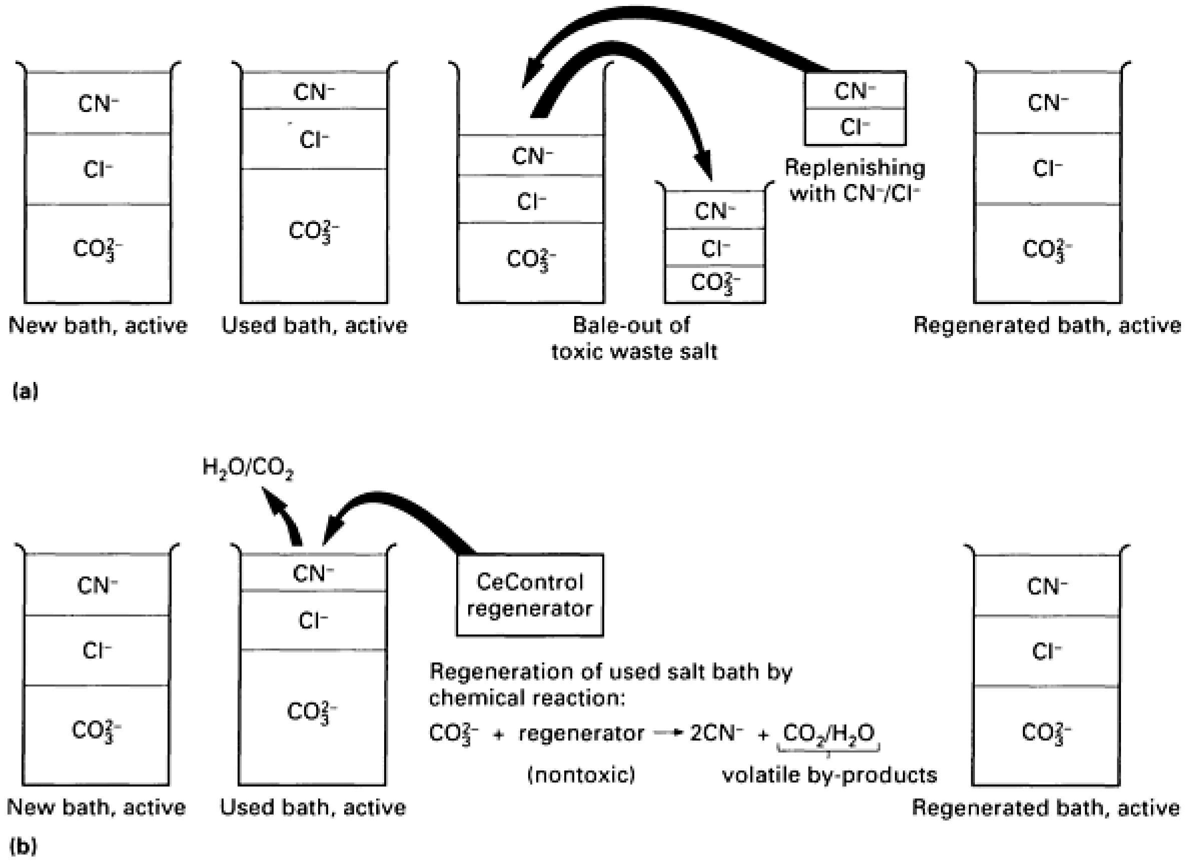

Fig. 5 Sequence of operations for two salt bath carburizing processes. (a) Conventional, requiring daily replenishment of bath with salts having high CN^- concentrations. (b) Durofer, in which CN^- level is maintained with addition of organic polymer material (CeControl regenerator) that converts carbonate in molten salt bath to CN^-

Process Control. The chemical reaction between the regenerator and the carburizing melt does not produce an increase in the molten salt volume, and, consequently, it is no longer necessary to bail out inactive salt. Therefore, the Durofer process does not produce toxic waste salt. The regenerator is manufactured in pellet form and is added to the molten bath by use of an automatic vibratory feeder. The equipment doses the molten salt with a regulated number of pellets at preset intervals, both when work is in the bath and during idling periods. Any deviation from the control range can be detected by regular analysis of the CN^- content and adjustments carried out on the autoregeneration system to compensate for any irregularity. As shown in Fig. 6, the advantage of automatic regeneration is that a very consistent CN^- level can be maintained in the bath, resulting in uniform and reproducible carburizing.

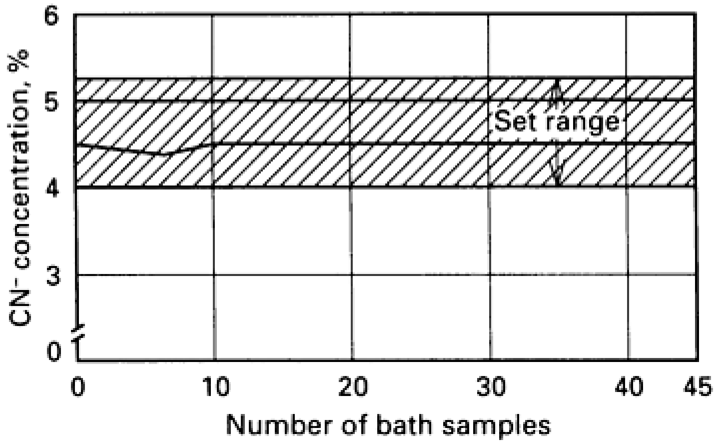

Fig. 6 The consistency of the CN- level maintained in the Durofer process. Test data compiled over 10 working days (3 shifts/day) in a carburizing bath at 930 °C (1705 °F) using CeControl 80 regenerator

Experience has shown that the optimum surface carbon value is 0.8% for alloy steels, and 1.1% is generally accepted as the optimum surface carbon value for unalloyed steels. A choice of base salt is available for use with the new regenerator to give these two carburizing conditions, designated CeControl 80B and CeControl 110B, respectively. Figure 7 shows carbon profiles obtained for samples of SAE 1015 steel after carburizing for 60 min at 930 °C (1705 °F) by the Durofer process using both of these base salts.

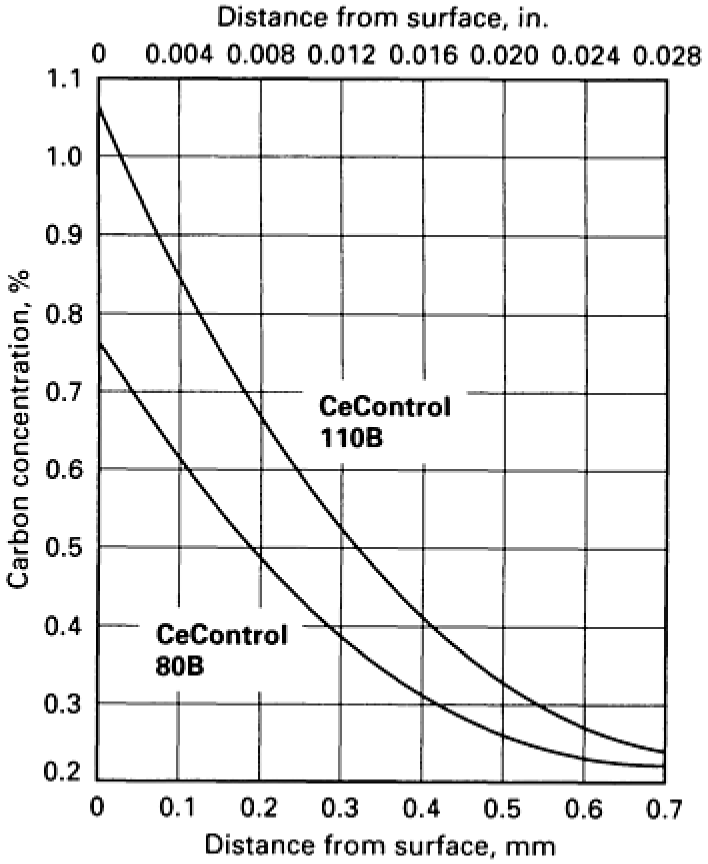

Fig. 7 Plots of carbon concentration versus carbon penetration for 1015 steels that were carburized at 930 °C (1705 °F) for 1 h with two different Durofer process base salt regenerators

Process Bath Preparation. The Durofer process bath is initially prepared by melting out the base salt, which may be either CeControl 80B or CeControl 110B, depending on the application requirements. The carburizing activity is promoted by adding CeControl regenerator via the automatic feeder, increasing the CN^- content up to about 4.5%. Control level is reached in approximately 5 h, when the addition rate is adjusted to that necessary to maintain control. The amount of regenerator required to maintain control is approximately 0.08 to 100 kg (0.18 to 220 lb) bath capacity per hour, for a working bath operating with a graphite economizer at 950 °C (1740 °F). Reduction of the molten salt level due to salt drag-out by the workload is restored by additions of the appropriate cyanide-free base salt.

Quenching. As in traditional salt bath carburizing, components carburized in the Durofer process can be quenched into water or oil. However, the composition of the Durofer bath also permits direct quenching into molten nitrate or nitrite salt baths to minimize distortion (Ref 8). In addition to this technical advantage, the chemical nature of the salt quench decomposes the CN^-, carried over on the components from the Durofer bath, to harmless carbonate. Thus, the need for detoxification of solid deposits in the quench medium and wash-water effluent is eliminated.

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Carbon Gradients

Figure 1 shows carbon gradients produced by liquid carburizing 1020 steel bars at 845, 870, and 955 °C (1550, 1600, and 1750 °F) for various lengths of time at carburizing temperature. Carbon-gradient data for two wrought alloy steels (3312 and 8620) and one cast alloy steel (4615 mod) are also shown. After carburizing, the 8620 steel parts were austenitized at 840 °C (1540 °F) and quenched in oil at 55 °C (130 °F). The 4615 steel parts were austenitized at 790 °C (1450 °F), quenched in salt at 190 °C (375 °F) for 3 min, and cooled in air.

Carbon penetration (case depth) in liquid carburizing is determined primarily by the carburizing temperature and the duration of the carburizing cycle. A simple formula for estimating total case depths (measured to base carbon level) obtainable in liquid carburizing is:

$$d = k\sqrt{t} \qquad \textbf{(Eq 17)}$$

where *d* is case depth, *k* is a constant that represents the penetration in the first hour at temperature, and *t* is the time at temperature in hours. Typical values of *k* at three different temperatures are 0.30 mm at 815 °C (0.012 in. at 1500 °F), 0.46 mm at 870 °C (0.018 in. at 1600 °F), and 0.64 mm at 925 °C (0.025 in. at 1700 °F).

Hardness Gradients

A hardness gradient or variation in hardness at different depths below the surface is established in parts that are quenched following liquid carburization. The data in Fig. 2 show typical hardness gradients obtainable with carbon and low-alloy steels and illustrate the influence of carburizing temperature, duration of carburizing, quenching temperature, and quenching medium. Data on 1020, 4620, and 8620 steels are plotted for cycles of 2, 4, 8, 15, 20, and 40 h. These

specimens were air cooled from carburizing temperatures of 870, 900, and 925 °C (1600, 1650, and 1700 °F), reheated in neutral salt at 845 °C (1550 °F), and quenched in molten salt at 180 °C (360 °F). Although the depth of case at maximum hardness is progressively extended in the alloy steels with increases in time and temperature, increases in carburizing temperature have the effect of foreshortening the curves plotted for the 1020 steel. Differences between the responses of 1020 and 8615 steels are shown to be less pronounced after carburizing at 925 °C (1700 °F) for 15 h and quenching directly from the carburizing temperature. A final series of curves indicates the results obtained with 1117 and 4815 steels after carburizing at 900 °C (1650 °F) for periods ranging from $\frac{1}{2}$ to 4 h. The 4815 steel was quenched in oil and the 1117 steel was quenched in a 10% brine solution.

The indentation hardness data presented in Fig. 3 for five different steels indicate the effects of normal variations in practice on the hardness gradient. The shaded bands represent the scatter in results obtained from multiple tests of each steel. Although similar surface hardnesses are obtained with all five steels, depth of hardness increases with the alloy content of the steel. A comparison among the hardnesses of these five steels at a depth of 1 mm (0.040 in.) illustrates this variation. Although a minimum case hardness of 60 HRC cannot be maintained to a depth of 1 mm (0.040 in.) with 1020 (0.30 to 0.60% Mn) steel, it can sometimes be achieved with 1113 (0.70 to 1.00% Mn) steel and can almost always be achieved with 1117 (1.00 to 1.30% Mn), 4615, and 8620 steels.

Cyaniding Time and Temperature

Bath operating temperatures for cyanide hardening vary between 760 and 870 °C (1400 and 1600 °F). Temperatures near the lower end of this range are favored for minimizing distortion during quenching from the bath temperature. Higher temperatures are selected to exceed the Ac_3 point of the steel, to achieve faster penetration, and, depending on alloy content, to produce a fully hardened core after quenching.

When low-carbon and alloy steels are to be cyanided to produce a surface capable of resisting high contact loads, the Surface usually must be backed up with a fine-grain, tough core. This requires an operating bath temperature of about 870 °C (1600 °F).

The high file hardness of salt bath cyanided steel parts is a combined effect of carbon and nitrogen absorption in the carbonitrided case (see Table 5). Usually, immersion times range from 30 min to 1 h and produce case depths and surface carbon and nitrogen concentrations corresponding to those in Table 5. Lower temperatures will provide results proportionately lower than those given in Table 5.

Table 5 Effect of cyaniding temperature and time on case depth and surface carbon and nitrogen contents

Material thickness, 2.03 mm (0.080 in.); cyanide content of bath, 20 to 30%

Steel	Case depth after cyaniding for:				Analysis after 100 min at temperature[a]	
	15 min		100 min			
	mm	in.	mm	in.	Carbon, %	Nitrogen, %
Cyanided at 760 °C (1400 °F)						
1008	0.038	0.0015	0.152	0.006	0.68	0.51
1010	0.038	0.0015	0.152	0.006	0.70	0.50
1022	0.051	0.0020	0.203	0.008	0.72	0.51

Cyanided at 845 °C (1550 °F)						
1008	0.076	0.0030	0.203	0.008	0.75	0.26
1010	0.076	0.0030	0.203	0.008	0.77	0.28
1022	0.089	0.0035	0.254	0.010	0.79	0.27

(a) Carbon and nitrogen contents were determined from analysis of the outermost 0.076 mm (0.003 in.) of cyanided cases.

Furnaces and Equipment

Liquid carburizing is carried out in a salt bath furnace that may be heated either externally or internally. In an externally heated furnace, heat is introduced into an annular space between the salt pot and the surrounding insulation, which usually is made of firebrick. In an internally heated furnace, heat is introduced directly into the salt. Both internally and externally heated furnaces generally have insulated lids that slide to open the bath and allow workpieces and fixtures to be positioned, usually with an overhead crane or with similar mechanized lifting equipment. Additional information is available in the article "Salt Bath Equipment" in this Volume.

Externally Heated Furnaces

Externally heated furnaces may be fired by gas or oil, or may be heated by means of electrical-resistance elements.

Gas-fired or oil-fired furnaces similar in design to the one shown in Fig. 8(a) are commonly used for liquid carburizing. These furnaces are generally lower in initial cost than electrode or resistance-heated furnaces and are simple to install and operate. To contain the molten carburizing salt, fuel-fired furnaces employ a steel or alloy pot, which may be either round or rectangular. Heat is applied by two or more self-cooling burners that fire tangentially between the outer pot wall and the inner surface of the furnace lining. The hot gases are vented through a flue, which is located near the top for atmospheric-type burners, and near the bottom for pressure-type burners and for atmospheric burners for which the flue is connected to a stack 1 to 2 m (3 to 6 ft) high to maintain negative pressure in the firing chamber. The combustion chamber is lined with firebrick and with additional insulation if required. A steel casing completely surrounds all sides of the furnace housing and provides adequate safety in the event of pot failure.

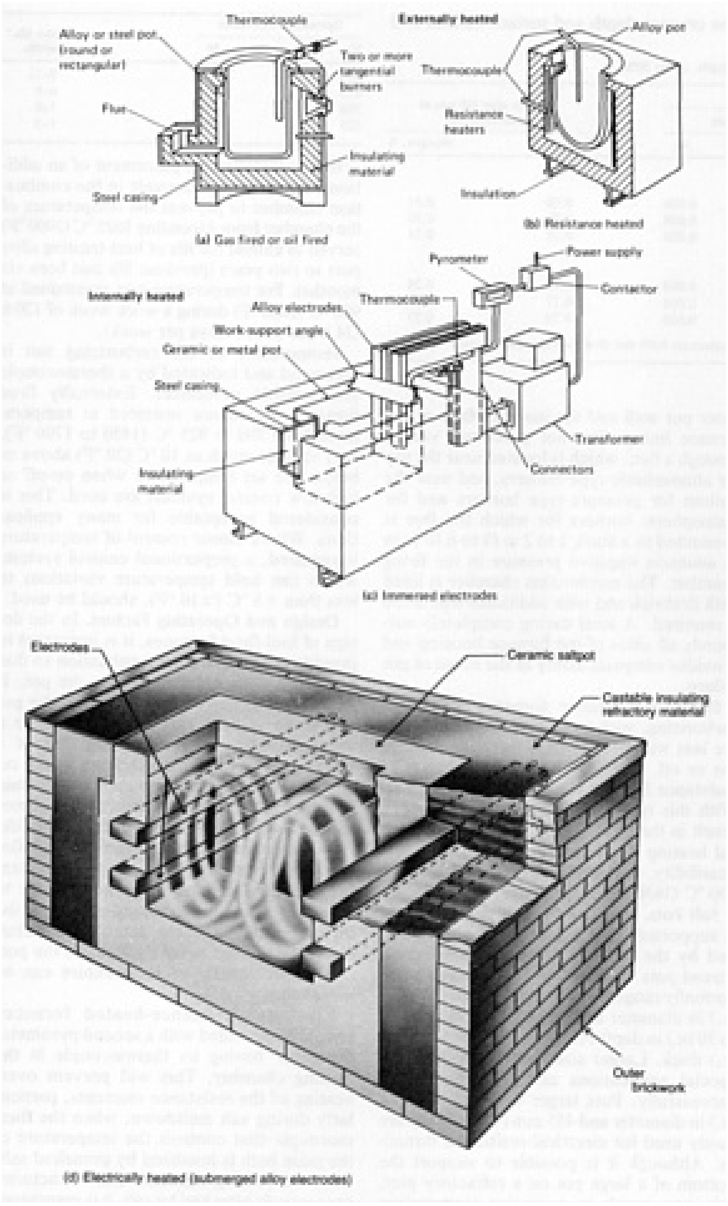


Fig. 8 Principal types of externally and internally heated salt bath furnaces used for liquid carburizing

Electrical-resistance furnaces for liquid carburizing, such as that shown in Fig. 8(b), are less widely used than furnaces fired by gas or oil. They are heated by a series of resistance heaters surrounding the salt pot. With this type of furnace, pot failure may result in the total destruction of the electrical heating elements; to guard against this possibility, carburizing temperatures below 900 °C (1650 °F) are preferred.

Salt Pots. Because the salt pot ordinarily is supported from a flange, pot size is limited by the strength of the material used. Round pots for furnaces fired by gas or oil normally range from 255 to 915 mm (10 to 36 in.) in diameter and from 205 to 760 mm (8 to 30 in.) in depth; they are about 9.5 mm ($\frac{3}{8}$ in.) thick. Larger sizes have been built for special applications and have performed successfully. Pots larger than 355 mm (14 in.) in diameter and 455 mm (18 in.) deep are rarely used for electrical-resistance furnaces. Although it is possible to support the bottom of a large pot on a refractory pier, this may result in excessive temperature gradients.

Pots may be press formed from a single piece of low-carbon steel or iron-nickel-chromium alloy; a composition of Fe-35Ni-15Cr is usually preferred for the latter. Less-expensive welded pots may be fabricated from either of these materials.

In a well-designed furnace, life of round alloy pots will vary with maximum operating temperature as follows:

Operating temperature		Service life, months
°C	°F	
845	1550	9-12
870	1600	6-9
900	1650	3-6

In one installation, placement of an additional control thermocouple in the combustion chamber to prevent the temperature of the chamber from exceeding 1095 °C (2000 °F) served to extend the life of heat-treating alloy pots to two years (previous life had been six months). Pot temperature was maintained at 900 °C (1650 °F) during a work week of 120 h (24 h per day, 5 days per week).

Temperature of the carburizing salt is measured and indicated by a thermocouple and suitable pyrometer. Externally fired furnaces which are operated at temperatures from 790 to 925 °C (1450 to 1700 °F), may vary as much as 10 °C (20 °F) above or below the set temperature when on-off or high-low control systems are used. This is considered acceptable for many applications. Where closer control of temperature is required, a proportional control system, which can hold temperature variations to less than ±5 °C (±10 °F), should be used.

Design and Operating Factors. In the design of fuel-fired furnaces, it is important to provide ample space for combustion so that the flame does not impinge on the pot. If flame impingement is unavoidable, the pot should be rotated slightly at least once a week. Rotation of the pot and use of a sleeve reduce local deterioration in the region of flame impingement and thus prolong pot life. The combustion-chamber atmosphere also has important effects on pot life. A system controlled to range from high fire to low fire is preferable to an on-off system for two reasons: the latter permits air to enter the combustion chamber during the off portion of the cycle, thereby accelerating scaling of the outer surfaces of the pot; and closer control of temperature can be achieved.

Electrical-resistance-heated furnaces should be provided with a second pyrometer controller having its thermocouple in the heating chamber. This will prevent over-heating of the resistance elements, particularly during salt meltdown, when the thermocouple that controls the temperature of the main bath is insulated by unmelted salt. Because heating elements and refractories are severely attacked by salt, it is mandatory that all salt be kept out of the combustion chamber. For this purpose, a mixture of high-temperature refractory cement, with a ceramic fiber for strength, may be used to seal joints where the pot flange rests on the retaining ring at the top of the furnace.

Regardless of the heating means, externally heated pots should be started on low fire (low heat input). After melting of the salt is observed around the top or side of the pot, the heat can be gradually increased to complete the meltdown. Excessive heating of the sidewalls or pot bottom during startup may create pressures sufficient to expel salt violently from the pot. For added safety, the pot should be covered during melt-down with either a cover or an unfastened steel plate.

Waste heat from flue gases may be fed to an adjacent chamber and used for preheating of work. Flue gases should always be visible to the operator; the presence of bluish white or white fumes at the vent is an indication that salts have entered the combustion chamber, and such situations require prompt corrective action.

Advantages and Disadvantages. Because of the ease with which they can be restarted, externally heated furnaces are well suited to intermittent operations. Another advantage of furnaces of this type is that a single furnace can be used for a variety of applications; a separate pot, containing the proper salt, can be used for each application.

Externally heated furnaces have several characteristics, however, that limit their usefulness in certain carburizing operations. They are less adaptable to close and uniform temperature control because they dissipate heat by convection, creating temperature gradients in the bath. Also, the temperature lag of the thermocouple and the recovery time of the furnace may result in overshooting or undershooting a desired temperature control point by as much as 14 °C (25 °F). In addition to requiring an exhaust system for flue gases, these furnaces may overheat at the bottom and sidewalls in restarting, creating in the thermally expanding molten salt a pressure buildup that may cause an explosion. Finally, externally heated furnaces are seldom practical for continuous high-volume production because of the limitations of pots with respect to size and maximum operating temperature. High maintenance cost is also a factor.

Immersed-Electrode Furnaces

The immersed-electrode furnace has greatly extended the useful range and capacity of molten carburizing baths. The electrodes can be removed and replaced without bailing out the furnace, and this design is suitable for both cyanide and non-cyanide carburizing processes. In this type of furnace, the molten salt is contained in a steel or ceramic pot surrounded by suitable insulating materials that separate it from an exterior casing of heavy-gage steel. The salt is heated by passing alternating current through it by means of immersed electrodes. Heat is generated by the passage of current through the salt. This heat is quickly dissipated by a downward stirring action created by current flows. The electrodes are attached by copper connectors to a transformer that converts the line voltage to a much lower voltage (9 to 18 V) across the electrodes. Bath temperature is automatically controlled by a thermocouple-activated system that regulates the input of electric power. A typical immersed-electrode furnace for liquid carburizing is shown in Fig. 8(c).

The depth of salt pots for immersed-electrode carburizing furnaces is usually limited to about 2 m (6 ft) for metal pots. Ceramic pot depth has no limit. Furnaces with pots up to 4.6 m (15 ft) long, and with power input of 360 kW, are presently in operation. They have heating capacities of about 320 kg/h (700 lb/h). In contrast, smaller units with salt pots having work spaces measuring 230 by 455 by 890 mm deep (9 by 7 by 14 in. deep), and with 15 kW power input, can heat about 23 kg/h (50 lb/h) to 925 °C (1700 °F).

Advantages and Disadvantages. Immersed-electrode furnaces do not require iron-chromium-nickel alloy pots. Carbon steel pots of welded construction, set in insulating brick but not cemented in place, have given service life as follows:

Operating temperature		Service life, years
°C	°F	
845[(a)]	1550[(a)]	2-3
870	1600	$1\frac{1}{2}$-2
900	1650	1-$1\frac{1}{2}$

(a) Max

These furnaces require minimum floor space and maintenance and can be used with all types of carburizing salts. Electrodes made of alloy steel should have an average service life equivalent to that indicated for steel pots in the above table. Worn electrodes can be replaced while the furnace is in operation.

Depending on the positioning of the electrodes, temperature control to within ±3 °C (±5 °F) is easily obtained with these furnaces; heat is generated within the bath, and overshooting is readily avoided. The furnaces lend themselves to mechanization and are suitable for high-volume production at operating temperatures from 815 to 955 °C (1500 to 1750 °F).

Maximum pot size is not restricted; pots may vary in length and width to suit requirements, and multiple pairs of electrodes can be installed to furnish the necessary heating capacity. Several batches of work may be carburized simultaneously and removed after different periods of time to produce a variety of case depths. Because the salt bath melts from the top downward, this type of furnace does not present a starting problem or an explosion hazard.

The immersed-electrode furnace is not recommended for intermittent operation. Depending on furnace size, reheating the salt charge may require a day or more. Pots are not intended to be interchangeable. Pot removal usually involves replacement of the surrounding insulation.

If an immersed-electrode-heated salt bath has been shut down completely and the salt has solidified, the salt between the electrodes must be melted with a torch before heating can be resumed. Insertion of an electric-resistance coil into the bath prior to salt solidification provides another means of remelting.

Submerged-Electrode Furnaces

Figure 8(d) illustrates the arrangement of components of a submerged-electrode furnace. The frame is made of heavy angle iron, and a steel plate is placed at the base beneath the brickwork. The outer brickwork consists of hollow ceramic tile or common building brick. The salt pot is made of burned alumina firebrick. The space between the sidewalls and the ceramic pot is filled with castable insulating refractory.

When salt is melted in the pot, it penetrates the refractory until it becomes cool enough to freeze. The resulting shell of solidified salt retains the liquid salt in the furnace. If the refractory develops a crack, bath temperature must be lowered to permit salt to solidify in the crack.

Water-cooled electrodes are submerged in liquid salt in the pot and are sealed in the refractory walls by frozen salt. Current travels between the electrodes, which are flush with the sidewalls. The path of current travel extends a few inches above the top of the electrodes.

Start-up and Shutdown. A submerged-electrode furnace can be started by adding molten salt from another furnace or by using a gas-fired torch or electric starting coil to melt a pool of salt that will wet both electrodes and provide molten salt for the current path. After the current path has been established in the molten salt between the electrodes, salt may be added to bring the bath up to working level. Additional salt will be required to maintain this level because a small amount will seep into the brickwork and freeze.

If the furnace must be shut down, the molten salt should be bailed from the furnace before it freezes. However, if the salt is allowed to remain in the furnace, a resistance-heated starting coil should be submerged in the bottom of the furnace while the salt is still molten. This coil remains in the frozen salt and is connected to the transformer leads to start up the furnace.

Advantages and Disadvantages. In common with immersed-electrode furnaces, submerged-electrode furnaces require minimum floor space and maintenance and are highly adaptable to mechanization. Because the submerged-electrode furnace employs water for cooling of the electrodes and transformer, it may be operated at a 50% overload without overheating the transformer, whereas the immersed-electrode furnace, being air cooled, should not be operated above a 10% overload unless designed for overload.

Because a ceramic pot is used, pot life can be 1 to 3 years. The electrodes are usually first to fail. The furnace can be rebuilt on a planned schedule during annual shutdowns.

Because of the erosive effects that water-soluble salts with high sodium carbonate or sodium cyanide contents have on ceramic pots, submerged-electrode furnaces can be used only with low-cyanide, low-carbonate salts. Baths with high cyanide or carbonate salt require a modified basic brick. The furnace shown in Fig. 8(d) with modified brick and submerged alloy electrodes will give many years of service in both cyanide and noncyanide operation.

Furnace Parts and Fixtures

Table 6 lists wrought and cast materials used for furnace parts and fixtures. As indicated, more than one material may be safely selected for a specific furnace part or fixture. Both cost of material and length of service usually increase with alloy content. Although length of service is influenced by both operating temperature and type of carburizing salt employed, the materials listed may be used in both the low- and high-temperature ranges--that is, at any temperature from 845 to 955 °C (1550 to 1750 °F).

Table 6 Recommended materials for furnace parts and fixtures when liquid carburizing at temperatures between 845 and 955 °C (1550 and 1750 °F)

Product	Material required for selected components[a]						
	Pots		Electrodes		Thermocouple protection tubes	Fixtures	Baskets
	Externally heated	Internally heated	Immersed	Submerged			
Wrought[b]	35-18[c]	Carbon steel[d]	446	Carbon steel	446	35-18[c]	35-18[c]
	Inconel	. . .	35-18[c]	35-18[c]	35-18[c]	Inconel	Inconel
	. . .	. . .	Inconel	. . .	Inconel	. . .	. . .
Cast	HT	[e]	HT	[e]	[e]	[e]	HT

(a) When more than one material is recommended for a specific part, each has proved satisfactory in service. Multiple choices are listed in order of increasing alloy content. Cost and expected service life usually increase as alloy content increases.

(b) Carbon steel has been used for most of the parts listed.

(c) Refers to a series of alloys generally of the 35Ni-15Cr type or modifications that contain from 30 to 40% Ni and 15 to 23% Cr and include RA-330, 35-19, Incoloy, and other proprietary alloys.

(d) For immersed-electrode furnaces. Pots for submerged-electrode furnaces are made of burned alumina firebrick.

(e) These types of parts are not usually cast.

Unless parts can be suspended in the salt bath by simple wiring or by placing them in a basket or similar container, some form of fixturing is required. Some typical workholding fixtures are shown in Fig. 9, together with methods of wiring small parts. The weights of specific parts may influence both the design of the fixture and the selection of material from which it is made.

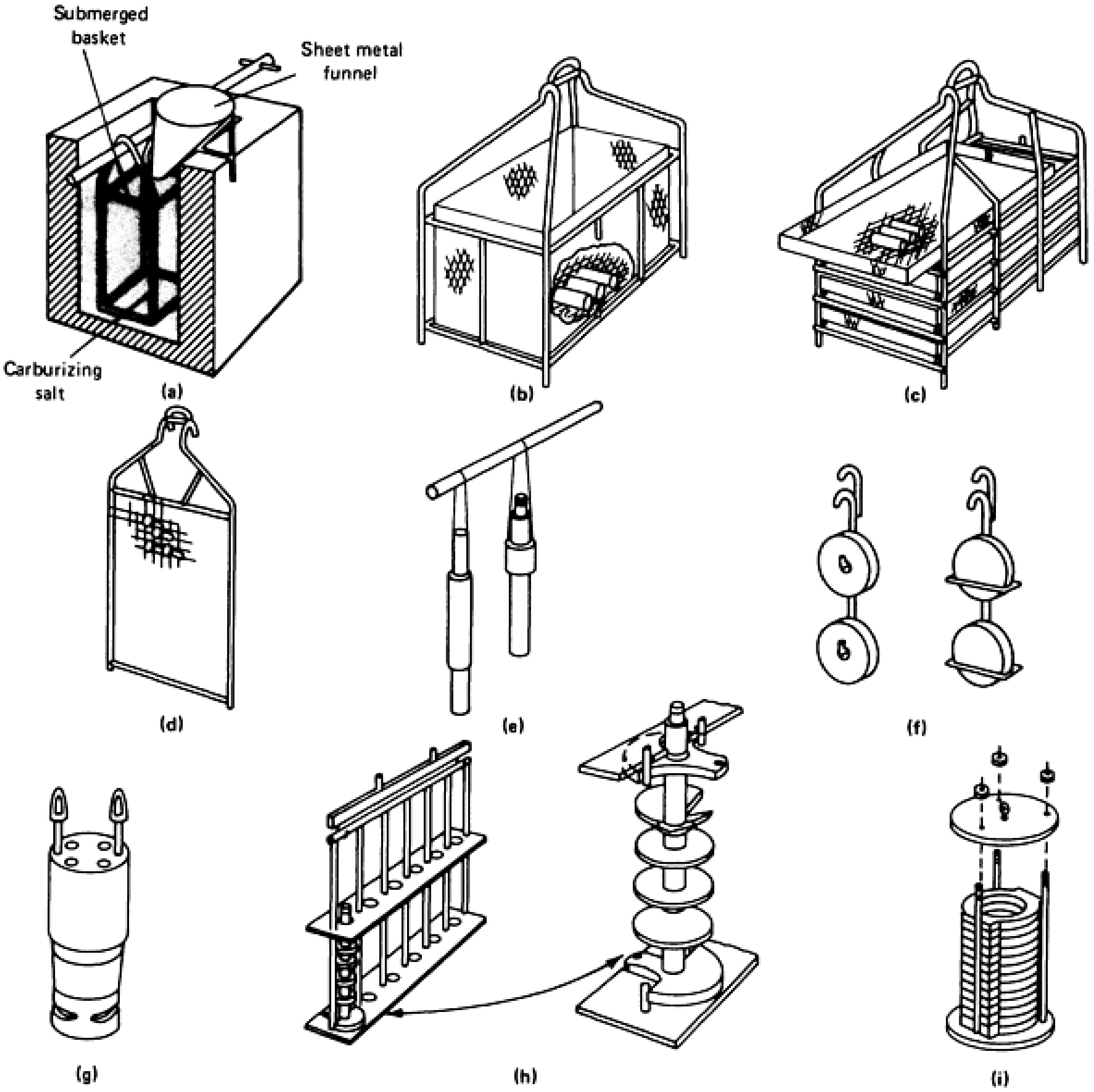


Fig. 9 Work-holding fixtures and wiring techniques used in liquid carburizing. (a) Typical holding basket for small parts, equipped with a funnel for loading parts into the basket without splashing. The funnel, which is made of sheet metal, also ensures that parts are coated with salt before they are nested together. Basket may be made of carbon or alloy steel rod and steel wire mesh. Work must be free from oil, or the parts will stick together. Parts must be dry. (b) Inconel basket of simple design. Upper loop of handle is for lifting; lower loop accommodates a rod that supports the basket over the furnace. (c) Simple basket with trays, intended for small parts. Trays provide maximum loading space without adversely affecting circulation. Entire fixture is made of Inconel. (d) Method of running flat parts. (e) Method of supporting small parts. Black annealed steel wire is used for parts weighing less than 4.5 kg (10 lb); annealed stainless steel wire is used for heavier parts. (f) Hooks, made of nickel alloy rod, for holding circular parts. (g) Method for holding large parts in which tapped handling holes are available or can be provided. Nickel alloys are used for such fixtures because of the need for high-temperature strength. Resistance to oxidation is not a factor, because liquid carburizing salts are reducing. (h) Rack for holding six small crankshafts; exploded view shows a crankshaft positioned in the rack. (i) Special rack for carburizing the outer surfaces of bearing races. Holding plates are made of mild steel; rods, of Inconel.

Holding fixtures and supports used in salt bath carburizing should be kept as simple as possible. Fixture weight should be minimized to conserve heat by lessening the load to be heated. Whenever possible, fixture components should be pinned or riveted rather than welded. This permits freedom of movement of the fixture during heating and quenching, thereby extending its life. Although weldments are not significantly affected by the carburizing bath, they are subject to the stresses imposed by cyclic heating and cooling and thus are susceptible to cracking. Finally, riveting and pinning permit easy replacement of those fixture components that can be replaced.

Additional information is available in the article "Heat-Resistant Materials for Furnace Parts, Trays, and Fixtures" in this Volume.

Automatic and Semiautomatic Lines

Figure 10(a) shows a fully automatic (jackrabbit) mechanism used for salt bath carburizing and hardening. The mechanism has synchronized, continuous-chain conveyors that carry the work through the various operations. Work suspended from horizontal bars is moved through baths at the proper speed by a main conveyor. Transfer conveyors carry the work from bath to bath. Completed work is picked up by a third conveyor and is dried by warm air in the enclosed upper portion of the structure while it is being returned to the loading point.

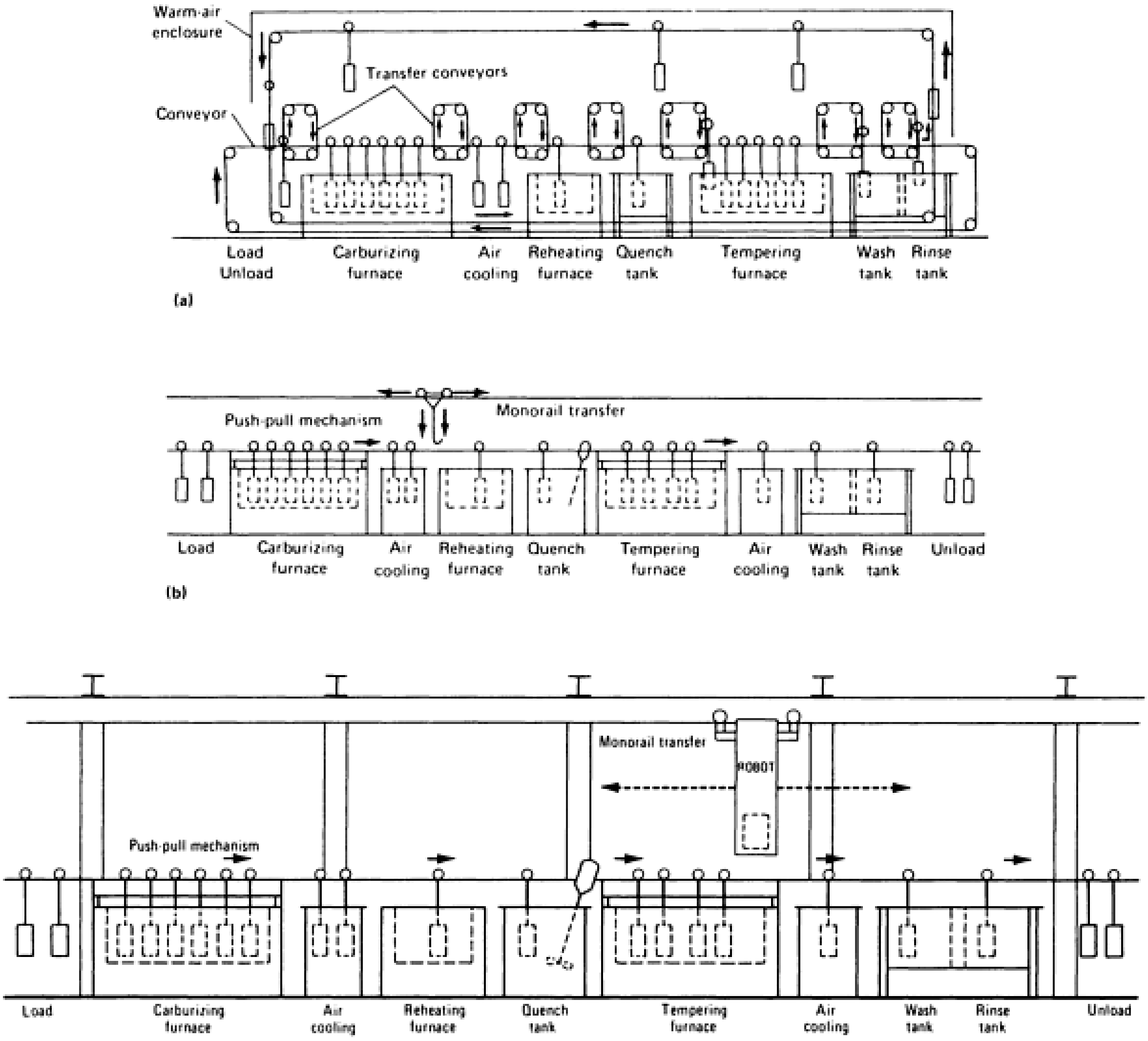


Fig. 10 Fully automatic and semiautomatic production lines for liquid carburizing and related operations (reheating, quenching, tempering, and washing). (a) Fully automatic carburizing line. (b) Semiautomatic carburizing line. (c) Fully automatic programmed-hoist carburizing line. See text for details.

The mechanism can be used only for work having similar requirements. It does not permit the time cycle of any one operation to be varied without affecting the cycles of the other synchronized operations.

Where part requirements vary, a semiautomatic mechanism, such as that shown in Fig. 10(b), may be used. Work is transferred between operations by an overhead monorail and is automatically advanced through the carburizing and tempering furnaces by means of a push-pull mechanism. This mechanism consists of two parallel beams with reciprocating push bars. Driven either hydraulically or electrically, the bars carry the dogs, which are spaced to advance the fixtures at the center of the furnace only a part of the stroke while advancing the end fixtures through the entire stroke. By closer spacing of the work at the center of the furnace and wider spacing at the ends, high productive capacity is achieved with ease of loading and unloading.

A semiautomatic line of this type permits the time cycle for any one operation to be varied without affecting other operations and is less likely to require modification if work requirements change. Figure 10(c) shows a fully automatic programmable-hoist carburizing line. One or more hoists travel simultaneously back and forth, automatically advancing the fixtures that carry the work through the required stations.

The hoist movement may be controlled by a solid-state programmable control, which provides functions that normally would require extensive wiring and hundreds of relays, counters, and switches. Once programmed, the controller will perform the functions specified by the user. Functions such as time cycles, sequences, and skips are entered easily or changed to meet metallurgical requirements. For example, some parts could be programmed to be carburized, air cooled, washed, rinsed, and returned for unloading. A pushbutton command would return the controller to the standard program.

Parts suitable for fully automatic or semiautomatic installations are those that can be fixtured by wiring, racking, or placing in baskets and that do not present problems of either buoyancy or drainage. Case-depth requirements ranging from 0.25 to 3.2 mm (0.010 to 0.125 in.) can be satisfied.

Process Control

Externally heated salt baths can be held within closer temperature limits (±8 °C, or ±14 °F) when a proportional control system employing electronic instrumentation is used. Control by means of valves (on-off or high-low control) requires mechanical instrumentation and is less accurate, although for a majority of applications it is entirely adequate.

Internally heated salt baths (immersed or submerged electrodes) may be regulated to ±5 °C (±9 °F) with either mechanical or electronic on-off controllers. In either type, the temperature-control instrument operates a relay that actuates a large circuit breaker that in turn connects or disconnects the 440-V power to the step-down transformer. Welded thermocouples may be used in installations that employ electrode heating. For safety, two thermocouples are recommended--one for temperature control and one for excess temperature cutoff.

Control of Bath Composition. Control of sodium cyanide content is the most important factor in maintaining the effectiveness of a liquid carburizing bath.

Analysis of a noncyanide liquid carburizing bath is achieved by a rapid performance test in which a 1008 steel wire 1.6 mm ($\frac{1}{16}$ in.) in diameter is immersed for 3 min in the bath, then is water quenched and mechanically bent through 90°. The bath is well activated if the wire breaks before reaching the full 90° bend. A more reliable test of activity can be made by running a 1012 silicon-killed test bar for 1 h, water quenching, and measuring Rockwell C hardness. Readings above 58 HRC indicate a well-activated bath.

Graphite Cover. A graphite cover must be maintained on the surface of a cyanide bath for reduced radiation loss and reduced cyanide loss at 870 to 955 °C (1600 to 1750 °F) and during idling. Either natural flake or artificial graphite powders may be used. The former provides a more fluid cover that has less tendency to cling to the work. However, because natural graphite has a higher ash content, it introduces more impurities into the bath, which can be a problem--particularly at low operating temperatures. Furthermore, to avoid corrosion of parts, natural graphite that contains sulfur should not be used.

A noncyanide liquid carburizing bath must also have a graphite cover. A higher rate of graphite consumption, compared with a cyanide bath, is characteristic. Frequent replenishment (commonly every hour) is necessary for maintenance of proper bath activity.

Daily maintenance routines for liquid carburizing furnaces, whether fuel-fired or electrode-heated, differ in only a few details. The following items, with exceptions as noted, comprise a typical daily maintenance schedule for all types of salt bath equipment:

- Check temperature-control system, using an auxiliary pyrometer and thermocouple. An indicating potentiometer with a long extension wire can be mounted near the furnaces and will provide accurate temperature checks faster than will a laboratory-type instrument
- Check color of exhaust smoke from the combustion chamber of fuel-fired furnaces. A bluish white or white smoke indicates salt leakage
- Remove sludge from bottom of pot while furnace is still at idling temperature, which normally is 705 to 730 °C (1300 to 1350 °F). The electrodes of internally heated furnaces should be scraped clean, and electric power should be shut off during the sludging and cleaning operation
- Add fresh salt to compensate for dragout losses. If required, make room for addition of fresh salt by bailing
- To help maintain bath composition and reduce surface heat losses, add graphite cover material to provide a thin but continuous cover
- Check bath activity by testing for cyanide content or by quenching and examining the fracture case depth
- If possible, rotate the pot of a fuel-fired furnace at least once a week to minimize the effects of flame impingement and thus extend pot life
- If a salt pot is leaking and the salt is still active, remove the salt and place it in sturdy steel containers. This salt may be broken up and re-used in starting another pot (however, it is not recommended that such salt be used thereafter for replenishment)
- Prior to replacement of a pot in a resistance-heated or fuel-fired furnace, the combustion chamber should be rebuilt if contaminated with salt to avoid rapid pot failure
- Consult operating and maintenance instructions provided by the furnace manufacturer and salt supplier

Shutdown and Restarting. For shutdowns of 2 days or longer, externally heated furnaces need not be idled; the heat may be shut off completely. During cooling and reheating, however, the pot should be covered to guard against violent expulsion of salt. The cover recommended by the manufacturer should be used.

It is generally advisable to idle electrode furnaces at 705 to 730 °C (1300 to 1350 °F), even over shutdown periods of one to two weeks. This simplifies restarting and eliminates possible damage to power transformers from condensation of moisture on the windings. For noncyanide carburizing furnaces with steel liners, idling above 845 °C (1550 °F) is recommended. During the idling period, the bath should be protected with a heavy carbon cover. The bath does not visibly fume at idling temperatures; therefore, ventilating air should be reduced. Excessive ventilating air should be avoided, because it will accelerate burn-off of the carbon cover. During the idling period, the transformer tap switch should be set at low voltage or idling tap. This will guard against possible overheating in the event that control-circuit difficulties arise while the equipment is unattended. An extra thermocouple and monitoring instrument equipped with warning alarms is recommended for use in such applications.

Control of Case Depth

The degree of uniformity of case depth obtained in normal production operations is indicated in Fig. 11 by data on 1020, 1117, and 8620 steels. Figures 11(a), 11(b), and 11(c) are based on information obtained with process-control specimens and show depth of case as a function of distance below the surface in terms of a hardness of 50 HRC or higher. These data indicate that variations in case depth can be held within narrow limits when controlled carburizing procedures are employed. At a carburizing temperature of 900 °C (1650 °F), the 1117 steel produced a deeper case to 50 HRC than did the 1020 and 8620 steels, which were carburized at 855 °C (1575 °F). Nevertheless, the total spread in case depth for any one of these steels did not exceed 0.13 mm (0.005 in.). Data presented in Fig. 11(d) indicate the range of hardnesses obtained at depths of 0.25 and 1.25 mm (0.010 and 0.050 in.) below the surface of liquid carburized 8620 steel. These data, based on 24 tests, indicate a slightly larger spread in hardness at 0.25 mm (0.010 in.) than at 1.25 mm (0.050 in.) below the surface.

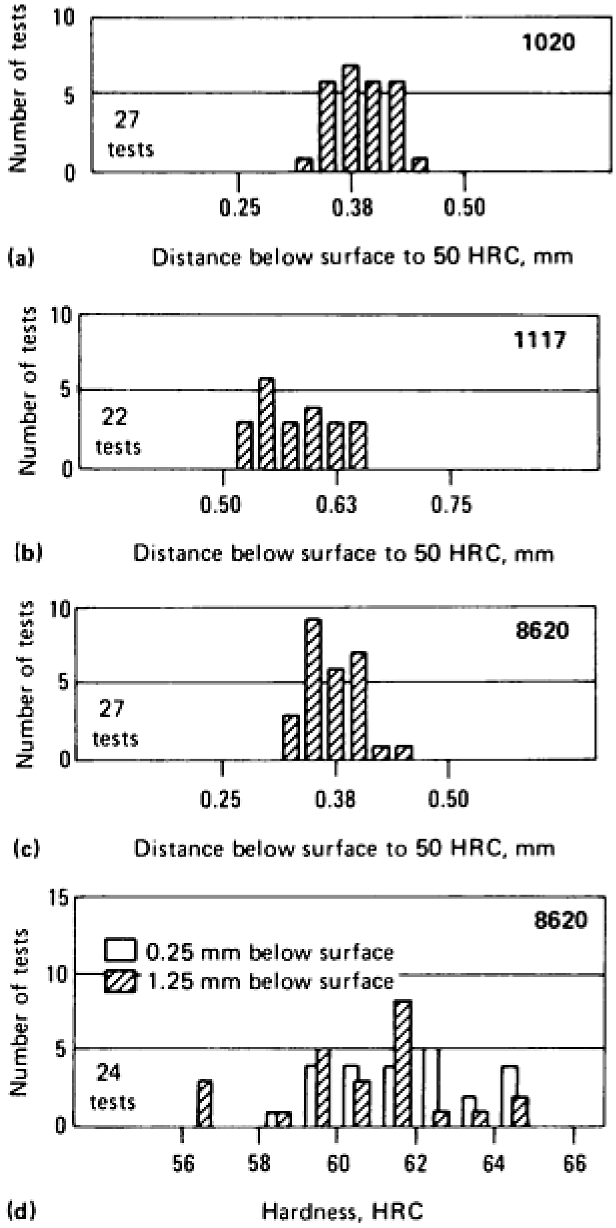
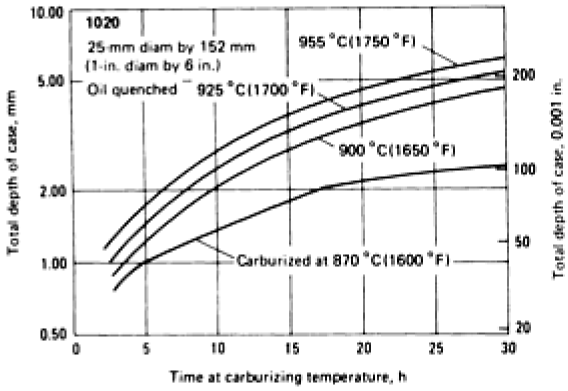
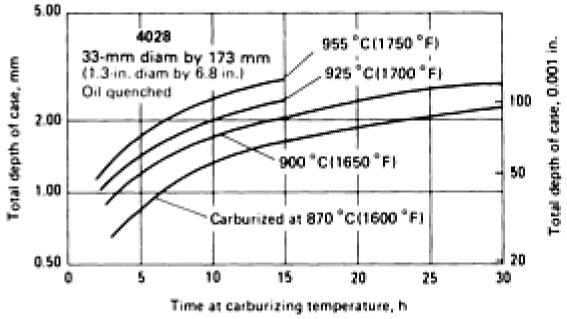


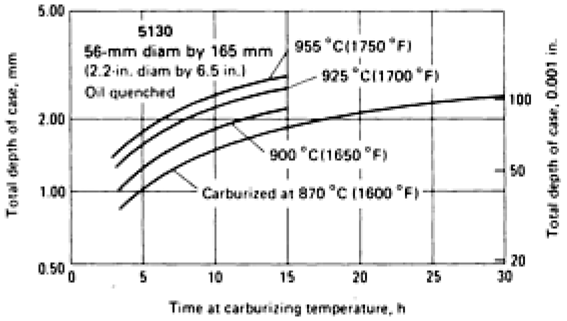
Fig. 11 Comparative case-depth and case-hardness data obtained for liquid carburizing process-control specimens made of three steels. (a) Data are for 11 mm (0.4375 in.) diam by 6.4 mm (0.25 in.) specimens carburized 2 h at 855 °C (1575 °F), brine quenched and tempered at 150 °C (300 °F). (b) Data are for 15.9 mm (0.625 in.) diam specimens carburized 2 h at 900 °C (1650 °F) and brine quenched. (c) Data are for 12.7 mm (0.50 in.) diam by 6.4 mm (0.25 in.) specimens carburized 2 h at 855 °C (1575 °F), oil quenched, and refrigerated to -85 °C (-120 °F). (d) Data are for 19 mm ($\frac{3}{4}$ in.) diam by 51 mm (2 in.) specimens carburized 2.5 h at 915 °C (1675 °F) and water quenched.

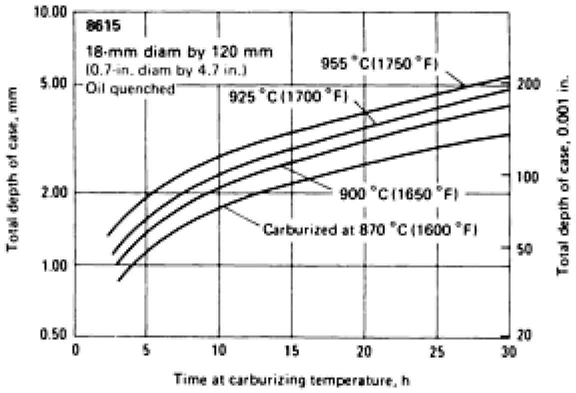
Whereas the information in Fig. 11 deals with carburizing cycles of 2 and 2.5 h at temperatures ranging from 855 to 915 °C (1575 to 1675 °F), the data presented in Fig. 3 pertain to a much longer carburizing time ($9\frac{1}{2}$ h) at 925 °C (1700 °F). The spread in case depth at 50 HRC is considerably wider than for the light-case work on which Fig. 11 is based.

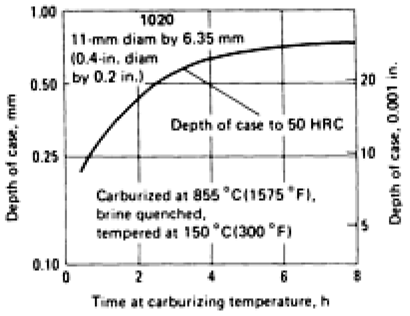
Additional data on case depth as a function of time and temperature are given for ten steels in Fig. 12. These data also reflect various criteria that have been applied to evaluate case depth--for example, data relating case depth to minimum hardness, carbon content, and pearlite content.

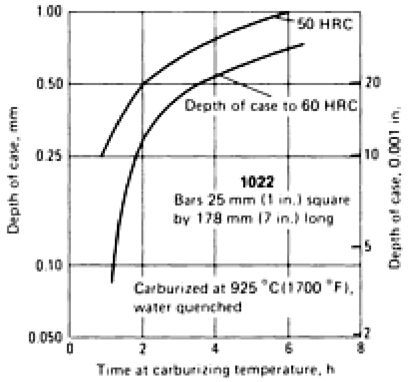

1020
25-mm diam by 152 mm
(1-in. diam by 6 in.)
Oil quenched
955 °C(1750 °F)
925 °C(1700 °F)
900 °C(1650 °F)
Carburized at 870 °C(1600 °F)
Total depth of case, mm
Total depth of case, 0.001 in.
Time at carburizing temperature, h

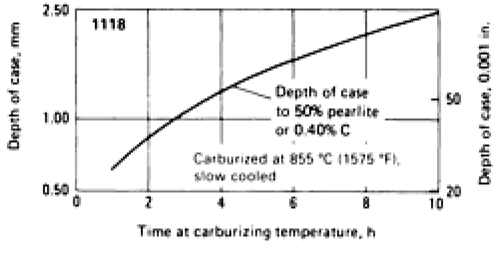

4028
33-mm diam by 173 mm
(1.3-in. diam by 6.8 in.)
Oil quenched
955 °C(1750 °F)
925 °C(1700 °F)
900 °C(1650 °F)
Carburized at 870 °C(1600 °F)
Total depth of case, mm
Total depth of case, 0.001 in.
Time at carburizing temperature, h


5130
56-mm diam by 165 mm
(2.2-in. diam by 6.5 in.)
Oil quenched
955 °C(1750 °F)
925 °C(1700 °F)
900 °C(1650 °F)
Carburized at 870 °C (1600 °F)
Total depth of case, mm
Total depth of case, 0.001 in.
Time at carburizing temperature, h


8615
18-mm diam by 120 mm
(0.7-in. diam by 4.7 in.)
Oil quenched
955 °C(1750 °F)
925 °C(1700 °F)
900 °C(1650 °F)
Carburized at 870 °C(1600 °F)
Total depth of case, mm
Total depth of case, 0.001 in.
Time at carburizing temperature, h


1020
11-mm diam by 6.35 mm
(0.4-in. diam
by 0.2 in.)
Depth of case to 50 HRC
Carburized at 855 °C(1575 °F),
brine quenched,
tempered at 150 °C(300 °F)
Depth of case, mm
Depth of case, 0.001 in.
Time at carburizing temperature, h


50 HRC
Depth of case to 60 HRC
1022
Bars 25 mm (1 in.) square
by 178 mm (7 in.) long
Carburized at 925 °C(1700 °F),
water quenched
Depth of case, mm
Depth of case, 0.001 in.
Time at carburizing temperature, h


1118
Depth of case
to 50% pearlite
or 0.40% C
Carburized at 855 °C (1575 °F),
slow cooled
Depth of case, mm
Depth of case, 0.001 in.
Time at carburizing temperature, h

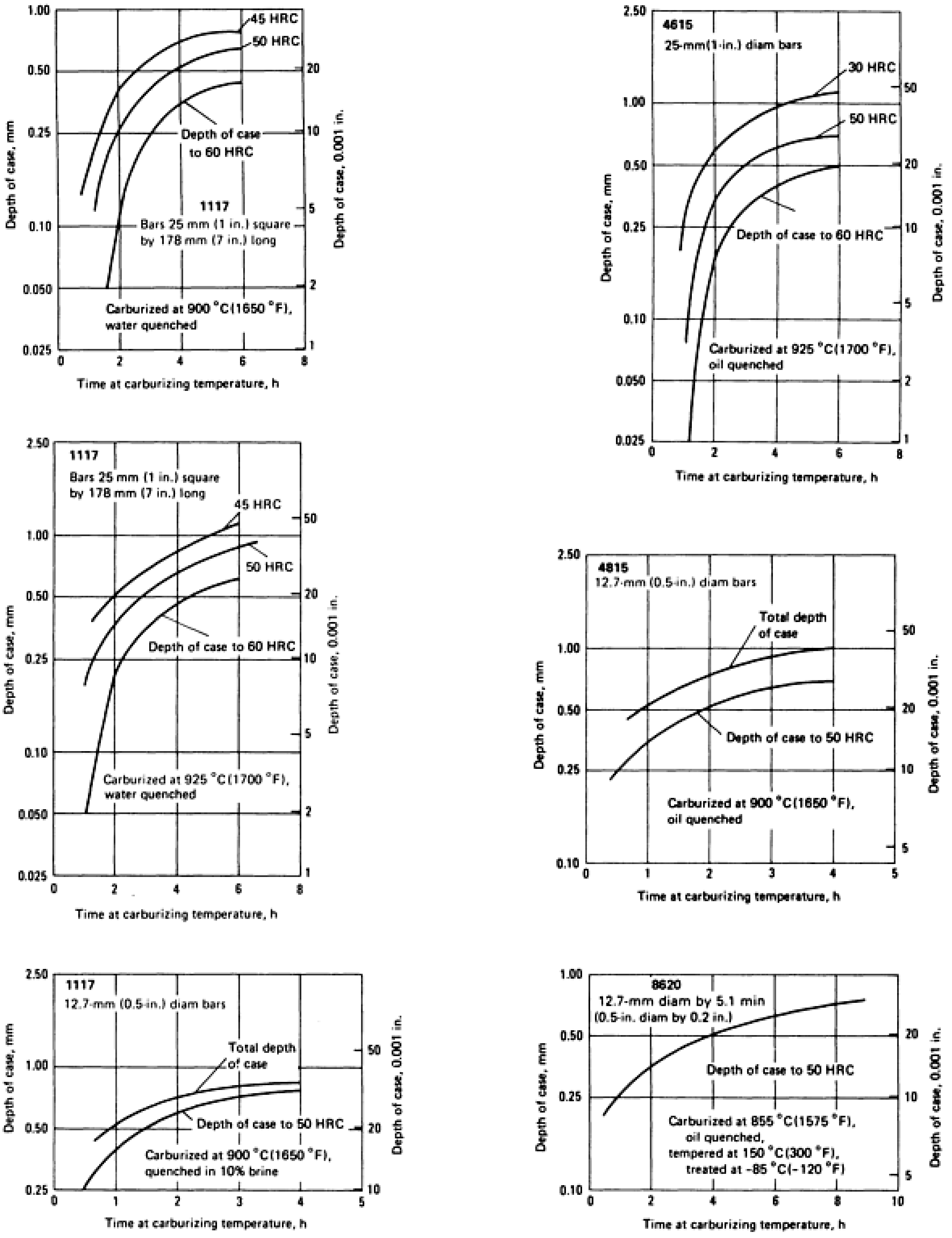


Fig. 12 Effect of time and temperature on case depth of liquid carburized steels

Dimensional Changes

All parts undergo dimensional changes as a result of carburizing and hardening. From a production standpoint, it is important to know the nature and amount of dimensional change, or distortion, that can be anticipated, and the corrective action that may be taken to hold dimensional changes to a minimum. The following examples relate dimensional change to several shapes that vary in complexity.

Example 1: Carburized, Quenched, and Tempered 8615H Steel Gear with 60 to 62 HRC Surface Hardness.

The small gear shown in Fig. 13(a) closed in along the bore from a minimum dimension of 17.22 mm (0.6780 in.) prior to heat treatment to a minimum of 17.14 mm (0.6750 in.) after heat treatment. In contrast, only slight contraction of the outer bearing surface occurred. The gears, made of 8615H steel, were carburized at 915 °C (1675 °F) to a depth of 0.51 to 0.64 mm (0.020 to 0.025 in.), reheated to 840 °C (1540 °F), quenched in oil at 55 °C (130 °F), and then tempered at 190 °C (375 °F) to a surface hardness of 60 to 62 HRC.

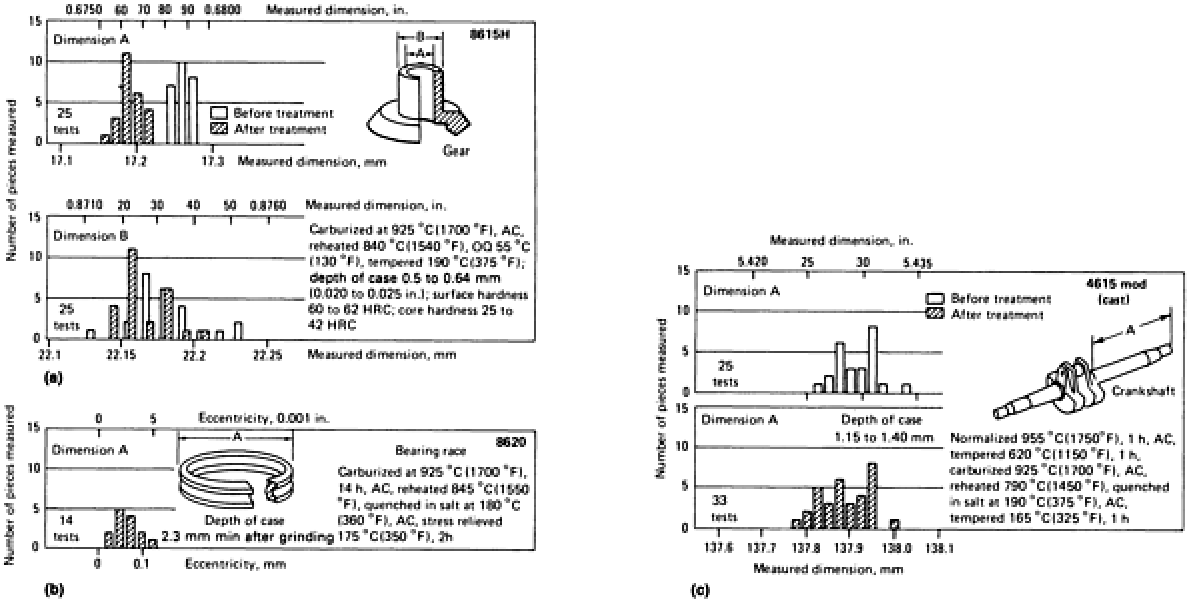


Fig. 13 Dimensional data relating selected low-alloy steel production parts before and after liquid carburizing and hardening. AC, air cooled; OQ, oil quenched

Example 2: Carburized, Quenched, and Stress Relieved 8620 Steel Gear with 61 to 63 HRC Surface Hardness.

The bearing race shown in Fig. 13(b) was subjected to more elaborate processing to minimize dimensional variations before and after carburizing. This 8620 steel forging was normalized and stress relieved prior to being carburized. After being rough ground, it was liquid carburized for 14 h at 925 °C (1700 °F) to produce a minimum case depth of 2.3 mm (0.090 in.). It was air cooled, reheated to 845 °C (1550 °F), and salt bath quenched at 180 °C (360 °F). After being cooled to room temperature, it was tempered for 2 h at 175 °C (350 °F). Final case hardness was 61 to 63 HRC; core hardness was 40 to 43 HRC.

To minimize distortion, which was excessive when these bearing races were wired, a fixture similar to that shown in Fig. 9(i) was used throughout the heat-treating cycle. As indicated by the dimensional data, the combination of fixturing and elaborate processing produced favorable results in terms of out-of-roundness and flatness. Dimensional discrepancy was held to 0.10 mm (0.004 in.) maximum, and in several instances, distortion was held to 0.025 mm (0.001 in.).

Example 3: Normalized, Tempered, Carburized, Quenched, and Retempered 4615 Modified Steel Crankshaft.

The crankshaft shown in Fig. 13(c), a shell-mold casting made of boron-modified 4615 steel, was initially normalized for 1 h at 955 °C (1750 °F) and then tempered for 1 h at 620 °C (1150 °F). After being machined, the part was liquid carburized at 925 °C (1700 °F) (case depth, 1.14 to 1.40 mm, or 0.045 to 0.055 in.), air cooled, reheated to 790 °C (1450 °F), quenched for 5 min in salt at 190 °C (375 °F), air cooled and tempered for 1 h at 165 °C (325 °F). The dimensional data, which apply to a length measurement at one end of the shaft only, indicate a high degree of dimensional stability with a slight tendency in the direction of shrinkage.

Quenching Media

Most conventional quenching media, including water, brine, caustic solution, oil, and molten salts, are suitable for quenching parts that have been liquid carburized. However, the suitability of each medium must be related to specific parts and depends primarily on the hardenability of the steel, surface and core hardness requirements, and the amount of allowable distortion.

Water and brine are the quenchants most commonly used for carbon steels. A water quench is usually maintained at 20 to 30 °C (70 to 90 °F) and agitated. Water helps to dissolve the film of carburizing salt and thus creates a localized brine that suppresses the vapor phase. With continuous use, salt concentration (chlorides, carbonates, and cyanides) increases, and fresh water must be added periodically to control the concentration of contaminants and maintain a desired temperature. Sodium chloride brine (5 to 10%) and caustic (3 to 5%) solutions are used to obtain more drastic quenching. The noncyanide liquid carburizing salt provides a brine-type quench when maintained around 10% concentration by water addition. The effectiveness of brine and caustic can be severely curtailed by an excessive accumulation of contaminants. When a caustic solution is used for quenching, care must be taken to ensure that racks, baskets, and fixtures are washed free from caustic and dried before being returned to the carburizing bath. Small amounts of caustic carried back to the bath will lower its cyanide content significantly.

A water-soluble polymer is sometimes used to modify the quenching rate of a water quench. However, such additives should be avoided in a quenchant used with a liquid carburizing line, unless frequent replacement or continuous salt removal by ultrafiltration can be employed. The polymers may be precipitated by salt carried into the quench, or salt buildup in the quench may render their effect variable. Either condition is undesirable.

Oil quenching is less drastic than water quenching and produces less distortion. It is often desirable to fortify the mineral oil with nonsaponifiable additives that increase its quenching effectiveness and lengthen its useful life. To minimize distortion, special oils are available that can be used at temperatures as high as 175 °C (350 °F). Normally, liquid carburized parts are quenched directly into agitated oil maintained with the range from 25 to 70 °C (80 to 160 °F).

Quenching oil should be kept free of moisture and should be agitated by propellers or impeller-type pumps. Compressed air should not be used for agitation. Because some salt will inevitably precipitate in the oil bath, periodic desludging is necessary. Screens should be placed in front of the lines leading to pumps to prevent entry of sludge.

Salt bath quenching in a nitrate-nitrite bath further minimizes distortion. Salt quench baths are compatible with cyanide as well as noncyanide liquid carburizing baths. *Caution: However, parts should never be transferred directly from a carburizing bath containing more than 5% cyanide to a nitrate-nitrite quench bath, because this will result in a violent reaction and may cause an explosion.* To avoid such reactions, immersion in a neutral salt bath (45 to 55% NaCl, 45 to 55% KCl) held at the desired temperature must precede quenching in a nitrate-nitrite bath. The neutral bath should be tested periodically for sodium cyanide content; it is general practice to limit cyanide content to a level of less than 5%. This level is never reached, as a rule, because of oxidation of the cyanide by oxygen in the air. The neutral stabilizing bath can be used alternatively for through hardening of carbon and alloy steels, provided that complete cyanide oxidation has not occurred.

Many liquid carburizing facilities case harden components at 925 to 955 °C (1700 to 1750 °F), and workpieces are then transferred directly to a neutral chloride salt at 845 °C (1550 °F) for stabilization and finally quenched directly into a marquenching oil at 175 to 260 °C (350 to 500 °F), depending on alloy and hardness requirements. Distortion of the workpieces is minimized when parts are air quenched after carburizing and then reheated prior to quenching.

All traces of nitrate should be removed from quenching fixtures before they are reimmersed in a carburizing bath. This can be accomplished by rinsing in hot water.

The buildup of high-temperature chlorides in a nitrate-nitrite bath impairs its quenching severity. It is desirable, therefore, to remove the chlorides as fast as they are being delivered. Various means of chloride removal are available, and the selection depends on furnace design. Where chloride is allowed to settle to the bottom of the quench area or an area provided for gravity separation, the chlorides can be collected in sludge pans; periodically, either the pans are removed or the bottoms of the pans are manually desludged. Some furnace designs employ continuous filtration of chlorides as the suspended crystals pass through filter baskets; the operator removes the baskets periodically to dump the collected chlorides and then returns the baskets to the furnace.

Maintenance of Quenching Baths. Although a limited amount of dissolved salt increases the efficiency of a water quench bath, amounts in excess of 10% retard the quenching rate. Controlled addition of fresh water to the bath, together with a continuous overflow, serves to keep salt concentration at an acceptably low level. It may be required that the overflow be chemically treated in a special reservoir prior to disposal in order to eliminate cyanide pollution (see the section "Disposal of Cyanide Wastes" in this article). For this reason, changing the water quench bath at scheduled intervals may be more convenient in small operations. For water tanks that are vigorously agitated, it is recommended that a false bottom--in the form of a perforated plate--be used to permit settling of heavier solids, which can be removed during periods of downtime.

Carryover of liquid carburizing salts into brine quench tanks actually helps maintain brine concentration. However, salt concentration should not exceed 10%. The same control of salt content applies to caustic tanks; concentration of caustic must be maintained by additions of sodium hydroxide to control the quench rate of the solution.

Some of the precautions that must be observed in the use of oil baths have already been discussed. It should be recognized that liquid carburizing salts do not dissolve in, or combine with, mineral quenching oils. Salt sludge must be removed periodically, either by mechanical means or by filtering through screens.

Proper maintenance of salt quench baths also requires sludging of contaminants. Use of separating chambers to collect these contaminants has already been discussed. Another technique involves continuous filtering out of higher-melting-point salts by pumping the contaminated quench salts through a filter maintained at a lower temperature. The contaminants are deposited on a wire-mesh basket, and the usable salts are returned to the quench tank.

Quenching Cyanided Parts. Cyanided steel parts are quenched in fast-quenching oils, water, or aqueous salt solutions. Selection of the quenchant depends on the composition of the steel, the required as-quenched hardness, and the shape of the workpiece.

Water or aqueous salt solutions should be as free as possible of dissolved gases, which may cause soft spots. For this reason, pumps or impellers should be used to agitate the quenching water or brine. Compressed air should not be used as the primary means of agitation; mechanical agitation is preferred.

For maximum hardness, the quenchant should be as cold as is feasible and should be well agitated. Typical quenchant temperatures range from room temperature to about 25 °C (75 °F) for plain water and up to about 50 °C (120 °F) for 5 to 10% aqueous salt solutions, including solutions of sodium chloride, sodium hydroxide, or proprietary salt mixtures that provide corrosion protection. Use of higher temperatures with water-based quenchants causes insufficient hardness or soft spots.

Quenching oils are commonly used at temperatures from 50 to 85 °C (120 to 185 °F). Only petroleum-base quenching oils should be used for quenching cyanided parts.

Salt Removal (Washing)

The ease or difficulty with which salt can be removed from liquid carburized parts depends primarily on how simply or intricately shaped the parts are and whether they were quenched in water or in oil. To some extent, removal of salt may be complicated by the presence of insoluble residues. Water-quenched parts of simple design and with no blind holes or deep recesses usually are easy to clean. They may be rinsed thoroughly in water at about 80 °C (180 °F) and then coated with a rust-preventive fluid or soluble oil. Parts that are rinsed free of cyanide by immersion in a chloride salt and then isothermally quenched in a nitrate-nitrite salt are easily cleaned by agitated hot-water washing and rinsing. It is also possible to reclaim the nitrate-nitrite salt from the wash water.

Oil-quenched parts are more difficult to clean because the oil must be removed before the salts can be dissolved. Some salts may be insoluble. Use of power washers with hot water or emulsion cleaners is effective. An economical cleaning procedure begins with soaking of parts in hot water to float off the oil and remove the soluble salts. The parts may then be transferred to a hot agitated dilute alkaline cleaner having high sequestering properties. (Silicated cleaners and those containing carbonates or phosphates are not recommended, because of the formation of insoluble barium compounds in the presence of barium-containing salts.) If a white, powdery overlay of barium carbonate remains on the parts, it may be removed--following removal of all cyanide--by immersion in a dilute solution of acetic or inhibited hydrochloric acid.

Complex parts with blind holes, recesses, and threads are difficult to clean, particularly if they have been oil quenched. Liquid carburizing of parts that contain blind holes for which the depth exceeds twice the diameter is not recommended unless such holes can be plugged. Agitated hot water or a steam jet is probably the best solvent for salt held in recesses, crevices, and blind holes. Normally, it will remove all soluble salts and will soften insoluble residues. When part shape and tolerances permit, tumbling for 10 to 30 min in a mild alkali and a small quantity of sand is most effective in removing insoluble surface residues.

Washing of Cyanided Parts. Cyanide-hardened parts are easy to wash, even after oil quenching, because cyanide and sodium carbonate are good detergents and because all the components of the salt bath are water soluble. The work may be soaked in a tank of agitated boiling water, rinsed in clean hot water, and then rustproofed (if required). Power spray washers, using hot water in a two-stage system, also give satisfactory results.

Typical Applications

The applicability of liquid carburizing is evidenced by the variety of parts listed in Tables 7 and 8, all of which were heat treated on a production basis. For ease of reference, the parts in Table 7 have been separated according to type of steel (carbon, resulfurized, or alloy), and the parts in each group have been arranged in alphabetical order. Tables 7 and 8 also provide details, wherever they were available, regarding case depth, carburizing temperature and cycle time, method of quenching, subsequent treatment, and surface hardness.

Table 7 Typical applications of liquid carburizing in cyanide baths

Part	Weight		Steel	Depth of case		Temperature		Time, h	Quench	Subsequent treatment	Hardness, HRC
	kg	lb		mm	in.	°C	°F				
Carbon steel											
Adapter	0.9	2	CR	1.0	0.040	940	1720	4	AC	(a)	62-63
Arbor, tapered	0.5	1.1	1020	1.5	0.060	940	1720	6.5	AC	(a)	62-63
Bushing	0.7	1.5	CR	1.5	0.060	940	1720	6.5	AC	(a)	62-63
Die block	3.5	7.7	1020	1.3	0.050	940	1720	5	AC	(a)	62-63
	1.1	2.5	CR	1.3	0.050	940	1720	5	AC	(a)	59-61
Disk	1.4	3	1020	1.3	0.050	940	1720	5	(b)	(b)	56-57
Flange	0.03	0.06	1020	0.4-0.5	0.015-0.020	845	1550	4	Oil	(c)	55 min(d)
Gage rings, knurled	0.09	0.2	1020	1.5	0.060	940	1720	6.5	AC	(a)	62-63
Hold-down block	0.9	2	CR	1.0	0.040	940	1720	4	AC	(a)	62-63

Insert, tapered	4.75	10.5	1020	1.3	0.050	940	1720	5	AC	[a]	62-63
Lever	0.05	0.12	1020	0.13-0.25	0.005-0.010	845	1550	1	Oil	[c]	[e]
Link	0.007	0.015	1018	0.13-0.25	0.005-0.010	845	1550	1	AC	. . .	. . .
Plate	0.007	0.015	1010	0.25-0.4	0.010-0.015	845	1550	2	Oil	[c]	[e]
Plug	0.7	1.6	CR	1.5	0.060	940	1720	6.5	AC	[a]	62-63
Plug gage	0.45	1	1020	1.5	0.060	940	1720	6.5	AC	[a]	62-63
Radius-cutout roll	7.7	17	CR	1.5	0.060	940	1720	6.5	AC	[a]	62-63
Torsion-bar cap	0.05	0.1	1022	0.02-0.05	0.001-0.002	900	1650	0.12	Caustic	[f]	45-47
Resulfurized steel											
Bushing	0.04	0.09	1118	0.25-0.4	0.010-0.015	845	1550	2	Oil	[c]	[e]
Dash sleeve	3.6	8	1117	1.1	0.045	915	1675	7	AC	[g]	58-63
Disk	0.0009	0.002	1118	0.13-0.25	0.005-0.010	845	1550	1	Brine	[c]	[e]
Drive shaft	3.6	8	1117	1.1	0.045	915	1675	7	AC	[h]	58-63
Guide bushing	0.2	0.5	1117	0.75	0.030	915	1675	5	[j]	. . .	58-63
Nut	0.04	0.09	1113	0.13-0.25	0.005-0.010	845	1550	1	Oil	[c]	[e]
Pin	0.003	0.007	1119	0.13-0.25	0.005-0.010	845	1550	1	Oil	[c]	[e]
Plug	0.007	0.015	1113	0.075-0.13	0.003-0.005	845	1550	0.5	Oil	[c]	[e]
Rack	0.34	0.75	1113	0.13-	0.005-	845	1550	1	Oil	[c]	[e]

				0.25	0.010						
Roller	0.01	0.03	1118	0.25-0.4	0.010-0.015	845	1550	2	Oil	[c]	[e]
Screw	0.003	0.007	1113	0.075-0.13	0.003-0.005	845	1550	0.5	Oil	[c]	[e]
Shaft	0.08	0.18	1118	0.25-0.4	0.010-0.015	845	1550	2	Oil	[c]	[e]
Spring seat	0.009	0.02	1118	0.25-0.4	0.010-0.015	845	1550	2	Oil	[c]	[e]
Stop collar	0.9	2	1117	1.1	0.045	925	1700	6.5	AC	[g]	60-63
Stud	0.007	0.015	1118	0.13-0.25	0.005-0.010	845	1550	1	Oil	[c]	[e]
Valve bushing	0.02	0.05	1117	1.3	0.050	915	1675	8	AC	[g]	58-63
Valve retainer	0.45	1	1117	1.1	0.045	915	1675	7	[j]	. . .	58-63
Washer	0.007	0.015	1118	0.25-0.4	0.010-0.015	845	1550	2	Oil	[c]	[e]
Alloy steel											
Bearing races	0.9-36	2-80	8620	2.3	0.090	925	1700	14	AC	[g]	61-64
Bearing rollers	0.20	0.5	8620	2.3	0.090	925	1700	14	AC	[g]	61-64
Coupling	0.03	0.06	8620	0.25-0.4	0.010-0.015	845	1550	2	Oil	[c]	[e]
Crankshaft	0.9	2	8620	1.0	0.040	915	1675	6.5	AC	[h]	60-63
Gear	0.34	0.75	8620	1.0	0.040	915	1675	6	AC	[g]	60-63
	0.03	0.06	8620	0.075-0.13	0.003-0.005	845	1550	0.5	Oil	[c]	[e]
Idler shaft	0.45	1	8620	0.75	0.030	915	1675	5	[i]	. . .	58-63

Pintle	4.5-86	10-190	8620	1.5	0.060	925	1700	12	[i]	. . .	58-63
Piston	0.20	0.5	8620	1.3	0.050	915	1675	8	AC	[g]	60-63
Plunger	0.45-82	1-180	8620	1.3	0.050	915	1675	8	[i]	. . .	58-63
Ram	2.3-23	5-50	8620	1.1	0.045	915	1675	7	[i]	. . .	58-63
Retainer	0.0009	0.002	9317	0.1-0.2	0.004-0.008	845	1550	0.33	Oil	[j]	[e]
Spool	0.45-54	1-120	8620	1.3	0.050	925	1700	7	[i]	. . .	58-63
Thrust cup	0.20	0.5	8620	1.1	0.045	915	1675	7	[i]	. . .	58-63
Thrust plate	5.4	12	8620	2.3	0.090	925	1700	14	AC	[g]	60-64
Universal socket	1.8	4	8620	1.5	0.060	915	1675	10	AC	[g]	58-63
Valve	0.01	0.03	8620	0.4-0.5	0.015-0.020	845	1550	4	Oil	[j]	60 min[d]
Valve seat	0.20	0.5	8620	1.1	0.045	915	1675	7	AC	[g]	60-63
Wear plate	0.45-3.6	1-8	8620	1.3	0.050	915	1675	7	AC	[g]	60-63

(a) Reheated at 790 °C (1450 °F), quenched in caustic, tempered at 150 °C (300 °F).

(b) Transferred to neutral salt at 790 °C (1450 °F), quenched in caustic, tempered at 175 °C (350 °F).

(c) Tempered at 165 °C (325 °F).

(d) Or equivalent.

(e) File-hard.

(f) Tempered at 205 °C (400 °F).

(g) Reheated at 845 °C (1550 °F), quenched in salt at 175 °C (350 °F).

(h) Reheated at 775 °C (1425 °F), quenched in salt at 195 °C (380 °F).

(i) Quenched directly in salt at 175 °C (350 °F).

(j) Tempered at 165 °C (325 °F) and treated at -85 °C (-120 °F)

Table 8 Typical applications of liquid carburizing in noncyanide baths

Part	Weight		Steel	Case depth		Temperature		Time, h	Quench	Subsequent treatment	Hardness, HRC
	kg	lb		mm	in.	°C	°F				
Production tools	0.5-2.0	1.1-4.4	1018	0.375	0.015	925	1700	0.5-1.0	Brine	. . .	50-60
Bicycle forks	1.4	3.1	1017[(a)]	0.05-0.08	0.002-0.003	925	1700	0.085	Brine	Temper at 425 °C (795 °F)	60
Shift lever and ball	~1.5	~3.3	1040, 1017[(b)]	0.25	0.010	925	1700	0.67	Air cool 30 s in brine	. . .	File hard
Screw machine spindles	0.8	1.8	4620, 8620	0.89	0.035	[(c)]	[(c)]	6.0	Molten salt, 205 °C (400 °F)	. . .	60-63
Clock screws and studs	0.005	0.011	1006, 1113	008-0.10	0.003-0.004	955	1750	0.2	Brine	. . .	62-64
Flat head screws	0.015	0.033	1122	0.15	0.006	925	1700	0.33	Molten salt, 290 °C (550	. . .	56

(a) Partial immersion.

(b) Carburizer brass braze.

(c) Preheat at 840 °C (1545 °F); carburize at 920 °C (1690 °F)

The parts listed in Table 7 were carburized in cyanide-type baths. Noncyanide carburizing baths can be used with slight adjustments in operating conditions to do much of the carburizing described in Table 8. Noncyanide carburizing is particularly applicable to parts treated at temperatures above 900 °C (1650 °F). Some specific applications for noncyanide liquid carburizing of production parts are listed in Table 8.

In general, liquid carburizing is best suited to small and medium-size parts. Very large parts, such as rock-bit drill rods 6 m (20 ft) long and rings 2 m (7 ft) in diameter, are too large to be conveniently processed in salt and are commonly carburized by pack methods. Because of the problems associated with salt removal, carburizing in salt baths is not recommended for parts containing small holes, threads, or recessed areas that are difficult to clean.

Stop-Offs and Selective Carburizing

Selective carburizing can be accomplished in liquid carburizing baths by stopping off carbon penetration with either copper plate or copper-base paint. Because cyanide-base salts can dissolve copper, salt baths with relatively low cyanide contents are necessary. One successful formulation operates at 8 to 10% NaCN with approximately 45% $BaCl_2$ energizer. Noncyanide carburizing salts will not dissolve copper.

When copper plate is employed to prevent carbon penetration, the copper layer should be fine-grained, dense, and without pinholes or other porosity. Smooth surfaces require lower plating thicknesses than do rough surfaces. Copper-plate thicknesses recommended for protection against liquid carburizing for various times are as follows:

Time, h	Copper plate thickness	
	mm	in.
Low-temperature salts		
<1	0.013	0.0005
1-5	0.020	0.0008
High-temperature salts		
<7	0.025	0.0010
7-15	0.040	0.0015

Partial Immersion. Another method for selective carburizing in liquid carburizing baths entails partial immersion of the workpiece in the salt bath so that only the immersed areas are carburized. With this method, unless a clean-cut breakoff between carburized and noncarburized areas is required, the use of copper plate or copper-base paint is unnecessary.

Oxidation of the work at the bath surface can be reduced if the parts are initially immersed an inch or two deeper than required, to coat them with salt, and are then withdrawn to the required depth. A piece of plain carbon steel pipe with the bottom closed by welding can be inserted in a corner of the bath to displace salt if a precise adjustment of the bath level is necessary. Typical parts that are well suited to carburizing by the partial-immersion technique are shown in Fig. 14.

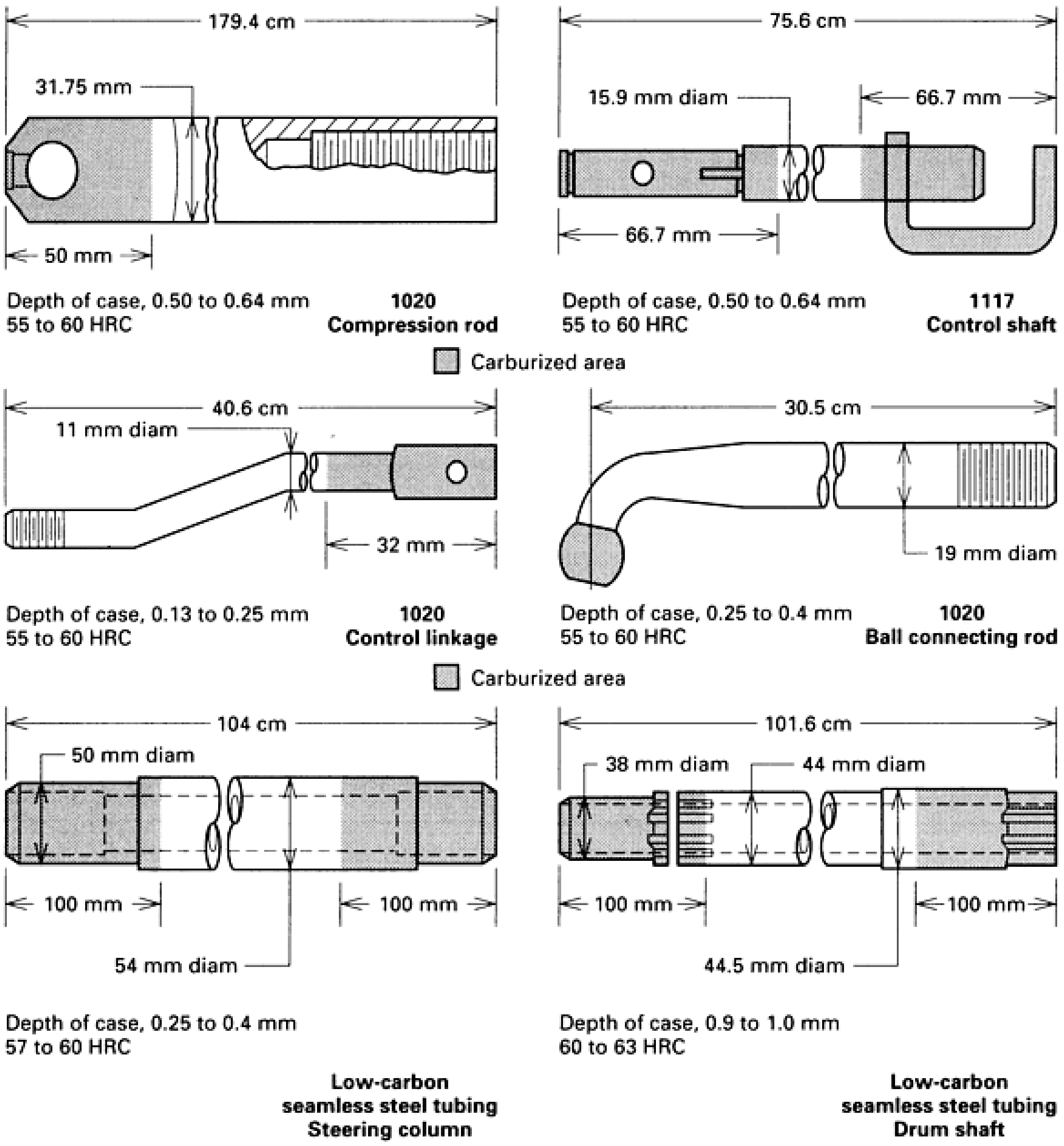


Fig. 14 Typical parts selectively carburized by partial immersion. Only the portion that is to be carburized is immersed in the bath. Area to be carburized is shaded.

Combined Carburizing and Brazing

It is possible to braze and carburize steel parts simultaneously in either a cyanide or a noncyanide liquid carburizing bath, provided that the operating temperature of the bath is high enough to cause the brazing alloy to flow. Initially, the parts are cleaned and degreased and then the components are assembled with brazing alloy enclosed in the joints. One suitable brazing alloy, in the form of wire or thin strip, contains 55% Cu and 45% Zn, melts at 880 °C (1620 °F), and makes a sound joint at 900 to 925 °C (1650 to 1700 °F). No flux is required.

The assembly is immersed in the liquid carburizing bath for a time long enough to produce the desired case depth and at a temperature high enough to cause the brazing alloy to flow. It is then quenched to harden the steel and complete the braze. Press-fit assemblies with carefully designed lap joints are ideal for this application.

Precautions in the Use of Cyanide Salts

Cyanides cause violently poisonous reactions if allowed to come into contact with scratches or wounds (on the hands, for example); they are fatal if taken internally. Also, fatally poisonous fumes are evolved when cyanides are brought into contact with acids. The white deposits that form on hoods and cooler furnace parts consist mainly of sublimed sodium carbonate, with small amounts of sodium, potassium, and barium salts, but may contain some cyanide as the result of splashing.

When cyanide salts are removed from the storage container, the container should be opened in the room in which the cyanide is to be used. The salts should be removed from the container with a metal scoop or gloved hands, or by being dumped out as required. When not in use, the container should be covered with its original cover or with a metal substitute cover.

The precautions that should be observed in handling cyanide-type carburizing salts are the same as for any other cyanide mixture. Work material must be clean and dry, and the bath must be enclosed and well ventilated. Even the slight amount of moisture that may be deposited on parts and fixtures as a result of atmospheric humidity will cause spatter in contact with molten salt. Accordingly, operators should be equipped with long protective gloves, protective aprons, and safety glasses or face shields. When adequate precautions are observed, carburizing salts should not present serious hazards to health or safety.

Remelting a frozen cyanide bath in externally heated furnaces can be potentially hazardous because of the expansion of the salt and gases as the salts are heated. This hazard is not encountered with immersed-electrode furnaces because the salts melt from the top down. If remelting is done in externally heated furnaces, however, the following precaution should be observed: a steel or cast iron wedge should be inserted in the center of the bath before the bath freezes. One end of the wedge should make contact with the bottom of the pot; the other end should extend at least 10 cm (4 in.) above the surface of the bath. Before the bath is remelted, the wedge should be tapped with a hammer, loosened and removed. The space previously occupied by the wedge will provide a vent for expanding salt and gases during remelting. No attempt should be made to remove a wedge from a bath that is not completely solidified, because molten salt may be forcibly blown out through the opening created.

Disposal of Cyanide Wastes

Cyanide wastes, whether dissolved in quench water or in the form of solid salt from pots, pose a serious disposal problem. The cyanide contents of these wastes must be chemically altered to render the material nonpoisonous before it is discharged into sewers or streams. Because of the toxicity of cyanide wastes, local ordinances and pollution authorities should be consulted regarding the proper disposal of wastes.

Chemical Treatment. The simplest treatment consists of oxidizing the cyanide in an alkaline solution to which is added either chlorine gas or its equivalent in the form of a hypochlorite compound, such as sodium or calcium hypochlorite (bleaching powder). The choice between gas or powder depends on the quantity of cyanide to be treated, on the availability of facilities and experienced personnel for handling the oxidizing agents, and on economics. For small quantities of cyanide solutions, it may be more practical to use a hypochlorite compound than to use chlorine gas.

Depending on the oxidizing agent employed, several reactions take place when cyanide is converted into a disposable form. One reaction with chlorine gas is as follows:

$$2NaCN + 4NaOH + 2Cl_2 + 2H_2O \rightarrow (NH_4)_2CO_3 + Na_2CO_3 + 4NaCl \quad \textbf{(Eq 18)}$$

This reaction indicates that, for each kilogram (2.2 lb) of sodium cyanide, 1.42 kg (3.13 lb) of chlorine gas and 1.6 kg (3.5 lb) of sodium hydroxide are required. Because of probable side reactions, however, practical experience indicates an actual requirement of slightly more than 2 kg (4.4 lb) of chlorine for each kilogram of sodium cyanide present in the waste solution. When a hypochlorite compound is used, the amount of powder required may be estimated on the basis of available chlorine content in the compound.

Solid cyanide wastes must be dissolved in water before they can be treated. A tank of suitable capacity, equipped with a coarse screen set well above the bottom, will facilitate solution of the solid material. The tank should also have an agitator, and, for chlorine gas, a perforated pipe placed well below the solution level is required.

When cyanide wastes are to be treated with chlorine gas, the cyanide content must first be determined and the proper amount of caustic added. The gas is then introduced slowly while the temperature of the solution is kept below 50 °C (120 °F). If a sodium hypochlorite solution is used, sufficient caustic should be added to raise the pH of the cyanide solution above 8.5. The reaction between cyanide and the oxidizing agent should continue until a slight excess of chlorine is present in the solution. This can be determined by testing with starch iodide paper or with a solution of potassium iodide and starch. Both the iodide paper and starch solution will turn blue in the presence of free chlorine.

Electrochemical Treatment. Although chemical treatment may be entirely adequate to meet local regulations, a recently developed electrochemical process destroys free cyanide with efficiency and economy superior to those of the chemical conversion processes. In the electrochemical process, cyanide wastes in aqueous solution are circulated through an electrochemical reactor. Within the reactor, an applied direct current potential oxidizes the free cyanide and cyanate according to the reactions:

$$2CN^- + 8OH^- \rightarrow 2CO_2 + N_2 + 4H_2O + 10e^- \quad \textbf{(Eq 19)}$$

$$2CNO^- + 4OH^- \rightarrow 2CO_2 + N_2 + 2H_2O + 6e^- \quad \textbf{(Eq 20)}$$

Free cyanide and cyanate are converted to the nontoxic gases carbon dioxide and nitrogen, which are allowed to escape freely from the vented storage tank into which the reacted solution is circulated.

The electrochemical process is most effective at high cyanide-ion concentrations. With continual recirculation between storage tank and reactor, cyanide can be reduced to 1 ppm or less in about 100 to 150 h. By combining electrochemical and chemical treatments, effective treatment can usually be achieved at minimum cost. Electrochemical removal is used to reduce cyanide concentration to ≈200 to 500 ppm, and then chemical treatment is used to complete the reduction.

Electrochemical treatment offers the following advantages:

- The process uses only electricity--no chemicals are required
- Cost per unit weight of cyanide treated is low, depending only on the cost of electricity (about 6.6 kW · h/kg, or 3 kW · h/lb of free CN^-)
- Capital investment is higher than alkaline chlorination
- The process is simple to control, requiring only periodic determination of cyanide concentration
- There are no toxic or otherwise harmful reaction products
- Upon reaching a concentration of 1 ppm cyanide, the oxidized effluent usually may be drained and further diluted by plant effluent
- The process can also be used to convert nitrite into nitrate

The only significant disadvantage is that the process is time-consuming when levels of cyanide below 200 ppm must be achieved. Increasing the number of reactors decreases process times.

Safety and Disposal of Noncyanide Carburizing Salts

Noncyanide carburizing salts are safe to dispose of directly in municipal or natural water if first diluted to acceptable dissolved-solids levels. There are no significant chemical hazards in the use of these salts. They are somewhat alkaline and should be washed from the skin or eyes if contact is made. When they are used as molten salts, the usual precautions apply: avoid introduction of moisture into the bath and prevent the hot salt from contacting the body.

Further information is available from Occupational Safety and Health Administration (OSHA) and Environmental Protection Agency (EPA) publications.

Vacuum Carburizing of Steels

Jeremy St. Pierre, C.I. Hayes, Inc.

Introduction

VACUUM CARBURIZING is a non-equilibrium, boost-diffusion-type carburizing process in which the steel being processed is austenitized in a rough vacuum, carburized in a partial pressure of hydrocarbon gas, diffused in a rough vacuum, and then quenched in either oil or gas. Compared to conventional atmosphere carburizing (see the articles "Gas Carburizing" and "Pack Carburizing" in this Volume), vacuum carburizing offers excellent uniformity and repeatability because of the high degree of process control possible with vacuum furnaces, improved mechanical properties due to the lack of intergranular oxidation, and potentially reduced cycle times particularly when the higher process temperatures possible with vacuum furnaces are used.

Process Overview

Vacuum carburizing a steel is typically a four-step process:

- Heat and soak step at carburizing temperature to ensure temperature uniformity throughout steel
- Boost step to increase carbon content of austenite
- Diffusion step to provide gradual case/core transition
- Oil-quenching step. In addition, a reheat step prior to quenching may also be necessary for grain refinement

Heat and Soak Step. The first step is to heat the steel being carburized to the desired carburizing temperature, typically in the range of 845 to 1040 °C (1550 to 1900 °F), and to soak at the carburizing temperature only long enough to ensure that the steel is uniformly at temperature. Oversoaking, particularly above 925 °C (1700 °F), can result in a reduction in toughness due to grain growth.

During the first step, surface oxidation must be prevented, and any surface oxides present must be reduced. In a graphite-lined heating chamber consisting of graphite heating elements, a rough vacuum in the range of 13 to 40 Pa (0.1 to 0.3 torr) is usually satisfactory. In a ceramic-lined heating chamber with silicon carbide heating elements, a partial pressure of approximately 40 to 67 Pa (0.3 to 0.5 torr) of hydrogen is effective. Steels with a high chromium content (M-50 NiL, X-2 Modified), a high silicon content (Pyrowear Alloy 53), or other high-oxygen affinity alloying elements usually require a higher vacuum level prior to carburizing but do not normally require preoxidizing.

Boost Step. Second is the boost step of the process. This step results in carbon absorption by the austenite to the limit of carbon solubility in austenite at the process temperature for the steel being carburized. The boost step is achieved by backfilling the vacuum chamber to a partial pressure with either a pure hydrocarbon gas (for example, methane, propane) or a mixture of hydrocarbon gases. Ammonia can be added if nitrogen alloying of the case is desired. An inert gas such as nitrogen can also be added to the gas or gas mixture.

Carbon transfer occurs by dissociation of the hydrocarbon gas on the surface of the steel with direct absorption of the carbon by the austenite and hydrogen gas being liberated. The reactions with methane and propane are:

$$CH_4 + Fe = Fe(C) + 2H_2 \quad \textbf{(Eq 1)}$$

$$C_3H_8 + 3Fe = 3Fe(C) + 4H_2 \quad \textbf{(Eq 2)}$$

At typical carburizing temperatures these reactions proceed rapidly from left to right of the given equations. Because these reactions are difficult to measure *in situ,* they cannot be used to control carbon potential when vacuum carburizing. Because there is no oxygen present, the oxygen-based methods of carbon-potential control used in conventional atmosphere carburizing cannot be used either (see the article "Control of Surface Carbon Content in Heat Treating of

Steel" in this Volume). However, at least one furnace manufacturer has reportedly designed a system for vacuum carburizing that measures and controls the carbon potential of the carburizing gas.

A minimum partial pressure of hydrocarbon gas is required to ensure rapid carburizing of the austenite. The minimum partial pressure required varies with the carburizing temperature, the carburizing gas composition, and the furnace construction. Above the minimum partial pressure, the partial pressure of carburizing gas used has no relationship to the carburizing potential of the atmosphere. Typical partial pressures vary between 1.3 and 6.6 kPa (10 and 50 torr) in furnaces of graphite construction and 13 kPa and 25 kPa (100 and 200 torr) in furnaces of ceramic construction. Partial pressures in excess of 40 kPa (300 torr) are not normally recommended because of the excessive carbon deposition within the furnace that accompanies higher partial pressures.

Diffusion Step. Third in the process is the diffusion step. If a steel were hardened with the carbon gradient resulting from the boost step only, particularly if no means of carbon-potential control were employed during the boost step, an undesirable microstructure adjacent to the carburized surface and an extremely abrupt case/core interface would result. The diffusion step enables the diffusion of carbon inward from the carburized surface, resulting in a lower surface carbon content (relative to the limit of carbon solubility in austenite at the carburizing temperature) and a more gradual case/core transition. The diffusion step is usually performed in a rough vacuum of 67 to 135 Pa (0.5 to 1.0 torr) at the same temperature used for carburizing. If carbon-potential control was used during the boost step, the diffusion segment might be shortened or eliminated.

Oil-Quenching Step. The fourth step of the process is quenching. If a reheat step is not going to be employed, and/or no further machining is required, the steel is directly quenched in oil, usually under a partial pressure of nitrogen.

When vacuum carburizing is performed at a higher temperature than is normally used with conventional atmosphere carburizing, cooling to a lower temperature and stabilizing at that temperature prior to quenching is usually required. Alternatively, if a reheat step is going to be employed for grain refinement, and/or further machining is required, the steel is gas quenched from the diffusion temperature to room temperature, usually under a partial pressure of nitrogen.

Reheating usually consists of austenitizing in the 790 to 845 °C (1450 to 1550 °F) range followed by oil quenching. When air-craft-quality gearing or bearings are being processed, reheating is usually preceded by a subcritical anneal. In some cases it is possible to gas pressure quench following carburizing, but this requires a high-performance gas pressure-quench system, light loads, thin sections, and moderate to high alloying. Interest in gas pressure quenching of carburized gearing is increasing, particularly with distortion-prone geometries. A diagram of temperature and pressure versus time for a typical vacuum-carburizing cycle with a reheat cycle is shown in Fig. 1.

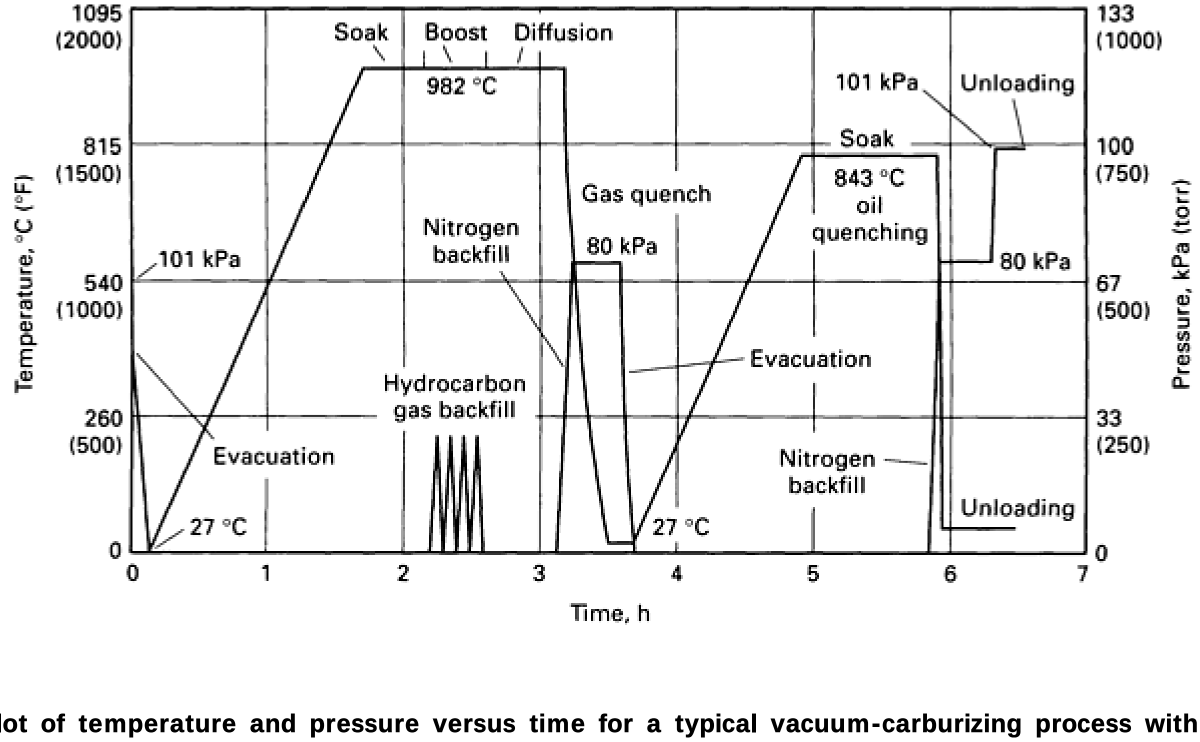


Fig. 1 Plot of temperature and pressure versus time for a typical vacuum-carburizing process with a reheat

cycle

Furnace Design. Vacuum carburizing is usually performed in a furnace specifically designed for this application, with or without oil and/or gas-quenching capability and modified with the controls and plumbing required for vacuum carburizing. The furnace can be of either graphite construction (graphite insulation and heating elements) or ceramic construction (refractory board insulation and silicon carbide heating elements). Graphite construction permits higher operating temperatures useful for a multipurpose furnace, whereas ceramic construction is well suited for vacuum carburizing because it can be safely operated in air at process temperatures for die quenching or for facilitating soot removal. Figure 2 shows a typical continuous ceramic construction vacuum-carburizing furnace. Figure 3 shows a typical batch graphite construction vacuum furnace with carburizing capability.

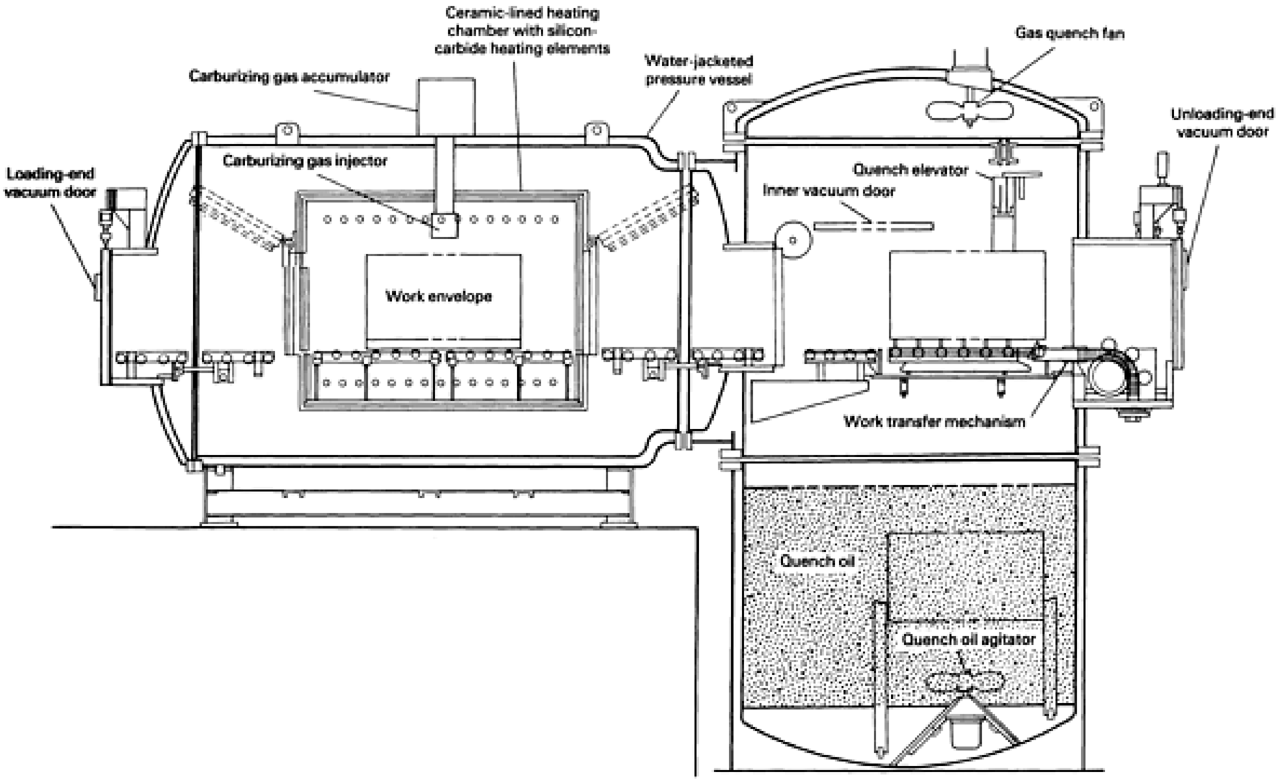


Fig. 2 A continuous ceramic vacuum-carburizing furnace

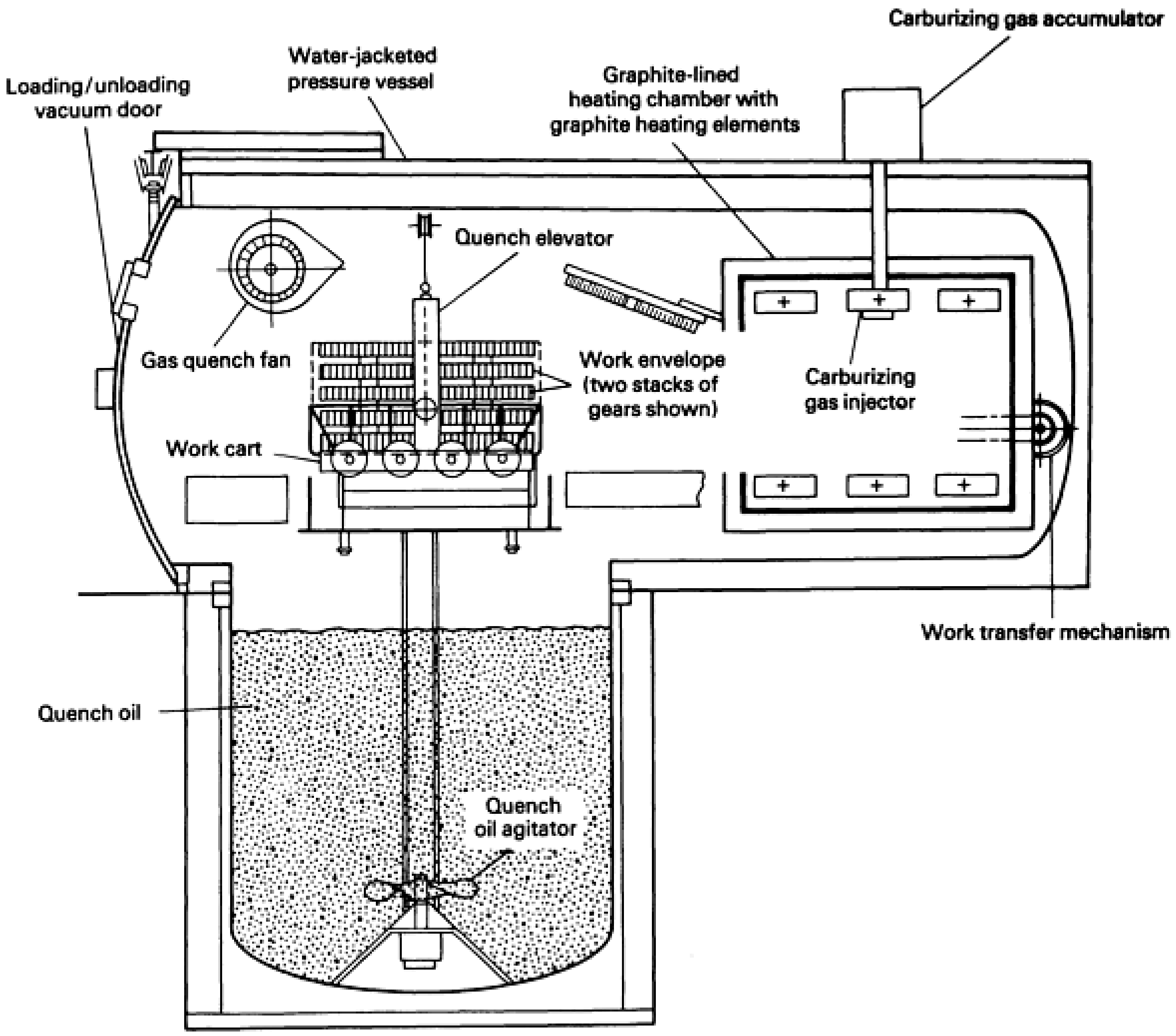


Fig. 3 A batch-graphite integral oil-quench vacuum furnace with vacuum-carburizing capability

Carbon Gradient and Case Depth Prediction

One approach for predicting the carbon gradient in a steel is to use a computer model to calculate the surface carbon content and the carbon profile. In the boost step of the process, the surface carbon content is usually increased to the limit of solubility of carbon in austenite at the process temperature. The surface carbon content and carbon profile resulting from the boost step can be predicted using diffusion theory. In the diffusion step, the carbon diffuses away from the surface. Because carbon is not gained or lost at the surface during the diffusion step, the final surface carbon content and carbon profile are also readily predicted using the same diffusion model. Accurate carbon-diffusivity data for the steel being processed are required if this approach is to produce a meaningful prediction. This approach can be further enhanced using a continuous cooling transformation (CCT) diagram calculated from the composition of the steel and quench rate data to predict case and core microstructures, hardness profile, and residual stress distribution. One major aircraft engine manufacturer is working on such a model for vacuum carburizing.

One method of simply and accurately predicting effective case depths is to use the following equations:

$$D = k\sqrt{t} \quad \textbf{(Eq 3)}$$

$$c = rt \quad \textbf{(Eq 4)}$$

$$t = c + d \quad \textbf{(Eq 5)}$$

where D is the effective case depth required, k is a carburizing constant for a specific carburizing temperature, t is the total time (that is, carburizing time plus diffusion time), c is the carburizing time, r is the boost/diffusion ratio, and d is the diffusion time.

Knowing the effective case depth required and the value of k for the material at the carburizing temperature to be used, Eq 3 can be solved for t or the total time. Knowing the value of r for the surface carbon content desired, also dependent on the carburizing temperature, Eq 4 can be solved for c or for the carburizing time. With t and c known, d or the diffusion time can be calculated using Eq 5. This method has been found to be accurate and repeatable as long as the case depth used to calculate k is accurately measured, the temperature control is accurate, and the actual carburizing and diffusion times used to produce the case depth/surface content from which k and r were determined are known. See Table 1 for typical carburizing constants and boost/diffusion ratios to obtain a surface carbon content of 0.8 to 0.9% with a low-alloy, low-carbon steel.

Table 1 Typical carburizing constants and boost/diffusion ratios needed to obtain a 0.8 to 0.9% surface carbon content in a low-alloy, low-carbon steel

Temperature		Carburizing constant		Boost/diffusion ratio, *r*
°C	°F	$k^{(a)}$	$k^{(b)}$	
840	1550	0.25	0.010	0.75
870	1600	0.33	0.013	0.65
900	1650	0.41	0.016	0.55
925	1700	0.51	0.020	0.50
950	1750	0.64	0.025	0.45
980	1800	0.76	0.030	0.40
1010	1850	0.89	0.035	0.35
1040	1900	1.02	0.040	0.30

(a) To obtain effective case depth (50 HRC hardness), D, in millimeters when $D = k\sqrt{t}$ and t is in hours.

(b) To obtain effective case depth (50 HRC hardness). D, in inches when $D = k\sqrt{t}$ and t is in hours

The two examples that follow demonstrate typical applications of Eq 3, 4, and 5.

Example 1: Workpiece Specifications Require an Effective Case Depth of 0.38 mm (0.015 in.) with a Nominal Surface Carbon Content of 0.85%.

The desired carburizing temperature is 845 °C (1550 °F). Using Table 1, *k* is 0.25 (0.010), and *r* is 0.75. Solving Eq 3 for *t* gives 2.3 h or 138 min total time. Solving Eq 4 and Eq 5 for *c* and *d* gives 104 min carburizing time and 34 min diffusion time.

Example 2: Workpiece Specifications Require an Effective Case Depth of 1.5 mm (0.060 in.) with a Nominal Surface Carbon Content of 0.85%.

The carburizing temperature to be used is undecided, therefore, carburizing temperatures of 925 °C (1700 °F) followed by cooling to a lower temperature and direct quenching, and 1040 °C (1900 °F) followed by reheating and oil quenching will be evaluated. Using Table 1, *k* at 925 °C (1700 °F) is 0.51 (0.020). At 1040 °C (1900 °F), *k* is 1.02 (0.040). Solving Eq 3 for *t* gives 8.7 h total time at 925 °C (1700 °F) and 2.2 h total time at 1040 °C (1900 °F). Therefore, carburizing at 1040 °C (1900 °F) will save 6.7 h; however, a reheat cycle will be required. If a reheat cycle is less than 6.7 h, a time savings may be possible by carburizing at the higher temperature.

Carburizing Gas Circulation

To obtain uniform case depths when vacuum carburizing, there are two principle requirements:

- Temperature uniformity of ±8 °C (15 °F) or better
- Uniform carburizing gas circulation

Pulse/Pump Systems. Effective at obtaining uniformity and minimizing gas consumption is the pulse/pump method, which is a method of gas circulation that has two stages. The first, or pulse, stage consists of repeatedly accumulating a small charge of carburizing gas external to the furnace and then releasing, or pulsing, the charge of gas into the heating chamber through an injector. This pulsing is repeated until the partial pressure setpoint is achieved. At this point, the spent carburizing gas is evacuated, or pumped. The cycle continues, alternately pulsing and pumping for the duration of the boost stage of the process. The principle operating variables of the method are accumulator pressure, release frequency, evacuation time, and carburizing gas partial pressure.

The advantage of the pulse/pump method is that effective gas circulation may be achieved at low partial pressures using relatively simple components. Methods using either hot (in the heating chamber) or cold (external to the heating chamber) gas fans require partial pressures of at least 40 kPa (300 torr) to be effective. With increased partial pressures of carburizing gas, heat losses increase and there tends to be greater soot deposition. Additionally, because of the environment in which the fans operate, they tend to require constant maintenance.

High-Temperature Vacuum Carburizing

The reduction in carburizing time associated with a higher carburizing temperature has long been appreciated. However, typical atmosphere furnace construction generally restricts the maximum carburizing temperature to approximately 955 °C (1750 °F). The higher temperature capability of vacuum furnaces, as compared to typical atmosphere furnaces, permits the use of higher carburizing temperatures with correspondingly reduced cycle times.

High-temperature vacuum carburizing can significantly reduce the overall cycle time required to obtain effective case depths in excess of 0.9 to 1.0 mm (0.035 to 0.040 in.). For obtaining smaller case depths, high-temperature vacuum carburizing does not offer any advantages because a grain refining step is required and the boost times tend to be too short for acceptable uniformity. Table 2 compares the time required to obtain 0.9 mm (0.035 in.) and 1.0 mm (0.050 in.) effective case depths via vacuum carburizing at both 900 °C (1650 °F) and 1040 °C (1900 °F) for an AISI 8620 steel. As is apparent from Table 2, significant reductions in the total cycle time can be obtained by using high-temperature vacuum carburizing.

Table 2 Comparison of time required to obtain a 0.9 mm (0.035 in.) and 1.3 mm (0.050 in.) effective case depth in an AISI 8620 steel at carburizing temperatures of 900 °C (1650 °F) and 1040 °C (1900 °F)

Effective depth	Carburizing temperature	Time, min

mm	in.	°C	°F	Heating to carburizing temperature	Soaking prior to carburizing	Boost	Diffusion	Gas quench to 540 °C (1000 °F)	Reheat to 845 °C (1550 °F)	Soak at 845 °C (1550 °F)	Oil quench	Total
0.9	0.035	900	1650	78	45	101	83	(a)	(a)	(a)	15	>322
		1040	1900	90	30	15	23	20	22	60	15	275
1.3	0.050	900	1650	78	45	206	169	(a)	(a)	(a)	15	>513
		1040	1900	90	30	31	46	20	22	60	15	314

(a) Not available

Metallurgists not familiar with high-temperature vacuum carburizing are often concerned that although reduced cycle times can be obtained by high-temperature carburizing, a degraded microstructure with reduced mechanical properties results. There is no evidence that any reduction in either monotonic or cyclic mechanical properties results from high-temperature vacuum carburizing, provided that the process is properly specified and controlled. One aircraft-quality gearing user has performed extensive work in the area of high-temperature vacuum carburizing and concluded that there is no loss of properties when either AISI 9310 or X-2 Modified are high-temperature vacuum carburized to aircraft-quality gearing process specifications.

There is also concern that the high process temperatures involved will result in excessive distortion and size change. Although it is true that some geometries are sensitive to the ultimate process temperature used, distortion can be minimized by using proper preheating/heating techniques, minimizing times at temperature, proper fixturing, and quenching techniques that are only severe enough to result in the desired microstructure and do not develop excessive nonuniform stresses within the part. Gas pressure quenching holds a lot of promise in this area, particularly with the new moderate- to high-alloy grades of carburizing steels being developed. As far as any dimensional change greater than normal is concerned, the uniformity and repeatability of the vacuum-carburizing process, even at elevated temperatures, allows for dimensional change during manufacturing planning.

Future Outlook

Vacuum carburizing is a sophisticated and powerful carburizing process. When it is properly specified in well-controlled and maintained furnaces, the process offers excellent uniformity throughout the load and good lot-to-lot repeatability--typically better than can be achieved with conventional atmosphere-carburizing methods. The excellent uniformity and repeatability of the process are well recognized in the quality gearing and bearing fields where the process enables less grinding stock to be left on surfaces that require finish grinding to size and/or closer tolerances on those surfaces that are used as heat treated.

Because of the precision with which process variables can be controlled and the tremendous flexibility of vacuum furnaces, vacuum carburizing is well suited to processing both the new, more highly alloyed, high-performance grades of carburizing steels and the current, moderately alloyed grades used commercially. Coupled with the rapidly developing field of gas pressure quenching, tremendous opportunities in higher-performance, low-distortion gearing can be realized with the process.

Vacuum carburizing offers advantages not only in manufacturing planning/process control and engineering, but also in manufacturing. Cycle times can be reduced, particularly if even slightly higher carburizing temperatures are used. Preheating and post-carburizing heat treatment can also be performed in a vacuum, resulting in very clean parts that do not require the postcleaning associated with conventional atmosphere carburizing. The equipment can be started and shut

down quickly using utilities only when the furnace is actually processing work, resulting in significant utilities savings. Heat and exhaust from vacuum-carburizing furnaces are much less than those emitted with conventional atmosphere-carburizing methods. Therefore, the furnace can be located adjacent to other machine tools in a comfortable working environment. Other high-temperature processes, such as brazing, can be performed in the same furnace (depending on furnace construction) and possibly can be combined to reduce cycle time along with the need to heat, cool, and handle the work twice.

Plasma (Ion) Carburizing of Steels

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Introduction

IN DIFFUSION PROCESSES involving the migration of interstitial elements through metals (as in the carburizing of steels), the rate of diffusion is influenced by temperature and the atomic concentration of the migrating species at the surface. The concentration of migrating species at the surface is further determined by the supply of species at the surface and their ease in entering the surface. The importance of these three factors (temperature, surface reactions, and species supply at the surface) on diffusion rates depends on the particular process.

Carburizing methods (be it pack, gas, vacuum, or a plasma technique) are seldom limited by iron-carbon reactions and the temperature dependence of diffusion, because carburizing requires austenitizing temperatures (which not only improve diffusion rates but also improve surface rates by the high solubility of carbon in austenite). Rather, the rate at which carburizing can proceed is more often limited by the rate at which active carbon can be generated and brought to the surface of the steel. Thus, the search for means to increase carburizing rates has centered on methods designed to overcome this limitation.

One method of increasing carburizing rates involves the use of plasma (ion) carburizing, which is basically a vacuum process utilizing glow-discharge technology to introduce carbon-bearing ions to the surface of steel for subsequent diffusion below the surface. Plasma carburizing is effective in increasing carburizing rates because the process effectively bypasses several steps in the dissociation process that produces active soluble carbon. With methane (CH_4) gas, for example, active carbon for adsorption can be formed directly from methane due to the ionizing effect of the plasma. Plasma carburizing thus allows higher process rates than conventional gas carburizing, which involves several reaction steps in the dissociation of methane into active carbon (see "Dissociation of Methane to Carbon in Gas and Plasma Carburizing" in this article).

Another possible advantage compared to gas carburizing in some applications of plasma carburizing is that higher temperatures are permissible, because the process is performed in an oxygen-free vacuum. This advantage is similar to the process of vacuum carburizing (described in the previous article in this Volume). However, vacuum carburizing exhibits some potential disadvantages when compared to plasma carburizing. Because vacuum carburizing is conducted at very low pressures, and the rate of flow of the carburizing gas into the furnace is very low, the carbon potential of the gas in deep recesses and blind-holes is quickly depleted. Unless this gas is replenished in these areas, a great nonuniformity in case depth over the surface of the part is likely to occur. If, in an effort to overcome this problem, the gas pressure is increased significantly, another problem arises, namely, free-carbon formation or sooting. Thus, in order to obtain cases of reasonably uniform depth over a part of complex shape, the gas pressure must be periodically increased to replenish the depleted atmosphere in recesses, and then reduced again to the operating pressure. Clearly, a delicate balance exists in vacuum carburizing where the process conditions must be adjusted to obtain the best compromise between case uniformity, risk of sooting, and carburizing rate. Plasma carburizing overcomes both of these major problems, yet retains the desirable features of a simple atmosphere and a higher permissible operating temperature.

General Process Characteristics

Physical Properties of Glow-Discharge Plasma. A plasma is an electrically generated "gaseous" mixture consisting of positively and negatively charged particles as well as neutral species. Although gaseous in nature, it has a cohesive and stable form with a net electrical charge of zero. Plasmas occur in many places throughout the cosmos, but do not exist in stable form on earth due to the rather special conditions they require for initiation. Nevertheless, the necessary conditions can be easily achieved and thus stable man-made plasmas can be produced. Such plasmas have been widely employed in a variety of important industrial applications such as welding, catalyzing chemical reactions, laser pumping, and polymer stabilization.

The plasma utilized for case carburizing is the glow discharge (Ref 1, 2). This plasma is shown on a plot of electron density versus electron energy in Fig. 1. It can be seen that a glow-discharge plasma contains a very high density of electrons ($1 \times 10^{12}/cm^3$) with an average energy in the range of 1 to 10 electron volts (eV)--an energy range very effective

in ionizing and dissociating diatomic molecules. Thus, a plasma provides a ready and prolific source of chemically active atoms, and in plasma (ion) carburizing this is its principal function.

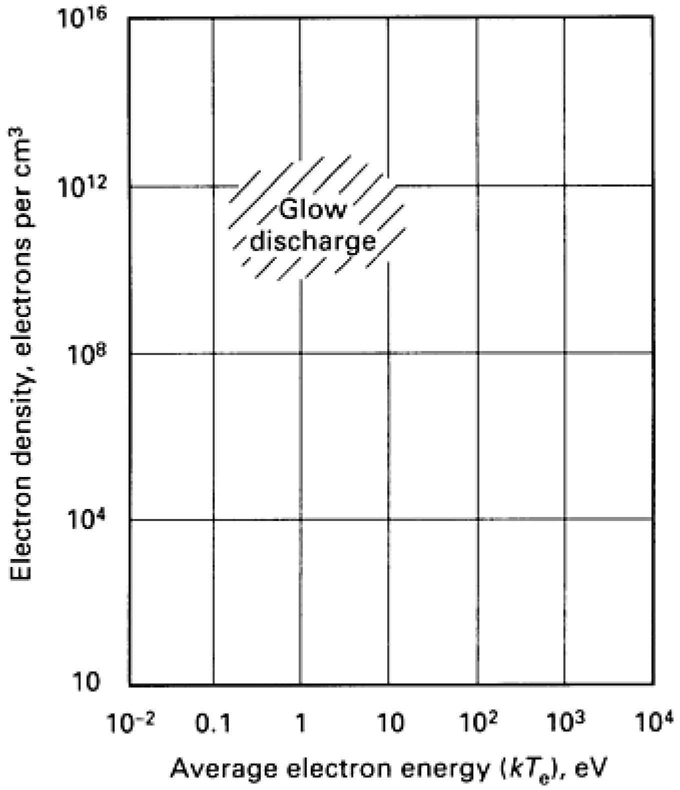

Fig. 1 Electron energy versus electron density in a glow-discharge plasma

A glow-discharge plasma can be easily established and maintained by placing two metal electrodes at opposite ends of a glass enclosure and evacuating it to a few hundred Pascals (Pa) of pressure (or a few torr of pressure with 1 torr = 1 mm of mercury pressure). Upon applying a dc voltage of a few hundred volts, a striated visible glow consisting of various regions (shown schematically in Fig. 2) is observed. All of the major regions are identified in Fig. 2, but in plasma (ion) carburizing, only the cathode and negative glows in the vicinity of the negative electrode are important. It is in this region of highest field strength (the cathodefall region) that ionization of the residual gas in the tube occurs. In fact, most of the advantages achieved by ion carburizing may be attributed to the physical processes which occur in this region. Much has been written on the details of the electron and ionic processes which occur in the cathodefall region (Ref 1, 2, 3), but suffice it to say, it is here that the electron and ion velocities are sufficiently high to dissociate molecules of the low-pressure gas and thus provide the active species required. Because this region is very near the cathode, it is also highly probable that these activated species will reach the cathode during their lifetime, and thus be available for reaction with the cathode surface or absorption into it.

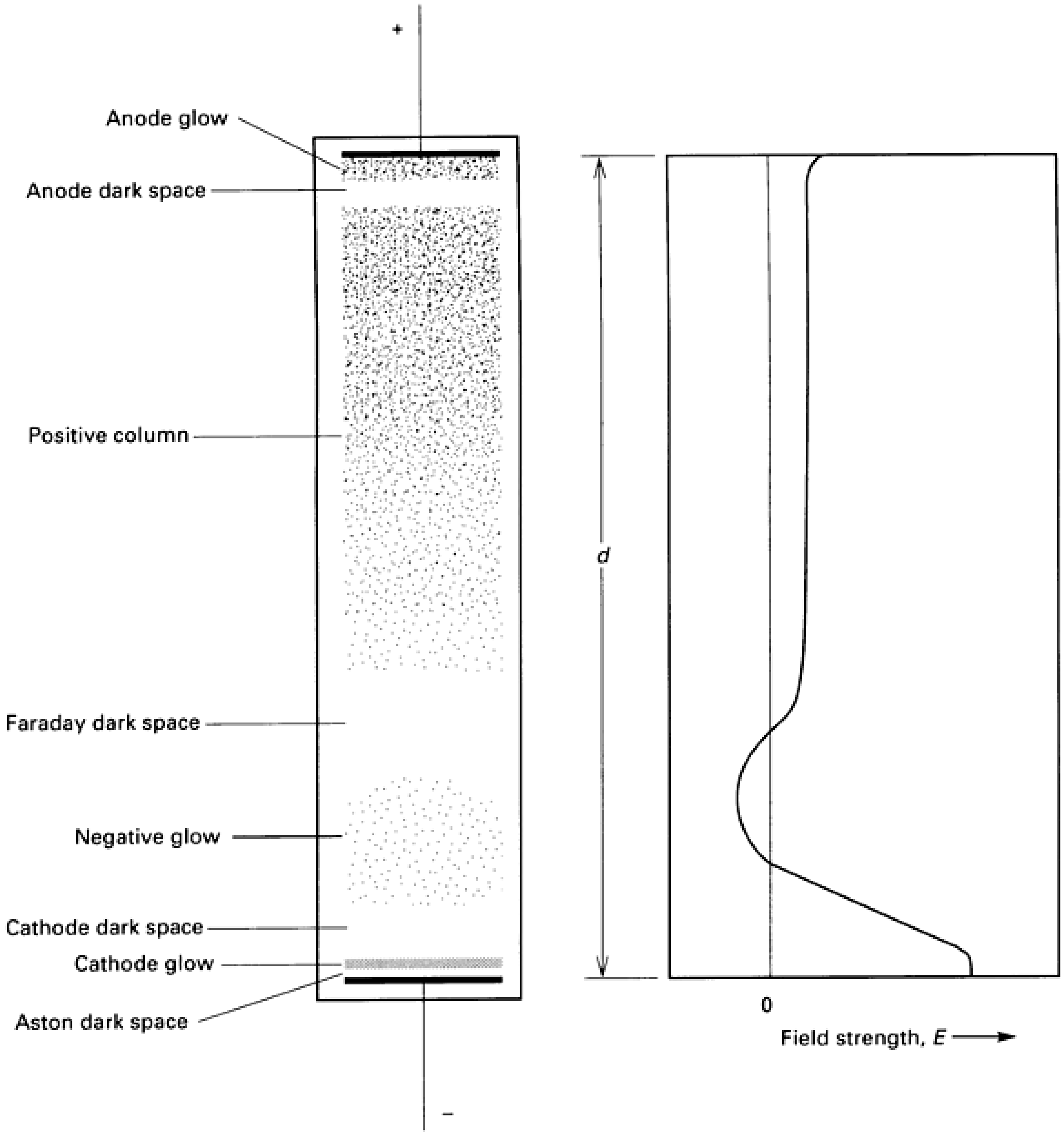

Fig. 2 Elements of a dc glow discharge in a gas at low pressure and field strength *E* versus distance *d* between the electrodes

Range and Limitations of Glow-Discharge Plasma. While glow-discharge plasma can be made to occur over a rather wide range of conditions, there are, nevertheless, some constraints that must be observed to ensure stability and a constant supply of active carbon. Referring again to Fig. 2, only the positive column constitutes a "true" plasma, that is, an ionized gas having no net space charge. This positive column, however, is not essential to the stability of the discharge, and may be eliminated by bringing the two electrodes closer together. In fact, if the pressure and the voltage are held constant and *d* in Fig. 2 is decreased, the positive column simply shrinks in length until it disappears as the anode enters the Faraday dark space (Fig. 2). Not until the anode approaches the negative glow do any of the discharge parameters change appreciably. Even with the anode very near the negative glow, the discharge is still stable, hut at a slightly higher voltage.

As *d* is further decreased, however, the voltage necessary to maintain stable operation will increase unless the pressure is increased in order to maintain approximately the same total amount of gas between the electrodes as when *d* was large. As shown by the Paschen curves in Fig. 3, the voltage required to maintain a stable discharge in a gas at low pressure is a function of both the pressure, *P*, and the distance, *d*, between the electrodes--actually, the product of *P* and *d.* Thus, as *d* is decreased, the pressure must be increased in order to permit operation at the minimum voltage. This dependence of the voltage on both *P* and *d* has important consequences in the practical application of plasma (ion) carburizing as will be shown later.

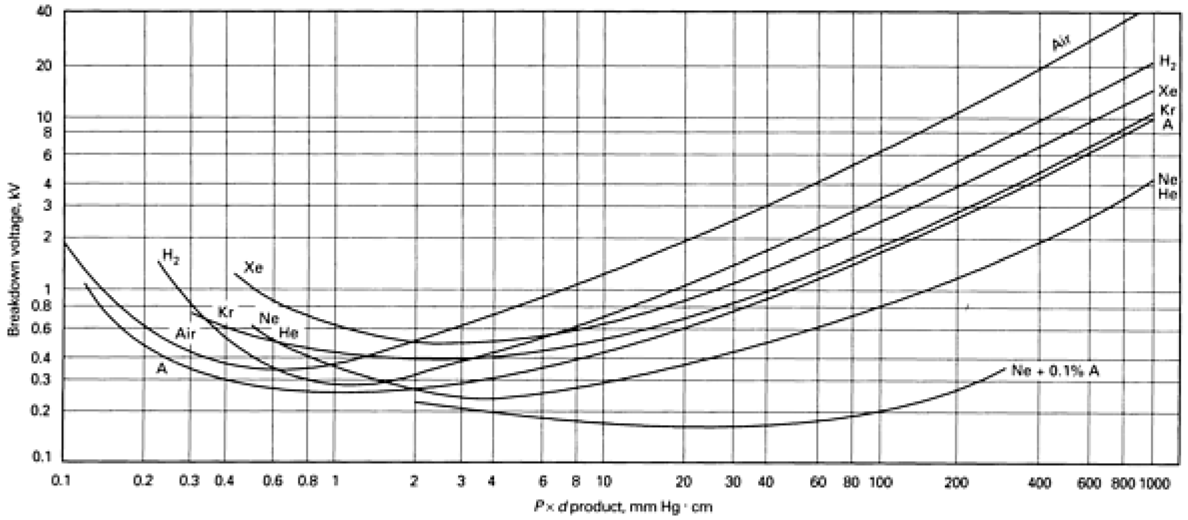

Fig. 3 Paschen curves for a dc glow discharge between parallel-plate electrodes for various gases showing the breakdown voltage versus the product of the gas pressure (*P*) and the distance (*d*) between the electrodes

Voltage Levels in Plasma Carburizing. Although it would be advantageous to be able to operate at the minimum voltage, in ion carburizing there are other more important conditions to be met. For example, it is essential that the plasma completely cover the cathode so that the case over the entire surface of the workpiece (the cathode) will be of uniform depth. A plot of voltage versus current in a gas at low pressure is shown in Fig. 4. The minimum voltage required to ensure complete coverage of the cathode is indicated by X, which is a voltage just above the constant voltage or "normal" glow region. Although the voltage must be high enough to ensure that the point X is on the positive slope region of the current-voltage (*I*-*V*) characteristic curve (for stability), it should not be any greater than that required for complete coverage because higher voltages simply increase the tendency of the discharge to pass into the arc mode (Fig. 4). Thus, in actual practice, the voltage is adjusted (for a given pressure and interelectrode distance, *d*), not only to ensure that the plasma sheath completely covers the workpiece but, simultaneously, to minimize the tendency of the discharge to abruptly enter the arc mode and damage the part.

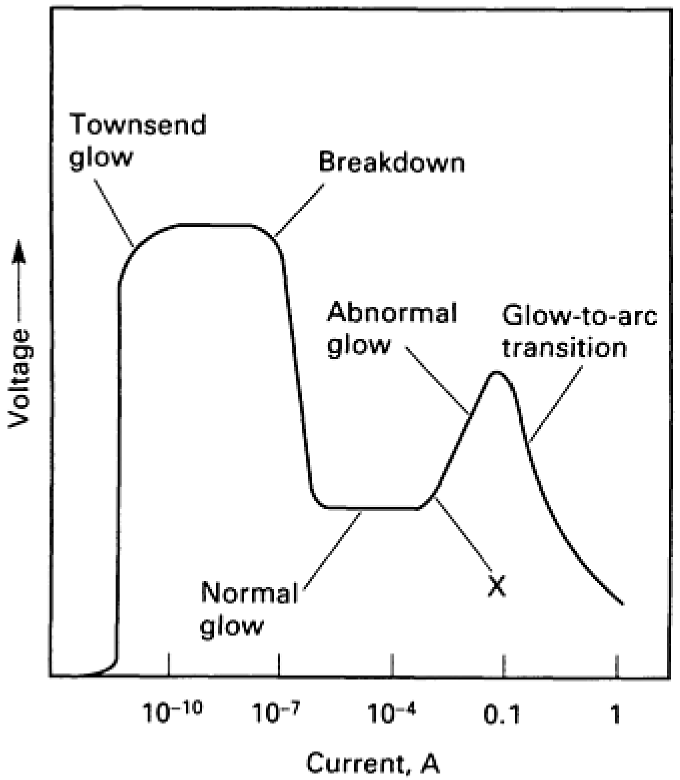

Fig. 4 Schematic current-voltage characteristic for electrical discharges in a gas at low pressure. X, minimum voltage required to ensure complete coverage of the cathode

Coverage and Wrap-Around Effect. While the need to adjust the operating conditions to ensure that the plasma sheath completely covers the workpiece may appear to be a troublesome constraint, this requirement is, in fact, an important advantage. Because a surface reaction will occur on the metal part only where the plasma is in contact with it, operation under conditions where complete coverage occurs ensures that the case will be of fairly uniform depth over the part--even on those areas that are not directly opposite (facing) the counterelectrode (the anode).

Deep recesses and "blind" holes are also carburized provided the depth-to-diameter ratio is not too large. To permit penetration of the plasma, a hole must have a diameter at least twice the thickness of the plasma sheath. The depth of the penetration of the plasma and therefore the extent of "down-hole" carburizing will depend on both the pressure and the interelectrode distance, *d.* This has important consequences in furnace design and furnace loading, as well as an influence on the operating parameters. This is discussed in greater detail in the section "Down-Hole Carburizing" in this article.

Dissociation of Methane to Carbon in Gas and Plasma Carburizing. In conventional gas atmosphere carburizing, the dissociative reactions that produce active soluble carbon from methane are shown in (a) to (f) in Eq 1:

$$\begin{array}{ll} \text{(a)} & CH_4\ \text{(gas)} \rightarrow \text{adsorbed (ad) } CH_4 \\ \text{(b)} & CH_4\ \text{(ad)} \rightarrow CH_3\ \text{(ad)} + H\ \text{(ad)} \\ \text{(c)} & CH_3\ \text{(ad)} \rightarrow CH_2\ \text{(ad)} + H\ \text{(ad)} \\ \text{(d)} & CH_2\ \text{(ad)} \rightarrow CH\ \text{(ad)} + H\ \text{(ad)} \\ \text{(e)} & CH\ \text{(ad)} \rightarrow CH\ \text{(ad)} + H\ \text{(ad)} \\ \text{(f)} & CH\ \text{(ad)} \rightarrow C\ \text{(dissolved)} \end{array} \qquad \textbf{(Eq 1)}$$

Of this series, (c) is the rate-limiting reaction (Ref 4, 5), and therefore the formation of active carbon for adsorption on the hot steel surface (reaction e) can proceed no faster than reaction (c) allows.

In a glow-discharge plasma, on the other hand, active carbon for adsorption can be formed directly from methane owing to the ionizing effect of the plasma. The rate-limiting reaction (c) of Eq 1 is thus effectively bypassed. This is not to say that all of the methane will be dissociated completely in one step. Intermediate dissociative steps may, and will, occur, but the end result is complete dissociation of the available methane. Herein lies the potential of plasma (ion) carburizing as a method of increasing the efficiency and rate of carbon delivery for subsequent dissolution in austenite. However, diffusion time is necessary or else deleterious carbides will form during cooling.

Diffusion Characteristics. Like vacuum carburizing, plasma carburizing is performed in an oxygen-free environment, which permits higher temperatures and thus higher diffusion rates. Higher temperatures also bring about some additional benefits arising from the increased solubility of carbon in austenite as the temperature is increased. As shown in the low-carbon region of the iron-carbon composition diagram in Fig. 5, by raising the temperature from the vicinity of 900 °C (1650 °F) (the normal carburizing temperature for conventional atmosphere carburizing) to 1040 °C (1900 °F), the limit of carbon solubility for carbon in austenite is increased from approximately 1.2 to approximately 1.6 wt% carbon (indicated by the arrows on the abscissa of Fig. 5). Because the surface of the hot steel part becomes saturated to this higher value very quickly in plasma carburizing, the diffusivity (and hence the carburizing rate) increases because of the effect of higher dissolved carbon concentrations on the diffusion coefficient (*D*) for carbon in austenite.

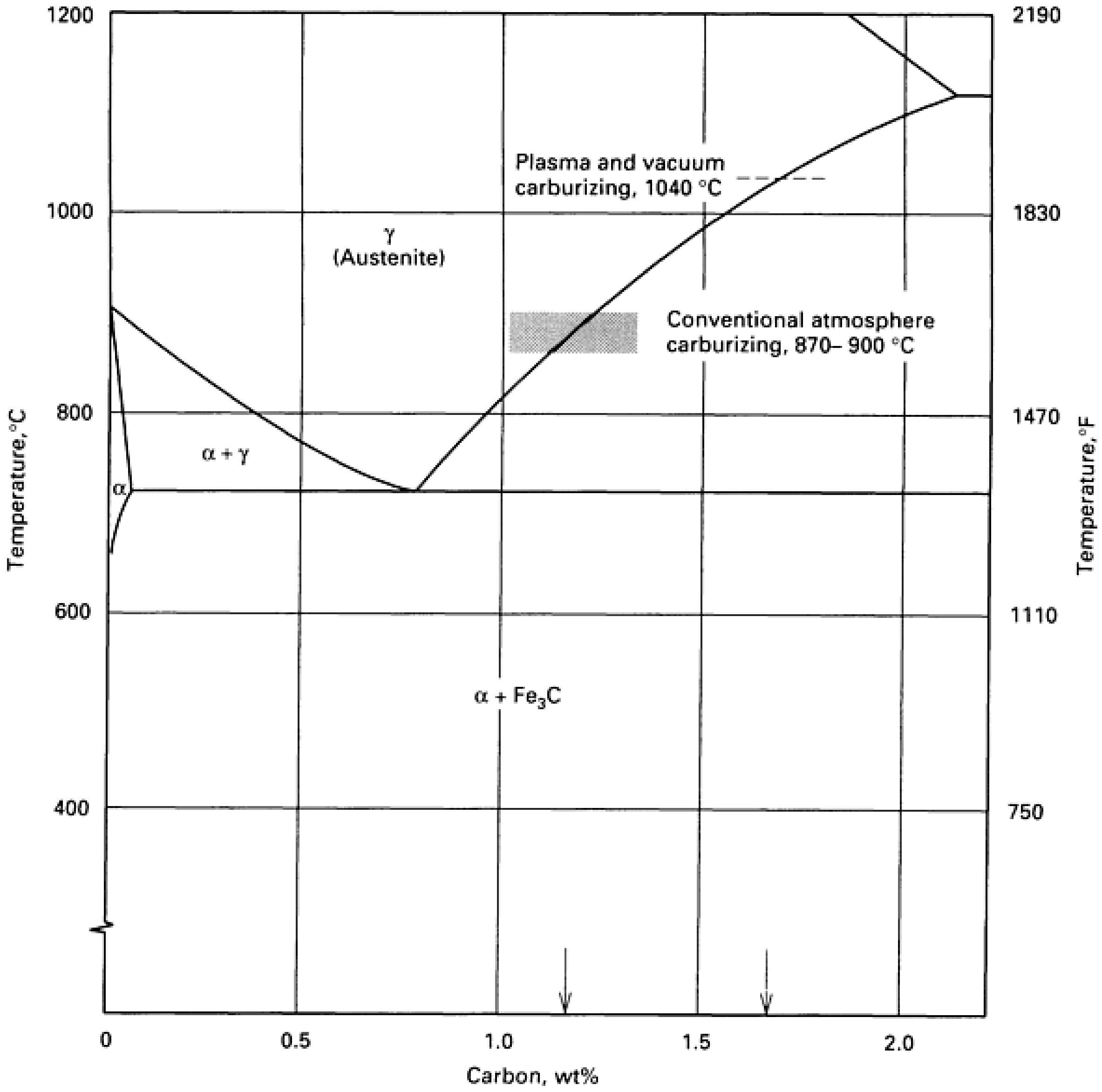

Fig. 5 Low-carbon region of the iron-carbon composition diagram. Arrows indicate the increase in the limit of carbon solubility for carbon in austenite.

The increase in the diffusion coefficient (*D*) with increasing carbon concentration is shown in Fig. 6. It may be seen that for carbon concentrations above approximately 1 wt% C, the diffusion coefficient increases very rapidly. For concentrations in the neighborhood of 1.5 to 1.6 wt% (the limit of solid solubility of carbon in austenite at the temperatures allowed in plasma carburizing), the diffusion coefficient (and hence the diffusivity) is more than twice that for a concentration below 1 wt%. Therefore, temperature has two effects acting simultaneously to increase the diffusion rate of carbon from the surface into the interior of the steel part: first, the effect of the increased temperature on the diffusivity, and second, the increased diffusivity brought about by the increased carbon solubility in the steel.

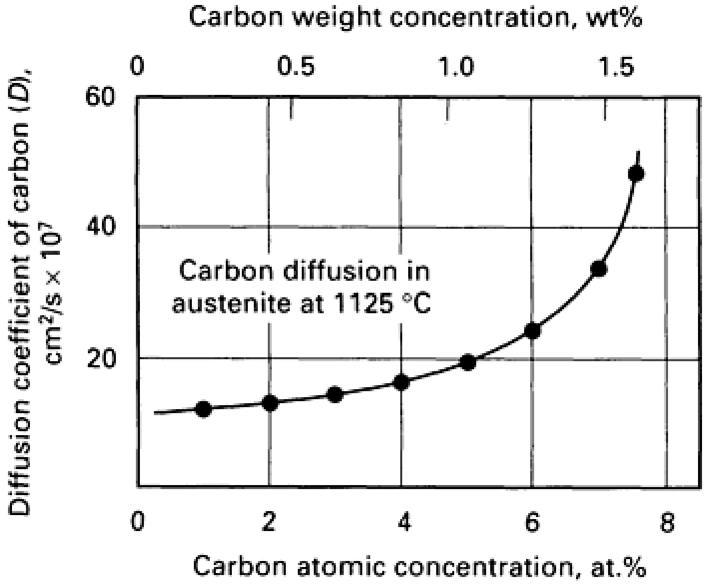

Fig. 6 Diffusion coefficient for carbon in austenite versus carbon concentration at 1125 °C (2060 °F). Source: Ref 6

In addition, because the rate of adding carbon is increased during plasma carburizing, the combined effect is to bring about a profound increase in the rate of carburizing. For example, at a temperature of 1050 °C (1920 °F), enough carbon can be added in only 10 min (Fig. 7) to obtain a case depth of 1 mm (0.040 in.). While an additional diffusion step of 30 min is required to develop the effective case depth of 1 mm (0.040 in.), all of the carbon needed was added in only 10 min from the methane plasma. As also shown in Fig. 7, six h is required to obtain a comparable carbon profile with conventional gas-atmosphere carburizing at 918 °C (1685 °F). Further discussion of the factors which lead to the increased carburizing rates may be found in Ref 8, 9, and 10.

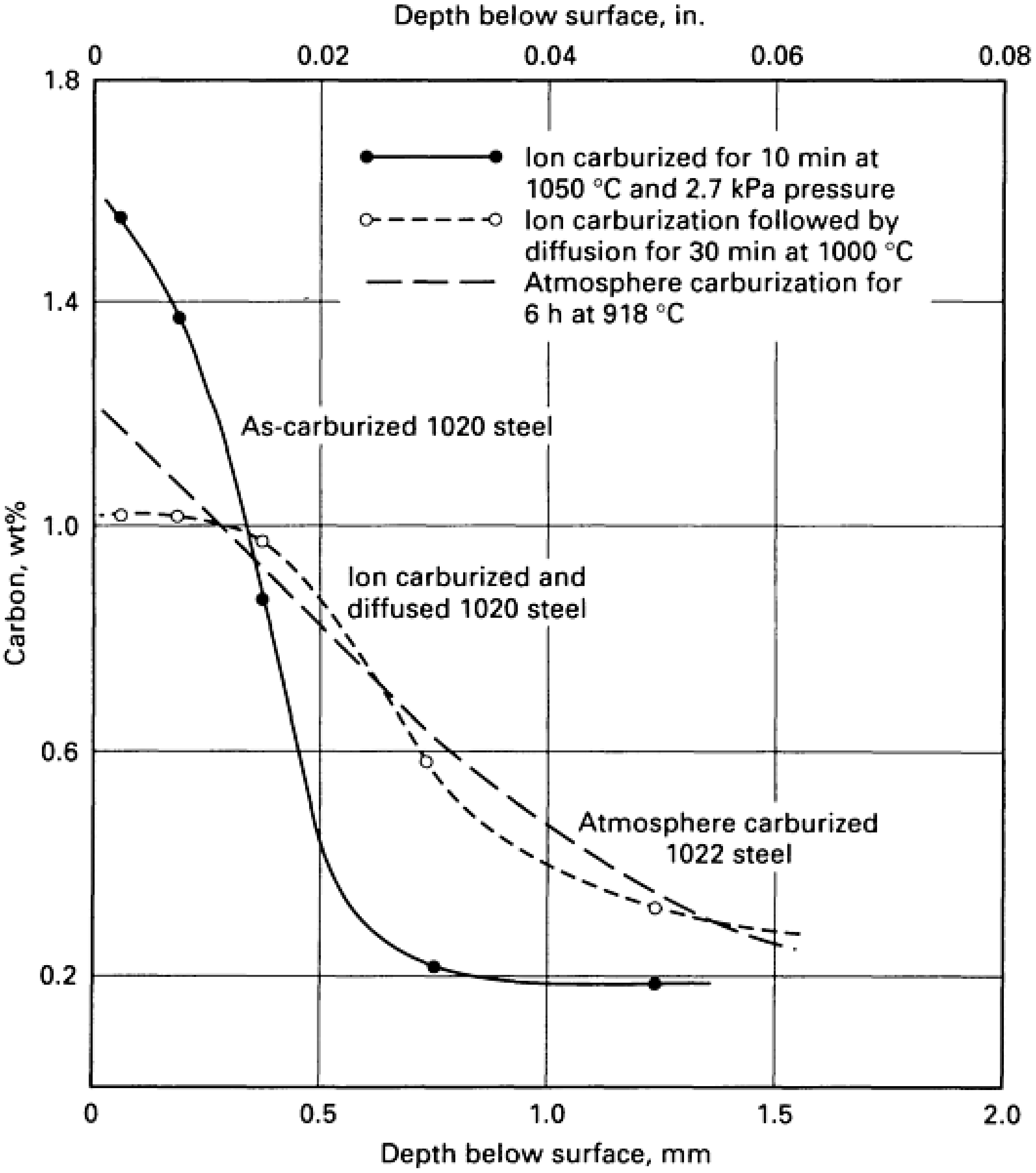

Fig. 7 Carbon concentration profile in AISI 1020 steel after ion carburizing for 10 min at 1050 °C (1920 °F) followed by vacuum diffusing for an additional 30 min at 1000 °C (1830 °F). A similar carbon concentration profile is obtained by atmosphere carburizing for 6 h at 918 °C (1685 °F) Source: Ref 7

Advantages of ion carburizing include several technical factors (such as carburizing and case uniformity) as well as economic and environmental factors. These advantages are briefly discussed below.

High Carburizing Rate. The marked increase in carburizing rate compared to gas or atmosphere carburizing is illustrated in Fig. 8. Shown are the carbon profiles obtained by plasma carburizing at 900 °C (1650 °F) for 10, 30, 60, and 120 min as well as that obtained by atmosphere carburizing for 240 min at the same temperature (Ref 7). It may be seen that the profile obtained by atmosphere carburizing for 240 min at 900 °C (1650 °F) may be obtained in one-half the time by plasma carburizing at the same temperature.

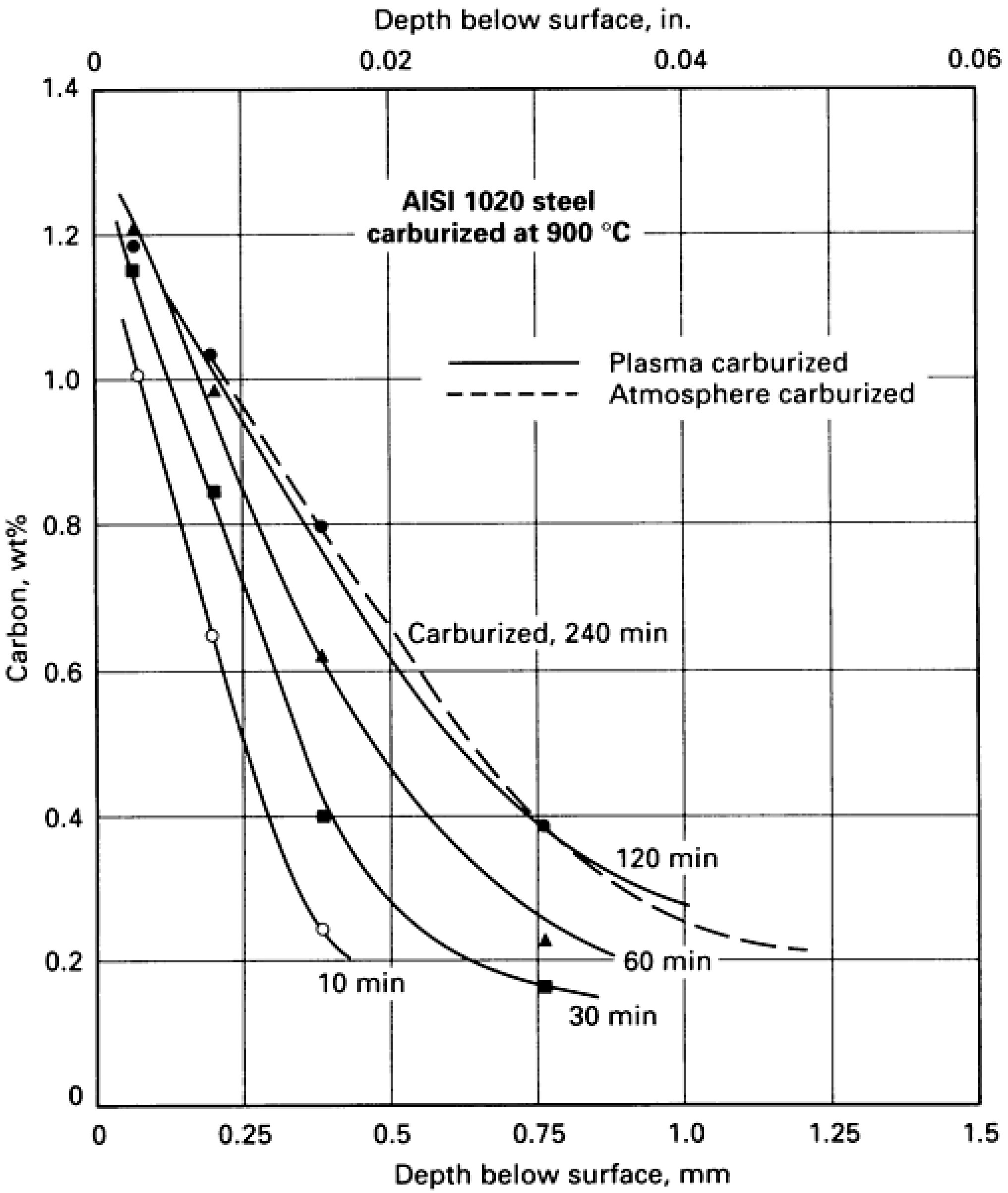

Fig. 8 Carbon concentration profiles in AISI 1020 steel after ion carburizing for 10, 20, 30, 60, and 120 min at 900 °C (1650 °F) Carbon profile after atmosphere carburizing for 240 min at 900 °C (1650 °F) shown for comparison. Source: Ref 7

A similar 2-to-1 advantage is illustrated in Fig. 9 for AISI 8620 steel carburized at 980 °C (1800 °F). Plasma carburizing for 15 min at this temperature matches the carbon profile which required 30 min with atmosphere carburizing. Compared to vacuum carburizing for 30 min, the case depth at the 0.8 wt% C level is 50% deeper with plasma carburizing.

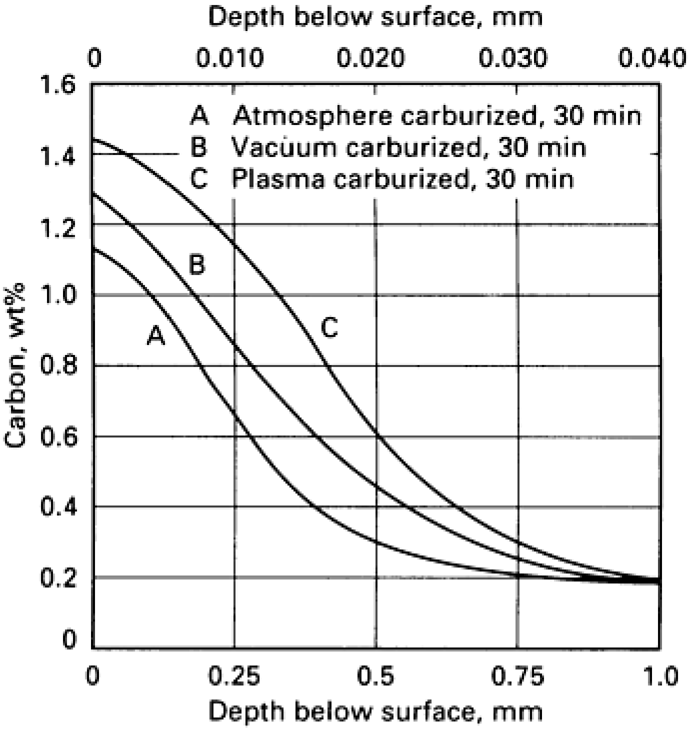

Fig. 9 Carbon gradient profile of atmosphere, vacuum, and plasma carburizing of AISI 8620 steel at 980 °C (1800 °F) saturation conditions for 30 min and followed by direct oil quenching. Source: Ref 11

Typical carbon and hardness profiles through an ion carburized case in the ascarburized and in the carburized-and-diffused condition are shown in Fig. 10. At a carburizing temperature of 1000 °C (1830 °F), a 1 mm (0.040 in.) case is typically obtained with a 10 min carburize, 30 min diffuse cycle.

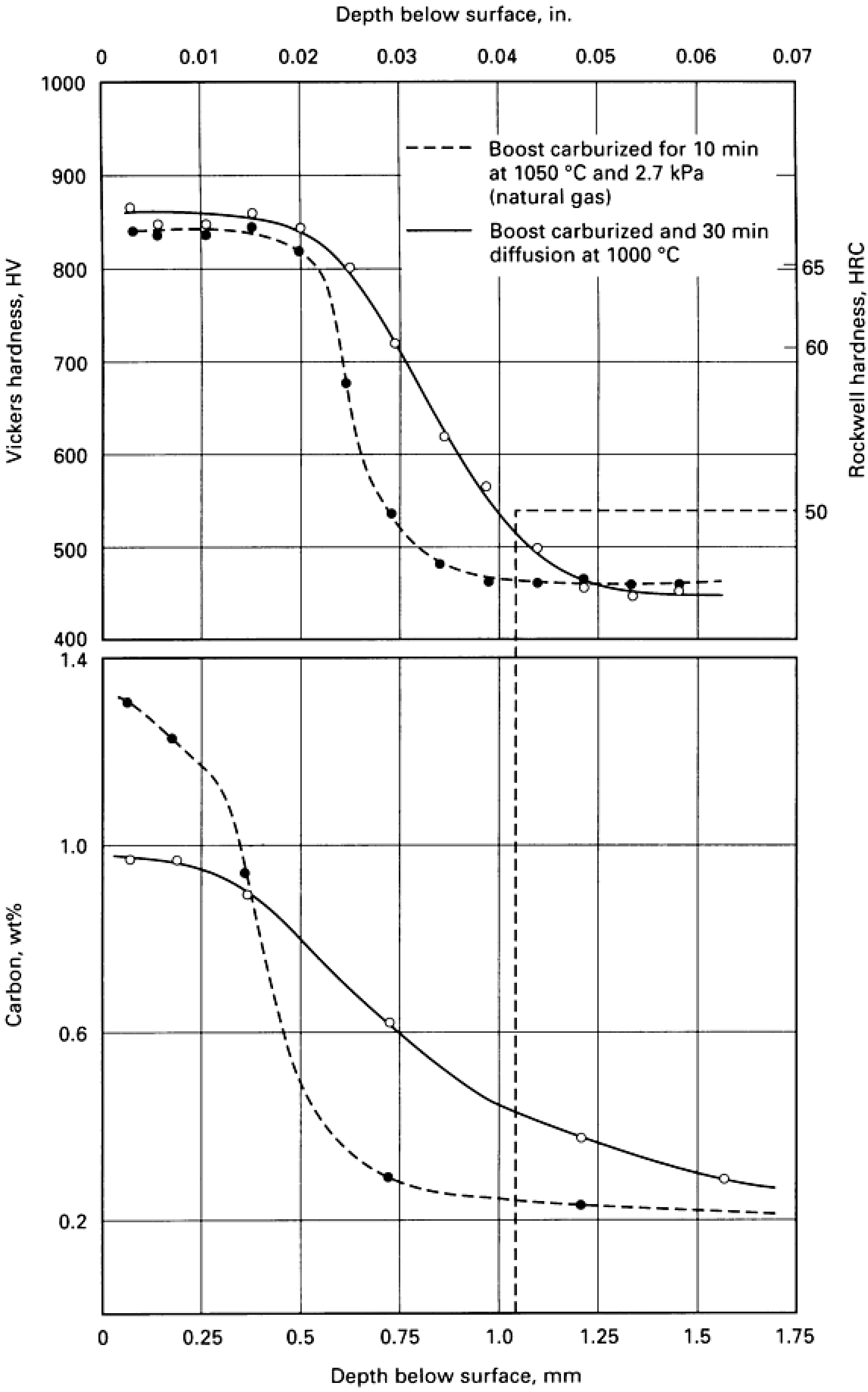

Fig. 10 Carbon concentration and hardness profiles in AISI 1020 steel after ion carburizing for 10 min at 1050 °C (1920 °F) followed by additional vacuum diffusing for 30 min at 1000 °C (1830 °F). Effective case depth is indicated by dotted line.

Improved Case Uniformity. Figure 11 illustrates the improvement in uniformity of case depth in gear-tooth profiles obtained with ion carburizing. Here the case depth profile after ion carburizing at 980 °C (1800 °F) is compared to that obtained with atmosphere carburizing at the same temperature. The improved case depth uniformity obtained by ion carburizing on a part having deep recesses is illustrated in Fig. 12. In this figure, the case uniformity obtained with ion carburizing is compared to that obtained with vacuum carburizing.

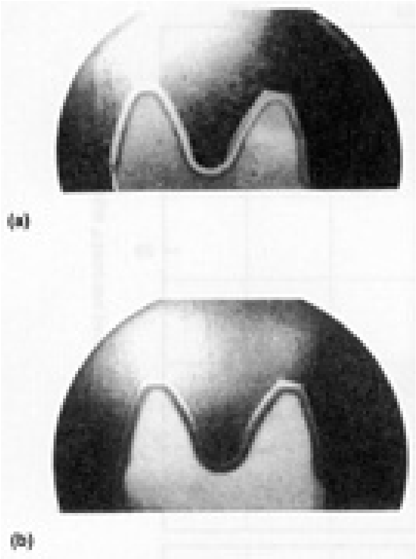

Fig. 11 Comparing uniformity of case depth over gear-tooth profiles. (a) Ion carburized at 980 °C (1800 °F). (b) Atmosphere carburized in a 980 °C (1800 °F) boost-diffuse cycle. Case depth in (a) exhibits more consistency, particularly in the root of the gear profile. Courtesy of Surface Combustion, Inc.

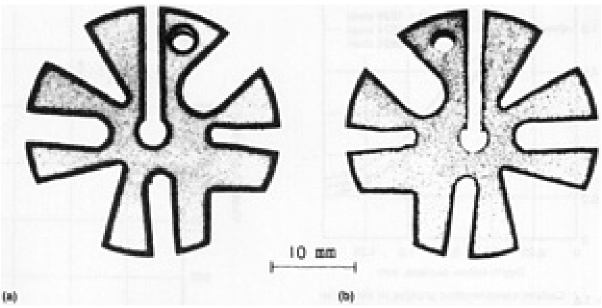

Fig. 12 Comparing uniformity of case depth over a part with deep recesses. (a) Ion carburized. (b) Vacuum carburized. Source: Ref 8

Blind-Hole Penetration. Ion carburizing improves blind-hole penetration, or "down-hole" carburizing. In Fig. 13, for example, plasma carburizing achieves a uniform plateau of case depth of up to an *L*/*D* ratio of about 12. Atmosphere carburizing achieved a uniform case depth for *L*/*D* ratios up to about 9 (Fig. 13).

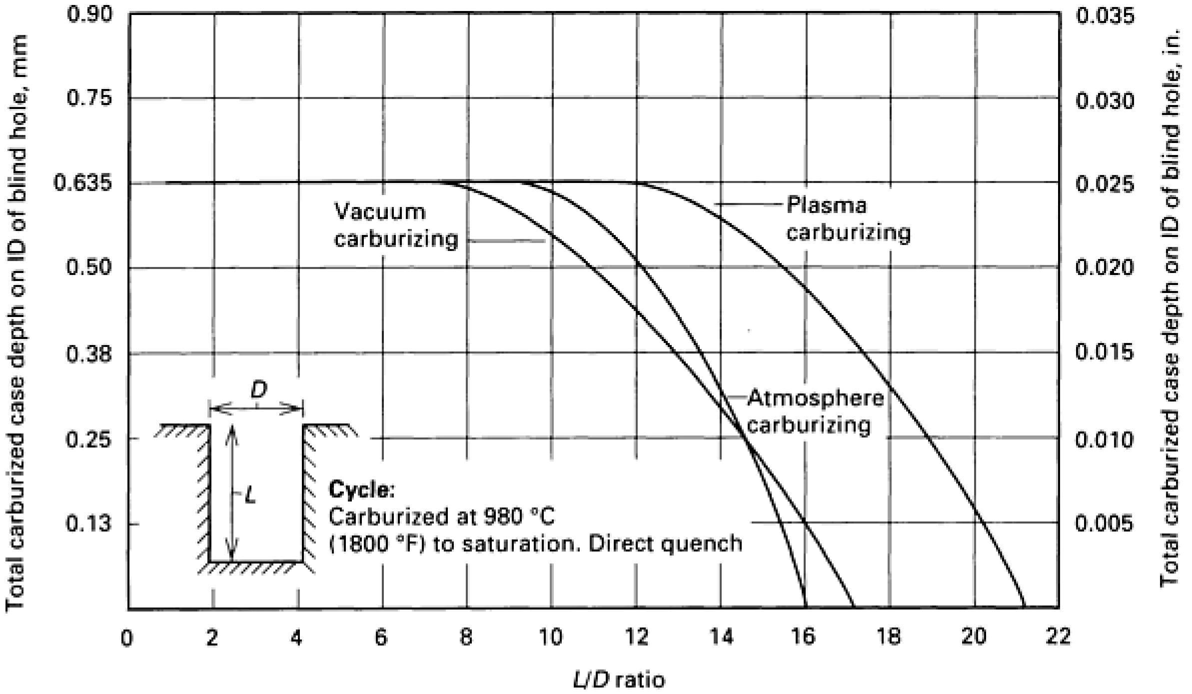

Fig. 13 Uniform case depth of 0.635 mm (0.025 in.) in a blind hole as a function of *L*/*D* ratios for plasma, vacuum, and gas carburizing. The curves were obtained by measuring case depths at different hole depths (*L*) in a 6.35 mm (0.25 in.) diam blind hole. Source: Ref 12

Insensitivity to Steel Composition. The rate at which steel may be ion carburized is quite insensitive to alloy composition, as illustrated in Fig. 14. Essentially the same profile and depth case are obtained in three steels of different alloy content.

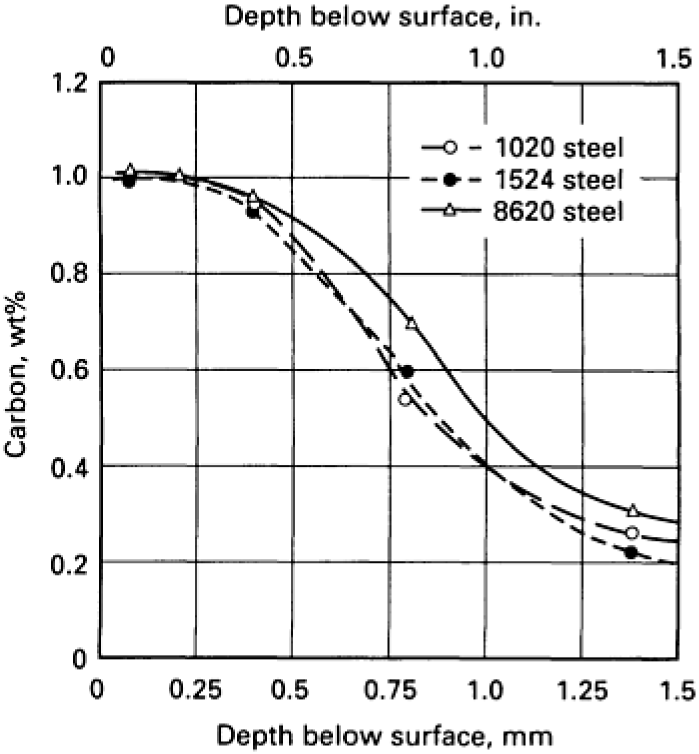

Fig. 14 Carbon concentration profiles in three carburizing steels after ion carburizing illustrating insensitivity to steel composition. Data are based on a boost-diffuse cycle of ion carburizing at 1040 °C (1900 °F) for 10 min followed by diffusion for 30 min at 1000 °C (1830 °F).

Ion carburizing is similarly insensitive to the hydrocarbon gas used as a carbon source. Figure 15 shows similar and comparable carbon and hardness profiles obtained by ion carburizing in methane, natural gas, and nitrogen-propane atmospheres.

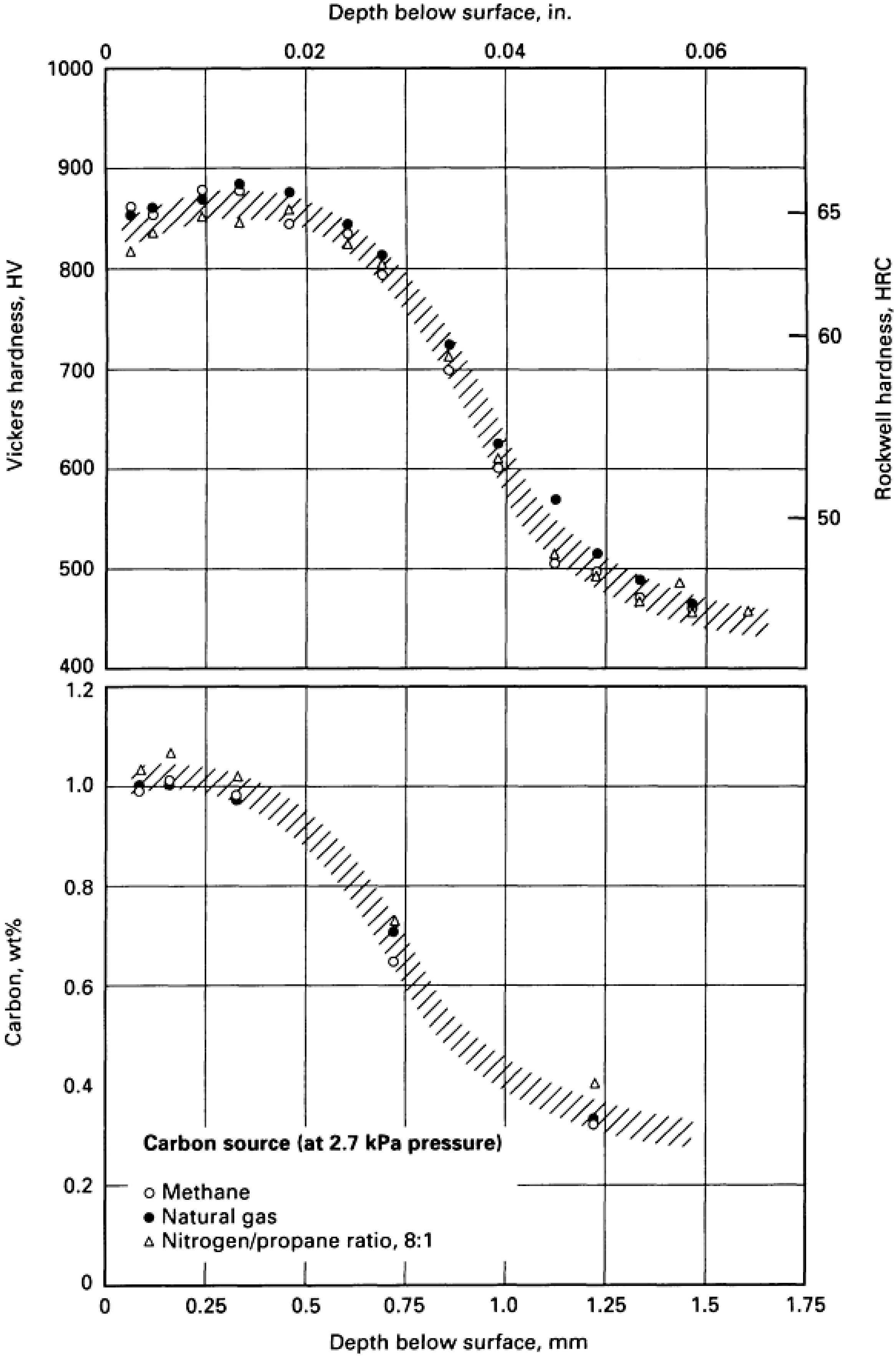

Fig. 15 Carbon concentration and hardness profiles through cases on AISI 1020 steel after ion carburizing in methane, natural gas, and in 8:1 nitrogen/propane combination. Data are based on a boost-diffuse cycle of ion carburizing for 10 min at 1050 °C (1920 °F) followed by 30 min of diffusion at 1000 °C (1830 °F). Source: Ref 13

Environmental Improvements. Plasma carburizing provides a much cleaner and safer environment than gas carburizing systems, and there is no fire hazard or toxic gases such as carbon monoxide from the flame screens on atmosphere furnaces. Because the carburizing zone is completely isolated from the surrounding work space, the furnace may also be placed in-line on the assembly floor. Furthermore, because the ambient temperature of the casing is near tap-water temperature, the furnace may be used in an air-conditioned environment.

Equipment and Operating Costs. Plasma carburizing is done in a special furnace using methane or propane gas at subatmospheric pressure for the carbon source, which eliminates the need for generated gas. Therefore, atmosphere generating equipment is not required, and simple gas-valve manifolds may be used with a resultant reduction in furnace capital equipment costs. However, when all ancillaries are taken into account, the costs of plasma versus atmosphere equipment are comparable.

In terms of an operating cost comparison, ion carburizing reduced the door-to-door processing time by 20% over atmosphere carburizing and by 5% over vacuum carburizing (Table 1). In comparing an electrically fired atmosphere furnace with an ion carburizing furnace, the cost per pound was reduced 45% (Table 1).

Table 1 Operating cost comparison of atmosphere, vacuum, and plasma carburizing methods for 144 gears with a gross weight of 560 kg (1235 lb)

	Atmosphere		Vacuum	Plasma
Cycle, h				
Carburize	2.5		0.9	0.6
Diffusion	0.0		0.7	0.7
Slow cool to 870 °C (1600 °F)	0.5		0.5	0.5
Door-to-door time, h	5.75		4.85	4.55
Atmosphere used, ft^3				
RX	3120 (600 ft^3/h)		. . .	. . .
CH_4	125		100	90
Utility costs/cycle[(a)] based on rates and conditions in:	Gas fired	Electric		
CH_4	$14.42	$2.07	$0.44	$0.38
H_2O	$4.18	$4.18	$7.06	$6.62
Electric	$5.02	$43.44	$20.62	$20.12
Cost/100 lb	$1.91	$4.02	$2.28	$2.20

(a) Utility rates: H_2O rate, $18.19/1000 ft^3; electric, 4.68 c/kWH; natural gas, $4.41/1000 ft^3. Common carburizing conditions: basket size, 24 in. × 36 in. × 5 in.; carburizing temperature of 980 °C (1800 °F); case depth, 1.4 mm (0.055 in.)

An ion carburizing furnace may be maintained in operating condition with 85 to 140 L (3 to 5 ft^3) per hour of air, thus providing minimum degradation of furnace elements and the hearth.

Efficiency in the Utilization of Carburizing Gas. In view of the very high carburizing rates achieved, and the relatively small amount of carburizing gas fed into the furnace, it is safe to assume that the efficiency in the utilization of the carburizing gas should be quite high. Although precise knowledge of this efficiency is not critical to the practice of plasma carburizing, the efficiency of gas utilization should be known so that the flow of carburizing gas through the furnace might be optimized to obtain the best balance between high utilization efficiency and carburizing rate. The quantities which must be measured to permit calculation of this efficiency are shown schematically in Fig. 16. As shown, the hydrocarbon utilization efficiency is given by the ratio:

$$h_h = \frac{V_i - V_c}{V_i} x100 \qquad \textbf{(Eq 2)}$$

The apparatus needed to make these measurements is shown schematically in Fig. 17. Basically, flow meters measure the volume, or mass, flow into the furnace and a large evacuated tank collects the entire effluent from the furnace during carburizing. To avoid contamination of the furnace effluent with vacuum pump oil vapors, the collecting volume is made large in comparison with the volume of the furnace so that it may serve as the vacuum pump for the entire system for the duration of the experiment. The experiment is run under steady-state conditions for 15 min. The collecting volume is then isolated from the system and backfilled with dry nitrogen. The amount of methane in collecting volume is measured with a flame-ionization analyzer which displays the methane concentration directly in parts per million.

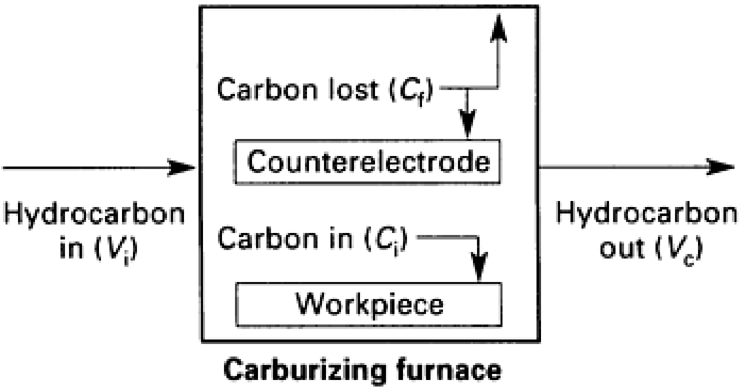

Fig. 16 Schematic measurement of hydrocarbon-utilization efficiency. Source: Ref 7

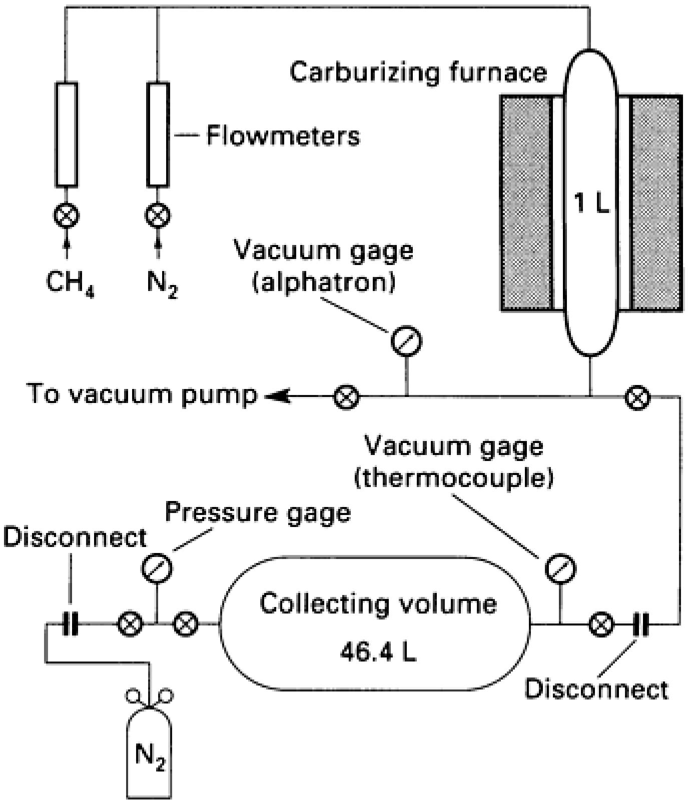

Fig. 17 Schematic of apparatus for measurement of hydrocarbon-utilization efficiency

Results obtained for a carburizing-gas space velocity of approximately one furnace volume per hour is shown in Fig. 18. Here the gas utilization efficiency is plotted versus the degree of dilution with nitrogen. For pure methane the efficiencies obtained are spread over a range of 40 to 75%. As the dilution with nitrogen is increased, the percentage of the methane consumed also increases. At a dilution of 9-to-1, efficiencies in the neighborhood of 90% are consistently obtained, but the carburizing rate is noticeably decreased as shown in Fig. 19. At a ratio of equal parts of nitrogen and methane, the carburizing rate is essentially the same as that obtained with pure methane (Fig. 19) but the efficiency of utilization (Fig. 18) is in the range of 70 to 80%, thus indicating that more hydrocarbon is being added than necessary. At this same dilution, but with the flow reduced by one half (approximately 0.5 furnace volumes per hour), the efficiency (shown by the open circle data points in Fig. 18) again increases to nearly 90%. As shown by the dashed curve in Fig. 19, however, the carburizing rate is less than that obtained with the 1:1 ratio at a flow rate of one furnace volume per hour. These results indicate that a furnace would have to be fine-tuned to achieve the optimum balance between carburizing rate and gas utilization efficiency. Because such a small amount of the hydrocarbon carburizing gas is needed, it is questionable whether efforts to achieve a high efficiency of gas utilization would be worth the risk of reducing the carburizing rate. In addition to carburizing rate, other factors, such as sooting, should govern the hydrocarbon dilution ratio and the atmosphere flow rate.

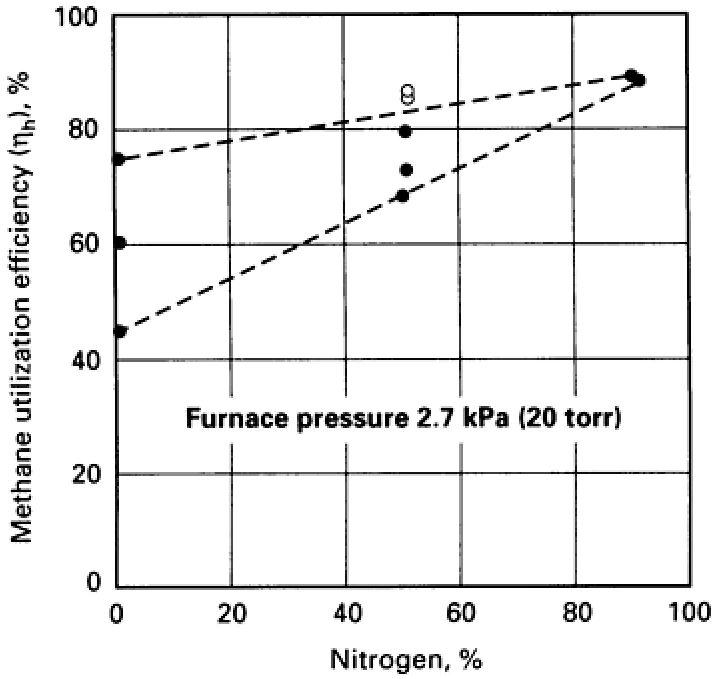

Fig. 18 Hydrocarbon-utilization efficiency (η_h) versus percent nitrogen in carburizing atmosphere. Source: Ref 7

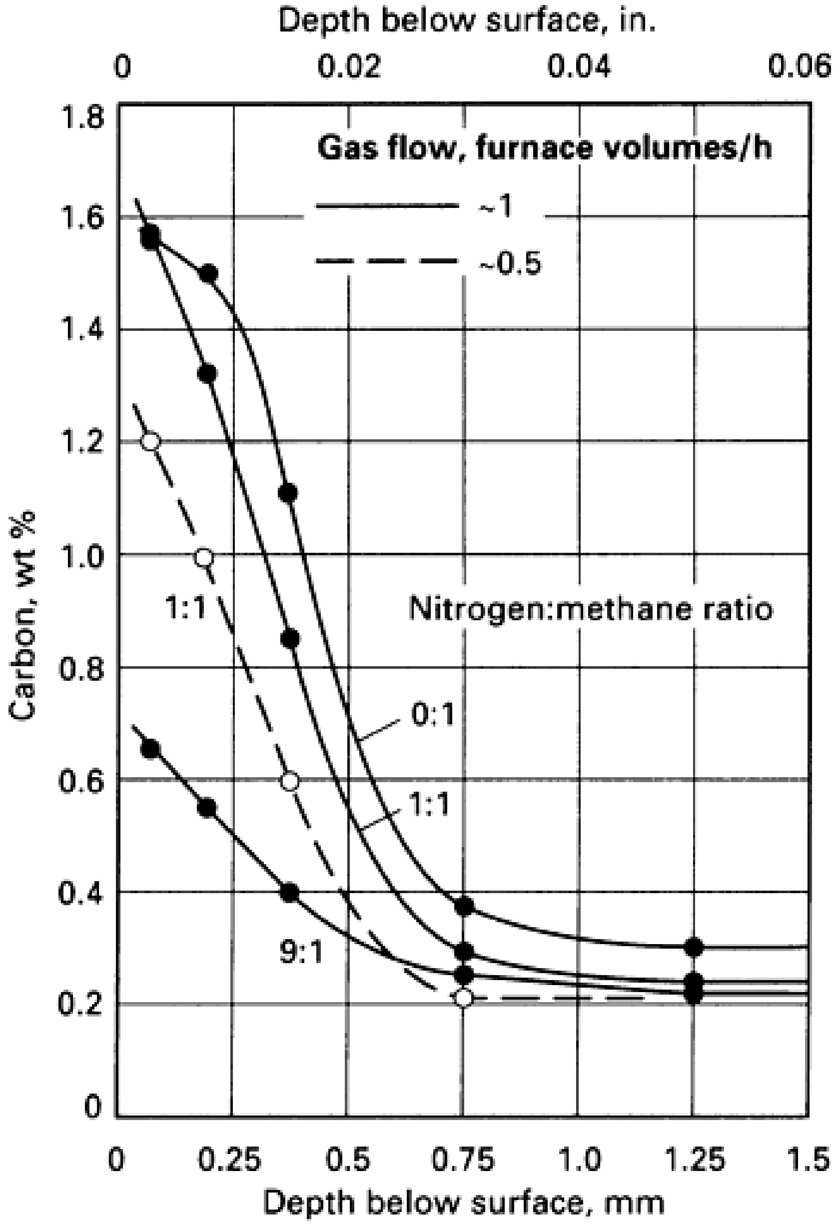

Fig. 19 Carbon concentration profiles in AISI 1524 steel after ion carburizing for 15 min at 1050 °C (1920 °F) in atmospheres and with flow conditions indicated

Equipment Requirements. The physical arrangement of the apparatus and electrical circuitry required for plasma carburizing is shown schematically in Fig. 20. In this arrangement, the workpiece (cathode) is at ground potential and the positive potential needed to establish and maintain the glow discharge is fed into the vacuum enclosure through a suitable insulated lead-through to a counterelectrode (the anode). Auxiliary heating elements (either radiant or induction), surround the workpiece to heat it to the carburizing temperature because the heat losses of the plasma are insufficient to heat the work load to the carburizing temperature (900 to 1000 °C, or 1650 to 1830 °F). An experimental carburizing furnace reflecting this arrangement is shown in Fig. 21. In this furnace, the workpiece and furnace are at ground potential and the high voltage is fed in through a water cooled insulated lead passing through the shell and the heating muffle (Ref 7).

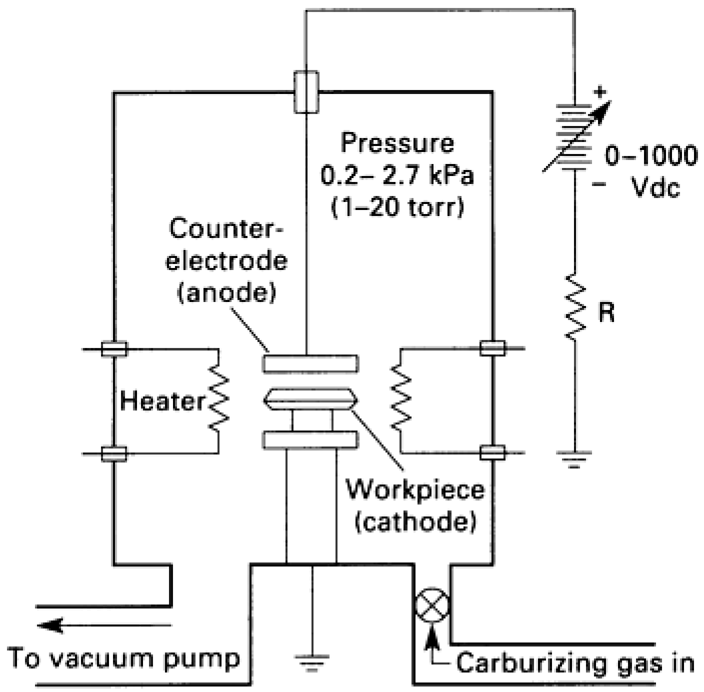

Fig. 20 Schematic of plasma (ion) carburizing apparatus

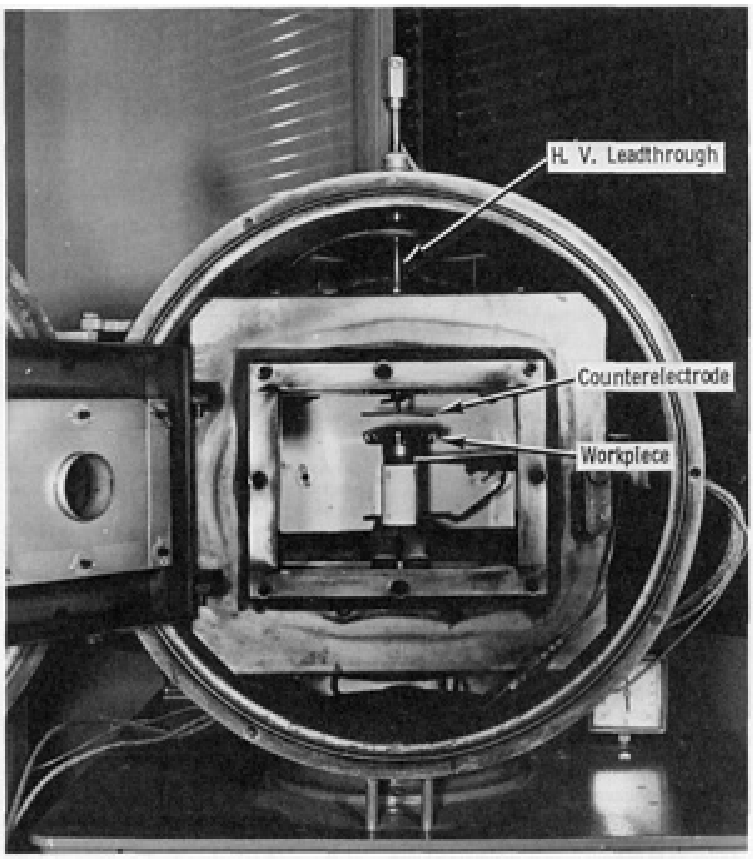

Fig. 21 Experimental plasma (ion) carburizing furnace. Courtesy of General Motors Research Laboratories

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Application to Carburizing Practice

Production Equipment. Figure 22 shows a production two-chamber ion carburizing furnace installation. The addition of the load support insulators and an ion power supply is the only difference between it and a two-chamber integral-oil-quench vacuum furnace. Depending on the manufacturer, these additions may require some periodic maintenance. The ion power supply, for example, needs its cabinet cooling filters cleaned regularly (once a month).

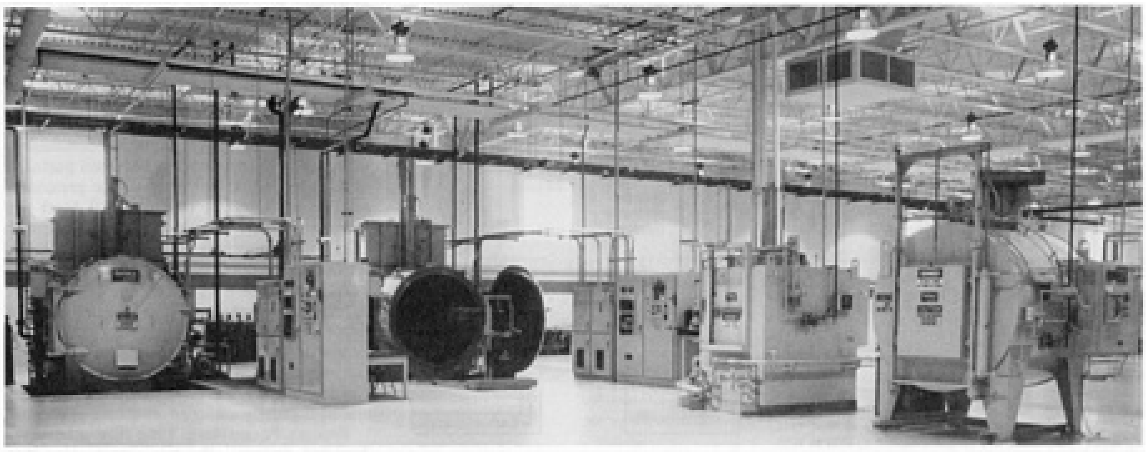

Fig. 22 Production installation of two dual-chamber ion carburizing furnaces. Courtesy of Surface Combustion, Inc.

Periodic maintenance of the furnace itself is minimal, although some plasma carburizing furnaces require cleaning of the load support insulators to remove carbon buildup and thus ensure electrical isolation. In some furnaces, load support devices are self cleaning with only monthly maintenance requirements.

If the load support insulators require cleaning, an air-burnout cycle can be used to remove the carbon deposits. In one manufacturer's equipment, for example, cleaning is accomplished by an automatic program cycle which adds 85 to 140 L/h (3 to 5 ft^3/h) of air to the furnace at 1150 °C (2100 °F) for 1 h. Under normal operating conditions a burnout cycle is recommended after 100 h of carburizing (plasma-on) time. An indication of the need for a burnout is a high count rate on the glow-interruption counter.

Loading Requirements and Limitations. In order to carburize, the plasma envelope must surround the component part. Thus, the parts must be fixtured or positioned such that they do not contact each other. In Fig. 23, for example, the load is composed of gears stacked in layers separated by a woven wire screen between layers. The component gears are carburized uniformly (±0.05 wt% C at the surface). The basket liner and the woven wire screens are chosen to minimize the contact area to the component parts. It is usually less than 3.2 mm (0.125 in.) diameter wire with a wide grid spacing. The parts cannot be shovel loaded because the plasma envelope would be mechanically masked. Thus the parts are positioned so that the plasma envelope of one component part does not touch the plasma envelope of its neighboring part. There is approximately 6.4 mm (0.25 in.) spacing between parts. It should be noted that at absolute pressures of 130 to

3330 Pa (1.0 to 25.0 torr) for plasma or ion carburizing, the methane (CH_4) concentration is too low to carburize without the plasma. To date, tests have indicated that a CH_4 atmosphere must be at a pressure of at least 13 kPa (100 torr) to carburize from the atmosphere alone. This is the minimum absolute pressure required for vacuum carburizing. Thus, the plasma in ion carburizing increases the carbon potential at a greatly reduced absolute pressure.

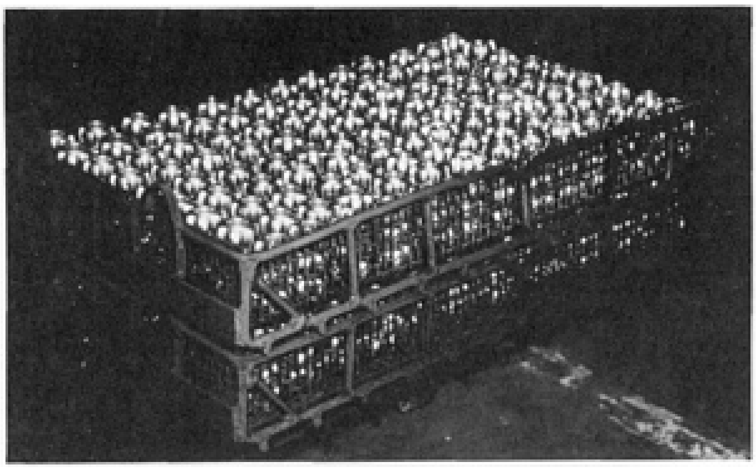

Fig. 23 Racked array of universal-joint components ready for ion carburizing. Two stacked fixtures constitute one furnace load of 1500 parts. Courtesy of Dana Corporation

Process Parameters. Like any other carburizing process, the two parameters that determine the surface carbon and the case depth for an alloy being carburized are time and temperature. The temperature, and indirectly the time, determine the grain size and mechanical properties to be achieved. A higher temperature is used to achieve more rapid diffusion rates. The use of higher temperatures, however, is not considered favorable by aerospace companies because the base properties of the steel are diminished. Higher temperatures also increase the potential for distortion.

Once a temperature is chosen, the time is determined from Harris's equation--case depth proportional to square root of the carburizing time. Diffusion time must be added or else deleterious carbides will still form upon cooling. Plasma carburizing is different from equilibrium atmosphere carburizing in that a constant carbon potential is not maintained, but rather the steel is taken to carbon saturation for the temperature chosen. Then by Fick's Law, the diffusion of the carbon occurs (without the plasma) as a function of time and temperature only. This establishes the surface at the desired carbon potential as well as the carbon gradient of the carbon case from the surface. This boost-diffuse method of carburizing is the only way plasma carburizing can provide predictable case depth from the time and temperature.

Process Pressure. After a time-and-temperature cycle is established, the operating absolute pressure is chosen. The operating pressure can be any value provided the plasma covers the parts and no hollow-cathode effect is evident. The pressure is usually chosen to be low, in the range of 130 to 670 Pa (1 to 5 torr), because optimum carburizing uniformity is achieved in this range. If the inside diameter is the critical area to be carburized, the pressure must be increased to the point that the plasma enters the cavity and covers the sidewall of the cavity. Likewise, if the plasma luminescence or visible glow overlaps within the cavity, a detrimental condition known as hollow-cathode effect can occur (see the section "Hollow-Cathode Problem" in this article).

The key to determining the necessary operating pressure involves a visual observation to ensure the plasma is covering the load. The visual check also verifies that no hollow-cathode effects are observed. Other than this effect, the absolute pressure value chosen is somewhat arbitrary.

Carbon Source. The gas utilized as the carburizing agent can be any hydrocarbon, however, the simplest and most commonly used hydrocarbon is CH_4. Propane (C_3H_8) can be used as well. In addition, a hydrocarbon such as CH_4 or C_3H_8 is used in combination with nitrogen mixtures for carbonitriding applications.

Carbon Mass Flow. The more important parameter than gas composition is the carbon mass flow into the plasma. The amount of carbon mass flow, however, is dependent upon the net surface area of the load that can absorb the carbon. Thus, the surface area of the load, the basket, and tray must be approximated to within 10% of its actual value.

As indicated in Fig. 24, the required uniformity of carburizing can be achieved if a minimum carbon mass flow into the plasma is achieved (Ref 14). A minimum mass flow of 3×10^{-4} grams of carbon per minute per square centimeter of

surface area achieves uniform carburizing This is equivalent to 0.37 L (0.013 ft^3) per minute of CH_4 per square inch of surface area. It is important to remember that this mass flow per unit surface area is based on only the surface area of the load that the plasma will carburize. Even though the baskets and the trays are within the plasma and are being carburized at a lower rate, because of their alloy content, they are not the active part of the load, which is absorbing the carbon. Thus, the surface area used in the calculation for the carbon mass flow should represent the net area that is active to the carbon. This will minimize any sooting of the component parts, baskets, and tray, but still provide optimum carbon for uniform carburizing.

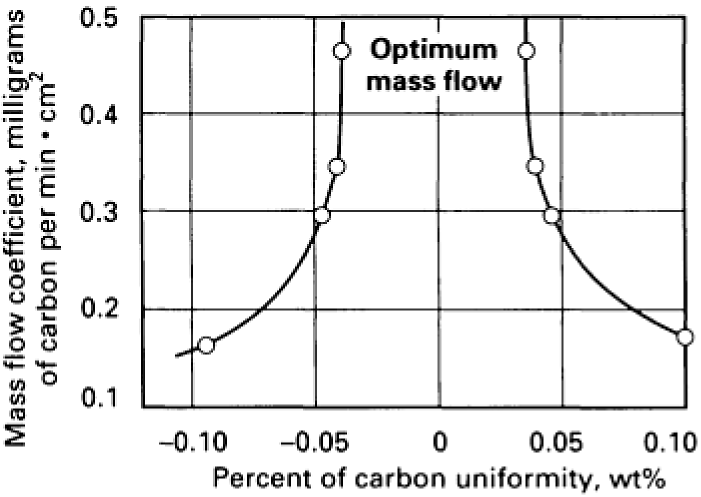

Fig. 24 Carbon mass flow to achieve surface carbon uniformity. Source: Ref 14

The minimum power density (Fig. 25), or the throwing power of the plasma per unit area, is given as function of temperature to achieve a uniform surface carbon potential within ±0.05 wt% C. As the temperature increases, more plasma power must be supplied to maintain carbon saturation level at the surface. As noted earlier, the carbon saturation level increases with temperature as well as the diffusion coefficient (Fig. 5 and 6), such that more carbon must be supplied. As indicated above, at the absolute pressures of 130 to 3330 Pa (1 to 25 torr), the only source of carbon is the plasma.

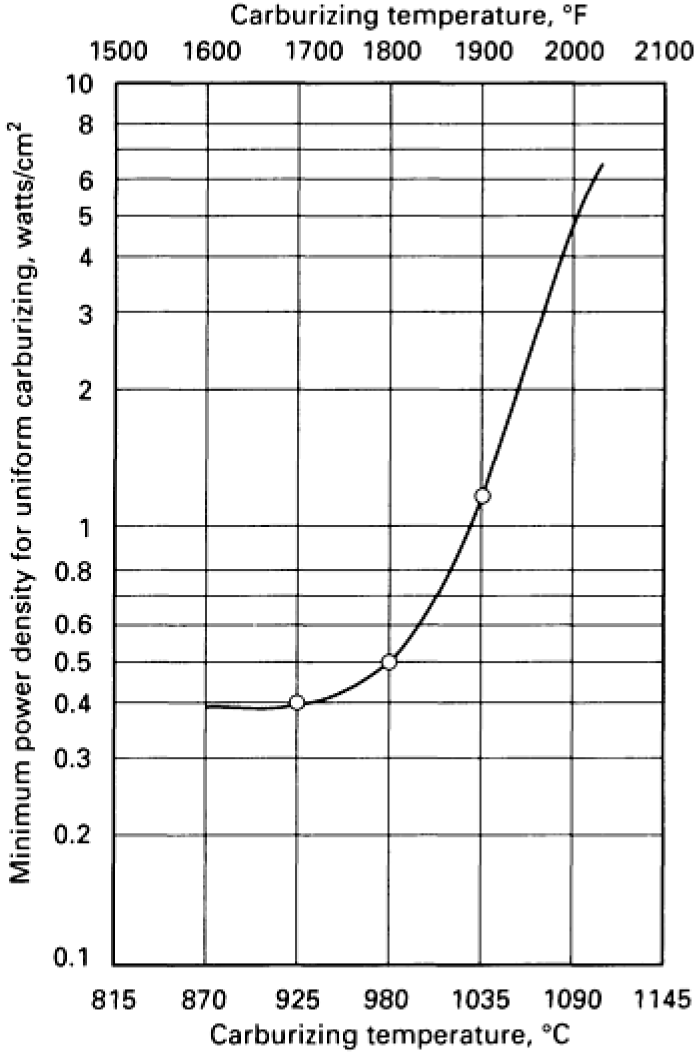

Fig. 25 Minimum power density as a function of the carburizing temperature. These minimum power densities are based on a constant dc supply. Results will differ if a pulsed power supply is used. Source: Ref 14

Again, the surface area must be known to utilize the power density or throwing power of the plasma of the value depicted in Fig. 25. Because the plasma must cover the whole load including the baskets and the tray, the plasma power required must be calculated by taking the total area multiplied by the power density of Fig. 25. The total area of the load must be calculated to within 10% of the actual area and the minimum power density utilized from Fig. 25. Power densities higher than the minimums of Fig. 25 can be used; however, the added power of the plasma can add sufficient energy to heat the load above the furnace operating temperature that is controlled by the resistance heaters. Figure 25 is the minimum watt density required for uniform carburizing and still maintain a ±14 °C (±25 °F) temperature uniformity during carburizing.

Down-Hole Carburizing. As indicated above, one of the operating parameters of the plasma is the absolute pressure. The control of the absolute pressure determines the depth to which the plasma penetrates a hole or cavity. The thickness of the cathode visible glow or luminescence is a function of the pressure, the gas composition, and the temperature. In order for the glow to appear down the cavity, the anode must still be in a line-of-sight with the cavity of the part. Empirically, this has been established at a length/diameter (*L*/*D*) ratio of 10/1. (The *L*/*D* ratio is the length of the hole or cavity divided by the diameter.) This empirical relationship is only applicable to blind-hole cavities.

Hollow-Cathode Problem. The above parameters give the optimum operating conditions for uniform carburizing. It was also indicated that in choosing the pressure, a visual observation of the load must be noted to ensure that the hollow-cathode effect is not present. When observing the load and any cavities within the load, the cathode glow or luminescence overlaps in the cavities, the current density cascades into extreme values and causes severe overheating or possibly melting.

Figure 26 is an empirical relationship that describes the region of hollow cathode at various temperatures and *L*/*D* ratios. These curves were established for a CH_4 atmosphere and would be shifted for other atmosphere compositions. To the right of the curves is the safe region and for a given *L*/*D* ratio the pressure is indicated where the cathode glow or

luminescence does not overlap. At this pressure, the current density remains stable, and no overheating occurs. The data in Fig. 26 were generated in a CH_4 plasma with the diameter of the cavities varying from 3.2 mm (0.125 in.) to 9.5 mm (0.375 in.). As indicated in Fig. 26, the safe region for a specific *L*/*D* is to the right of the curve at each temperature. As indicated above, the thickness of the cathode visible glow or luminescence is a function of the pressure, gas composition, and temperature. The glow luminescence becomes thicker as the temperature increases due to the kinetic activity. Thus, a hollow cathode may exist at one pressure and temperature, but disappear as the temperature is lowered or the pressure is increased. Figure 26 gives a starting point, however, the visual observation of the load is still required to ensure against hollow-cathode effects.

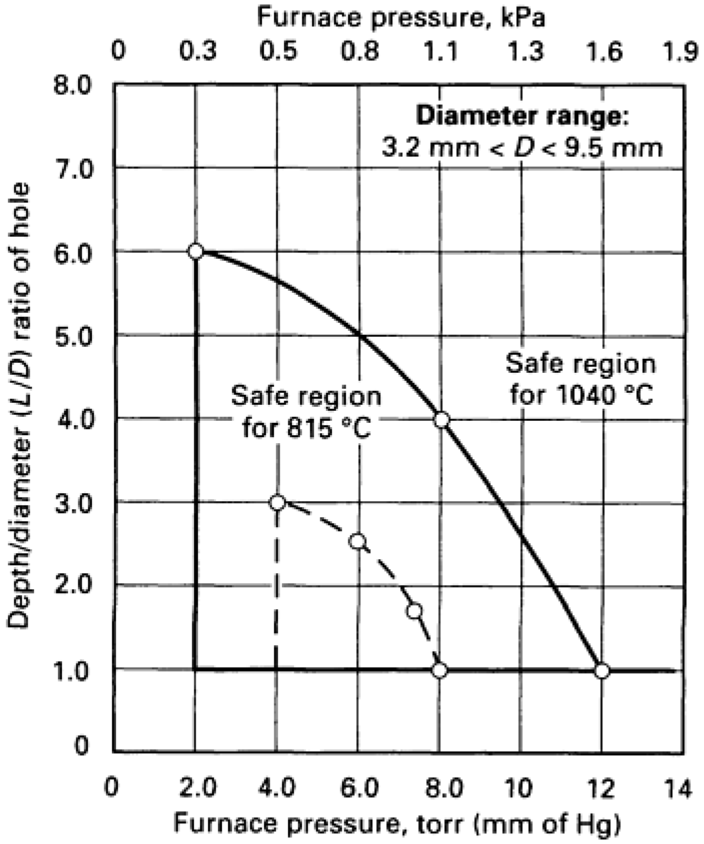

Fig. 26 Hollow cathode regions as a function of pressure for two different operating temperatures

Properties of Ion Carburized Parts. Aside from the faster carburizing rates associated with the fast rate of reaching carbon saturation, plasma (ion) carburizing offers some additional metallurgical advantages. Because the glow-discharge parameters can be adjusted to give more control of the carburizing mechanism (carbon saturation and, in turn, diffusion), greater uniformity of the carburized case can be achieved.

Because carburizing and oil quench hardening occurs under a vacuum, grain boundary oxides do not form in plasma carburizing. This elimination of intergranular oxides improves fatigue performance in the unground condition (see, for example, Ref 15). In atmosphere carburizing, grain boundary oxides to a depth of 0.05 mm (0.002 in.) to 0.12 mm (0.005 in.) are commonly found. The carbide level in the microstructure is no different than that found in atmosphere carburizing.

Parts in a load can be mechanically masked effectively by simply preventing the glow discharge from coming into contact with the areas not to be carburized, for example, by stacking or proper fixturing. Likewise, copper plating selected areas is effective for masking. The water-based and organic-based paint-on stop-offs have not been effective to date in masking for plasma carburizing. The plasma tends to spall off the coatings used and at high pressures the plasma gets under the coating and carburizes the area that was masked.

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Microstructures and Properties of Carburized Steels

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Introduction

CARBURIZING is a remarkable method of enhancing the surface properties of shafts, gears, bearings, and other highly stressed machine parts. Low-carbon steel bars are fabricated, by forging and machining, into finished shapes and then are converted by carburizing into a composite material consisting of a high-carbon steel case and low-carbon steel core. When this steel composite is quenched to martensite and tempered, the high hardness and strength of the case microstructure, combined with the favorable case compressive residual stress developed by interactions between the case and core during quenching, produce very high resistance to wear, bending fatigue, and rolling-contact fatigue.

The furnaces, atmospheres, control, and kinetics of carburizing are described in other articles in this Volume. The purpose of this article is to describe the microstructure, properties, and performance of carburized steels. At first glance, the microstructures of carburized steels appear to be quite straightforward: high-carbon martensite gradually replaced by martensite of lower carbon content with increasing distance from the carburized surface. This view of the microstructures of carburized steel is essentially correct. Lightly tempered martensite is the dominant microstructural constituent of properly carburized steel. However the martensite changes in morphology, amount, and properties as a function of distance from the surface. Other microstructural constituents may also be present and may significantly affect the performance of carburized parts. These other microstructural components include retained austenite; carbides of various origins, sizes, and morphologies; inclusions; processing-induced surface oxides; prior austenite grain boundaries embrittled by phosphorus segregation; and nonmartensitic transformation products of austenite, such as bainite and pearlite.

Because most carburized parts are subjected to cyclic loading, by far the most important property or measure of their performance is fatigue resistance. Hardness is another property commonly measured in carburized steels and is used as a quality control parameter to document carburizing success and to establish case depths. However, although many carburized steels have the same hardness profiles, they may have different microstructures and perform quite differently. Mechanical properties as measured by tensile testing are of little value because of the gradients in microstructures and properties between the surface and center of carburized steels. Thus strength and fracture toughness, which are useful in estimating critical flaw or crack sizes, are largely inferred from measurements on through-hardened steels of medium and high carbon content, although some measurements of fracture toughness have been made on carburized specimens (Ref 1, 2).

Throughout this article, the various microstructural components are described. Where possible, the effect of microstructure on properties, primarily hardness and fatigue resistance, are incorporated into the discussion of a particular microstructural feature.

Much of the published work on carburizing is devoted to processing (Ref 3, 4), aided by computer modelling and control technology (Ref 5, 6). Nevertheless, the understanding of the role microstructure plays in optimizing the performance of carburized steels continues to grow. Parrish thoroughly reviewed microstructures and properties of carburized steels up to 1977 (Ref 7) and, with Harper, authored a comprehensive treatment of all aspects of gas carburizing (Ref 8). An atlas of the microstructures of carburized steels has also been published (Ref 4). Proceedings of recent conferences on carburizing include articles on structure-property correlations as well as processing advances (Ref 1, 5, 6). The above list of major references is far from exhaustive, especially in view of the many articles published in journals, but it provides a good starting point for readers interested in more information regarding the processing, selection, and performance of carburized steels.

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Carbon and Hardness Profiles

The object of carburizing is to produce a high-hardness, high-carbon case on a low-carbon steel core with low-to-medium hardness. This objective is accomplished by the introduction of carbon into austenite by various gas-metal surface reactions (Ref 9, 10) and the diffusion of carbon through the austenite from the surface into the core (Ref 9, 11). The austenite is then quenched and is converted to microstructural gradients by solid-state phase transformations during cooling. The microstructural gradients in turn produce hardness gradients. Figures 1 and 2 show, respectively, typical carbon and hardness gradients from test bars of gas-carburized SAE 8620 steel. The microstructural gradients associated with such carbon and hardness gradients are described in the section below. Residual-stress gradients, which develop because of transformation and temperature gradients during quenching, are described in the section "Residual Stresses" in this article.

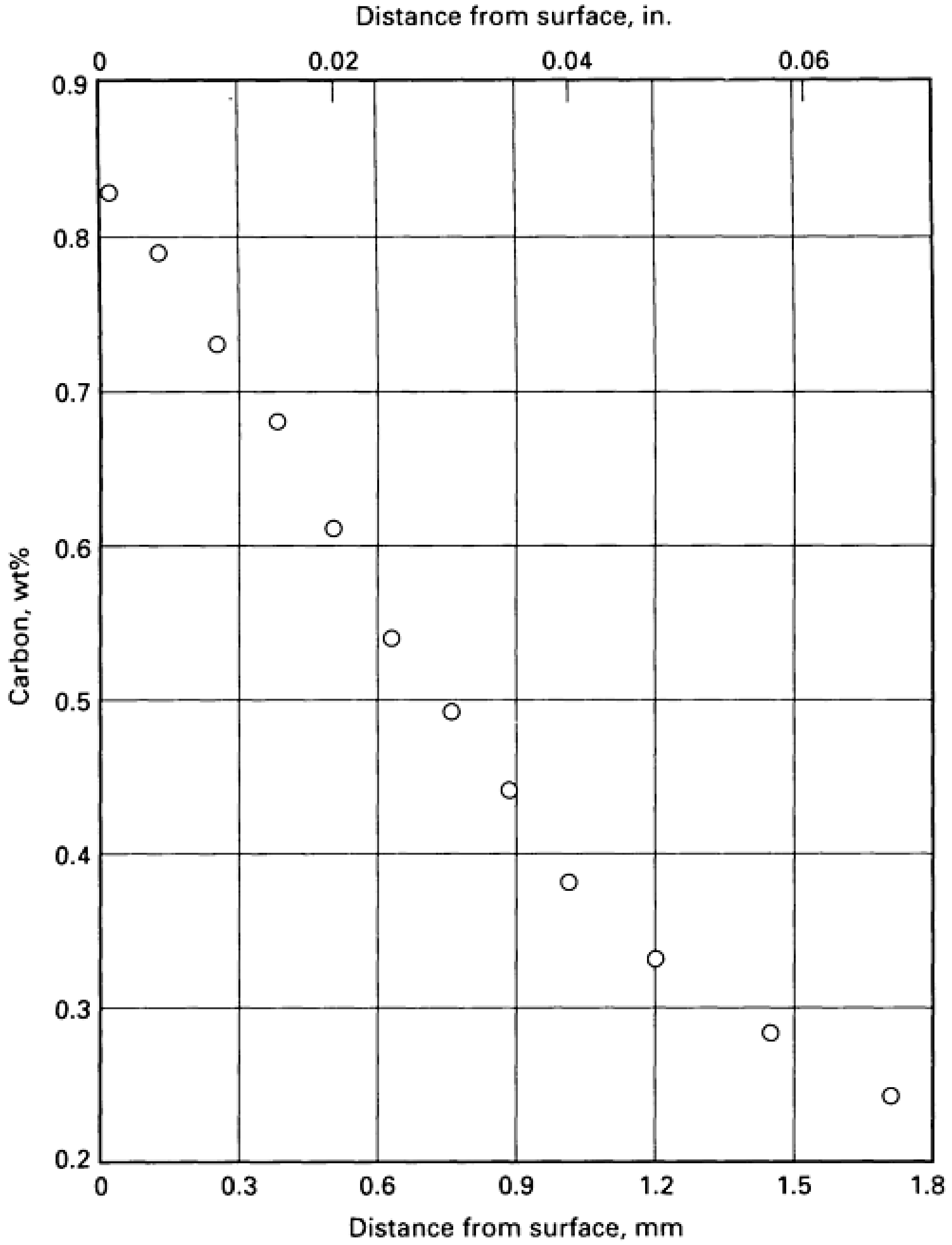

Fig. 1 Carbon gradient in a 25 mm (1 in.) diam test bar of 8620 steel after gas carburization at 925 °C (1700 °F). Source: Ref 12

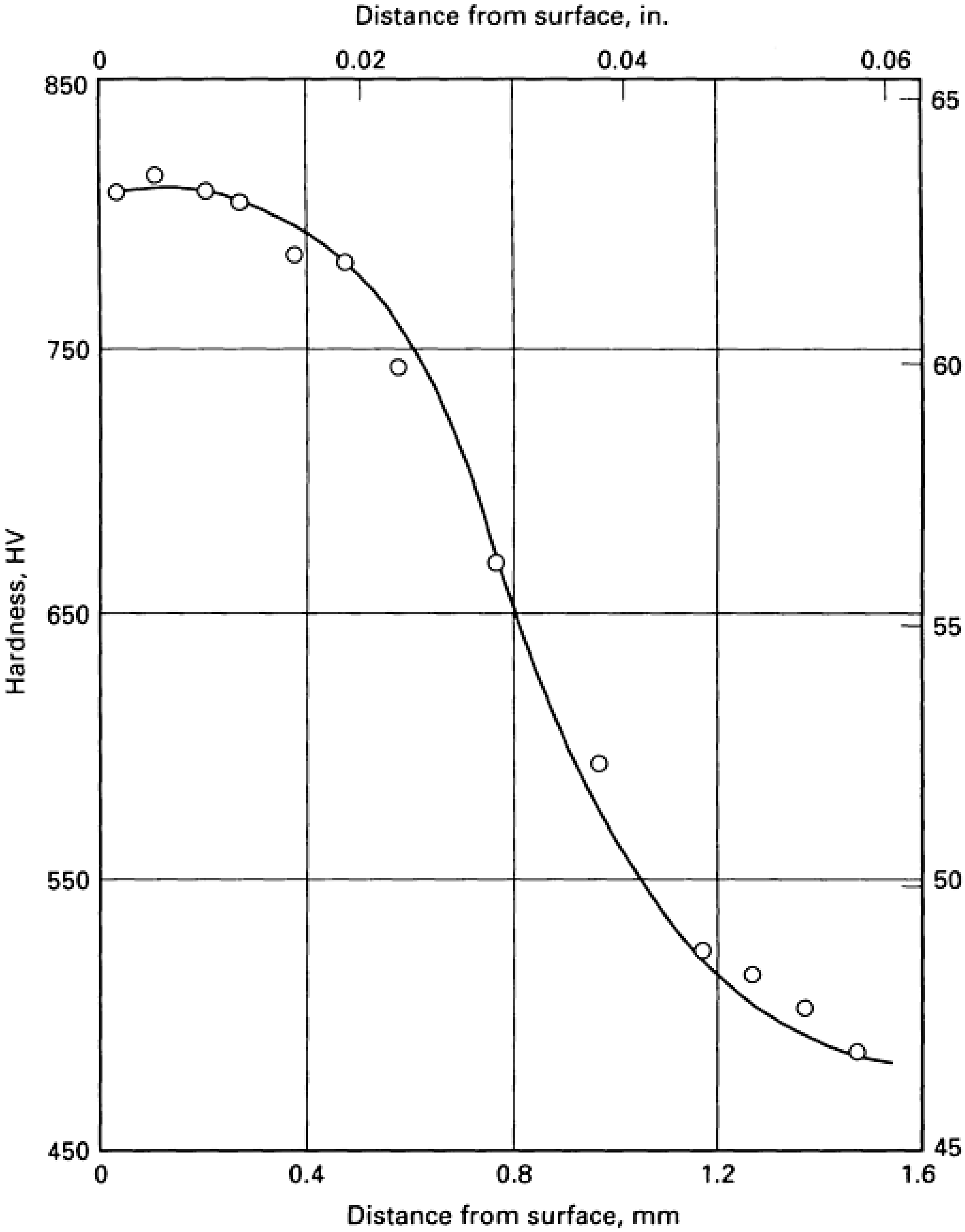

Fig. 2 Microhardness profile of 16 mm (0.63 in.) test bar of 8620 steel after gas carburization at 925 °C (1700 °F). Source: Ref 12

Case Depth Measurement. There are several ways to measure the depth of the case produced by a given carburizing schedule (Ref 4). Total case depths can be estimated from etching differences between the case and core. One of the most commonly accepted techniques is to section a part or test bar and measure the hardness profile. The perpendicular distance from the surface to the point where the hardness drops to a given hardness, often specified as 50 HRC (510 HV), is defined as the case depth (see the article "Methods of Measuring Case Depth" in this Volume for further information).

Factors Affecting Case Depth. Many factors, especially those that control surface carbon concentration, such as time and temperature during the various stages of a carburizing process, affect case depth. Frequently the first stage of carburizing introduces a high surface carbon content, on the order of 1.1 to 1.2 wt%, depending on the maximum solubility of carbon in austenite at the temperature of that stage. Such carbon contents would produce undesirable quenched microstructures. Therefore to produce optimum surface carbon concentrations of 0.8 to 0.9%, the second stage of carburizing is performed with lower carburizing atmosphere carbon potentials. Carbon already introduced in the first stage then adjusts to the lower surface potential and also diffuses deeper into the core. This two-stage approach is commonly referred to as the boost-diffuse method of carburizing.

Hardenability, as measured by the hardness method, also affects case depths. Generally, it is assumed that austenite of a given carbon concentration transforms to martensite of a given hardness. However, in carburizing steels with low hardenability or in massive carburized parts, which cool slowly, the austenite may transform to bainitic or pearlitic microstructures of lower hardness than martensite. Therefore, identical carbon gradients may produce quite different hardness gradients, depending on hardenability considerations.

Part shape or geometry also affects case depth. Access of the carburizing atmosphere or the quench severity may be affected by complex part shapes. For example the case depths of carburized gear teeth vary between the pitch line and root areas. Figure 3 shows recommended locations for hardness traverses and core hardness measurements for gear teeth, and Fig. 4 shows differences in pitch line and root traverses for a carburized 8620H gear. The effective case depth is less at the root than at the pitch line.

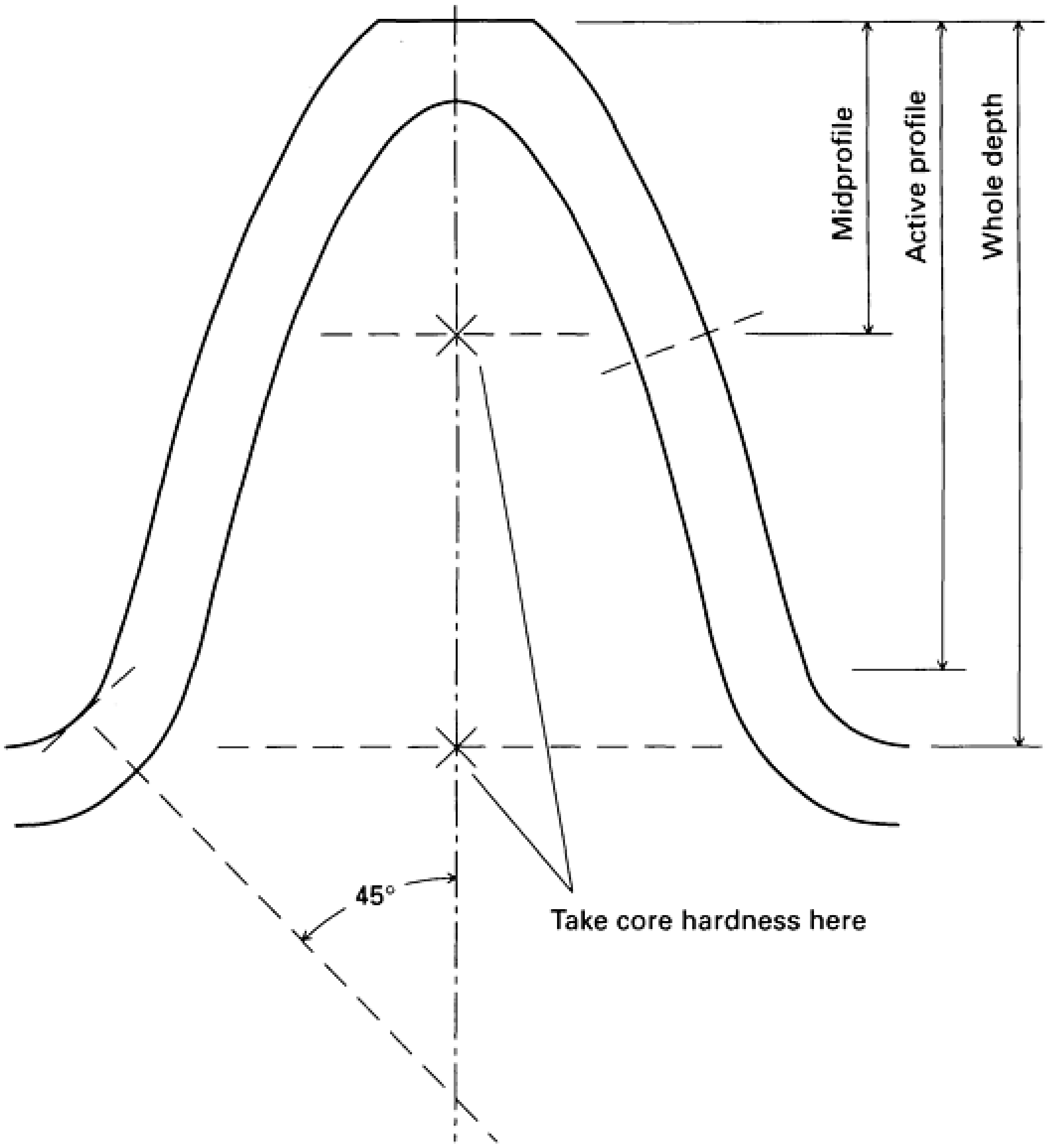

Fig. 3 Recommended locations for hardness traverses (dashed lines normal to tooth surface at midprofile, the pitch line, and root radius) and core hardness measurements of a gear tooth. Source: Ref 13

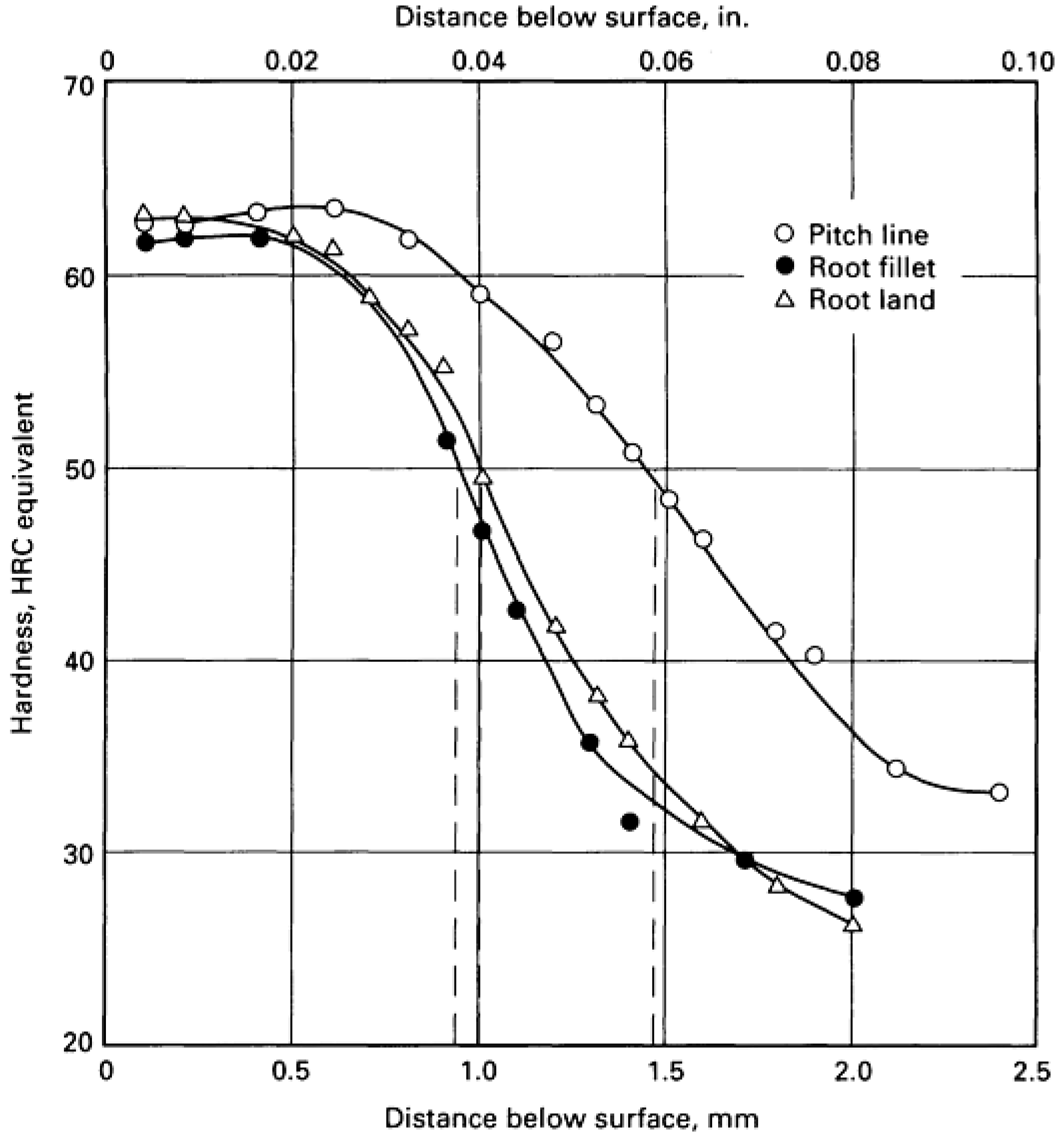

Fig. 4 Hardness profiles and effective case depths at 50 HRC for root and pitch line locations of a carburized and hardened 8620H steel gear. Source: Ref 4

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Martensite and Austenite

Figure 5 shows the typical martensite-austenite microstructure formed close to the surface of carburized steels quenched directly after carburizing. The high-carbon martensite (dark) is formed by a diffusion-less, shear transformation of the austenite and has a morphology characterized by nonparallel plate-shaped crystals (Ref 15, 16). The martensite plates have $\{225\}_A$ and $\{259\}_A$ habit planes with many equivalent variants and therefore assume the many orientations shown in

the micrograph. The sizes of the martensite plates are determined by the austenite grain size and the continuous formation of additional plates with decreasing temperature. The first plates form at the martensite start (M_s) temperature and span the austenite grains; the longest dimension of these plates is therefore equivalent to the austenitic grain size. With decreasing temperature, more martensite plates form between large plates, and they become finer as the austenite is increasingly partitioned by more transformation. According to this sequence of martensite formation, the finer the austenite grain size, the finer is the array of martensite plates.

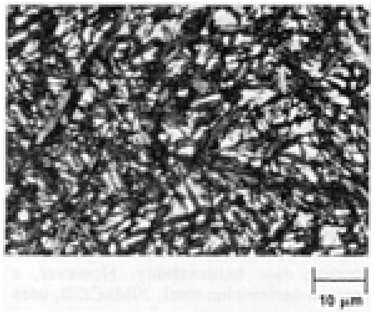

Fig. 5 Plate martensite-austenite microstructure in case of carburized and direct-quenched SAE 4121 (formerly EX24 steel) (0.89Mn-0.55Cr-0.24Mo). Light micrograph. Source: Ref 14

The white areas of Fig. 5 are regions of austenite that have not transformed. This austenite is referred to as retained austenite and is present because of the high stability of high-carbon austenite. Increasing carbon content significantly lowers M_s temperatures and depresses the entire temperature range for martensitic transformation to below room temperature. Consequently there are always significant amounts of retained austenite in the cases of carburized steels quenched to room temperature. Retained austenite plays a significant role in the fatigue of carburized steels, as discussed below, and amounts on the order of 30 to 35% are common in the near-surface cases of specimens quenched directly after carburizing.

Carburized parts may be cooled to room temperature after carburizing and reheated for hardening (Ref 17). Such reheating treatments invariably refine austenitic grain size. If reheating is performed above A_{cm}, that is, the temperature that defines the boundary between the austenite and austenite-cementite phase fields in steels, the structure is completely converted to austenite. Grain size is kept fine by setting austenitizing temperatures just above A_{cm}.

Reheating carburized steels below A_{cm} causes spheroidized carbides to be retained in the case austenite. As a result, the carbon content of the austenite is reduced, M_s is increased, and the quenched microstructure has less retained austenite. Also the carbide particles inhibit grain growth and maintain very fine austenitic grain sizes. Figure 6 shows a martensite-carbide microstructure formed by reheating and quenching a carburized 8620 steel. The small, white, spherical particles are carbides retained during austenitizing and quenching. The matrix structure etches dark and consists of martensite and retained austenite too fine for resolution in the light microscope.

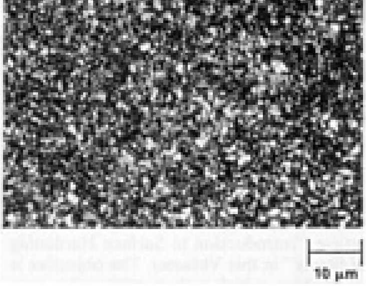

Fig. 6 Martensite-dispersed carbide microstructure in case of reheated and quenched carburized 8620 steel. The carbides are the circular, white features dispersed in the dark, martensitic matrix. Light micrograph. Source: Ref 14

The hardness and strength of martensite increase with increasing carbon content (Ref 16). Therefore the highest hardness of a hardened carburized steel is at or close to the surface. Hardness may peak at a distance from the surface if large amounts of retained austenite, which is much softer than martensite, offset the high hardness of martensite immediately adjacent to the surface where the carbon content, and therefore the retained-austenite content, are at their highest levels. With increasing distance from the carburized surface, the carbon concentration of the martensite decreases, and hardness drops (Fig. 2 and 4). Retained austenite also decreases with increasing distance from the surface; as the carbon

concentration of the austenite decreases (Fig. 1), the M_s temperature increases and more martensite forms on cooling to room temperature. Figure 7 shows retained austenite gradients in direct-quenched and reheated carburized 8620 steel specimens. The dramatic reduction of retained austenite content as a result of reheating below A_{cm} (double reheat) is apparent.

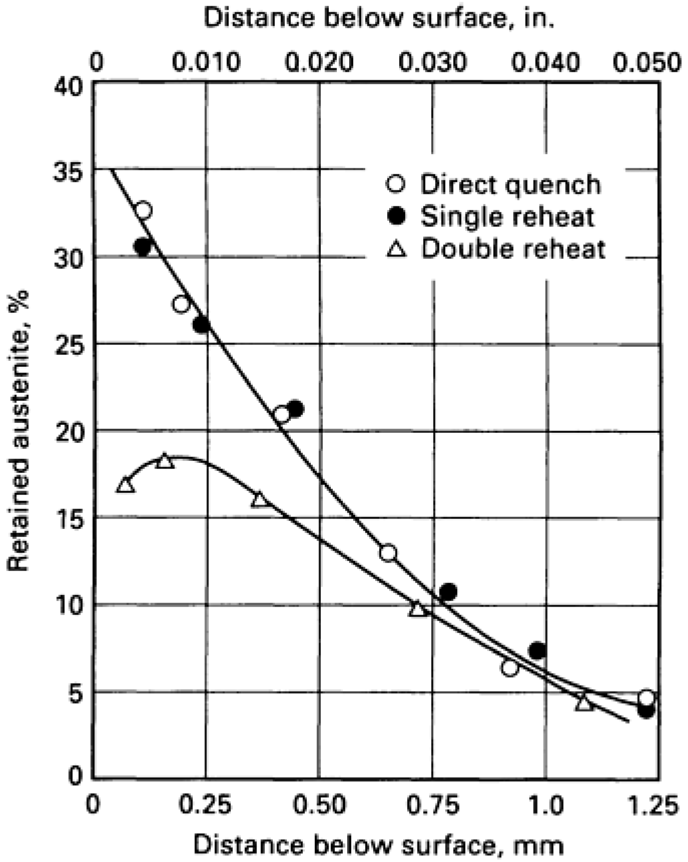

Fig. 7 Retained austenite, measured by x-ray diffraction, as a function of distance from the surface of an 8620 steel carburized at 925 °C (1700 °F). The single and double reheats were accomplished by heating to 845 and 790 °C (1550 and 1450 °F), respectively. Source: Ref 18

The core microstructures of carburized steels are determined by the low carbon content and base hardenability of the carburizing steel. If the steel has low hardenability, the low-carbon core may transform to ferrite and small amounts of pearlite, depending on quench rate. If the steel has high hardenability, the core may transform to martensite. For most highly stressed applications, a martensitic core is desired. Low-carbon martensite has higher strength and fracture resistance or toughness than do ferrite-pearlite microstructures. This increased strength is necessary to prevent subsurface crack initiation, sometimes referred to as case crushing (Ref 8, 13, 19). This mode of fracture occurs at case-core interfaces when heavy contact loads create stresses that exceed the strength of the microstructure at some distance below the surface. Subsurface crack initiation is prevented by producing deeper cases by carburizing for longer times, by using alloy steels with higher base hardenability that transform completely to martensite in the core as well as the case, or by increasing core carbon content. Thus strength is raised above applied stresses at critical subsurface locations.

Figure 8 shows the martensitic core microstructure of a carburized steel containing 1.06% Mn, 0.52% Cr, 0.50% Ni, and 0.17% Mo. The low-carbon martensite is referred to as lath martensite, and the morphology consists of fine laths arranged parallel to one another in regions termed packets (Ref 15, 16). The packets are visible in the light microscope, but most of the laths or individual crystals of martensite are too fine to be resolved by light microscopy.

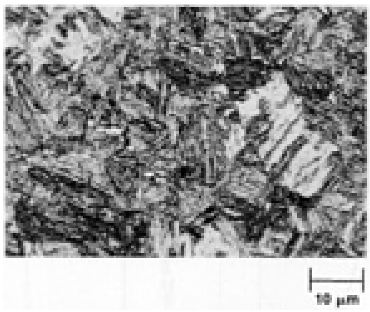

Fig. 8 Lath martensite microstructure in core of gas-carburized type 8719 steel containing 1.06% Mn, 0.52% Cr, 0.50% Ni, and 0.17% Mo. Light micrograph. Source: Ref 20

As-quenched carburized steels are generally tempered between 150 and 200 °C (300 and 400 °F). This final heat treatment step increases toughness slightly and relieves some residual stresses, but case hardness and compressive residual stresses are largely preserved. These changes in properties are accomplished by very fine scale changes of the microstructure. The major change consists of the precipitation of a transition carbide from the martensite supersaturated with carbon by quenching (Ref 16). This carbide, termed eta (η)-carbide, has been shown to have an orthorhombic crystal structure and to precipitate in rows of very fine particles, about 2 nm in size, within the martensite plates. These microstructural changes are much too fine to be resolved in the light microscope, but are reflected by an increased tendency of the martensite plates to appear black after etching. Retained austenite is not transformed by tempering at temperatures of 200 °C (400 °F) or lower. Therefore, the typical polished and etched case structure of a carburized steel consists of dark-etching martensite in a matrix of retained austenite, as shown in Fig. 5.

Figure 9 shows impact and fracture toughness measured for hardened 52100 steel as a function of tempering temperature. The microstructures consisted of retained carbides in a matrix of tempered martensite, typical of that formed in bearing steels or in the surface of carburized steel reheated below the A_{cm} (Fig. 6). The toughness of the 52100 steel was low, even after tempering at 200 °C (400 °F). Other studies show that plane-strain fracture toughness (K_{Ic}) for high-carbon martensite-austenite microstructures tempered between 150 and 200 °C (300 and 400 °F), equivalent to the near-surface case microstructures of carburized steels, ranges between 15 and 25 MPa $\sqrt{m}$ (14 and 23 ksi $\sqrt{in}$) (Ref 22).

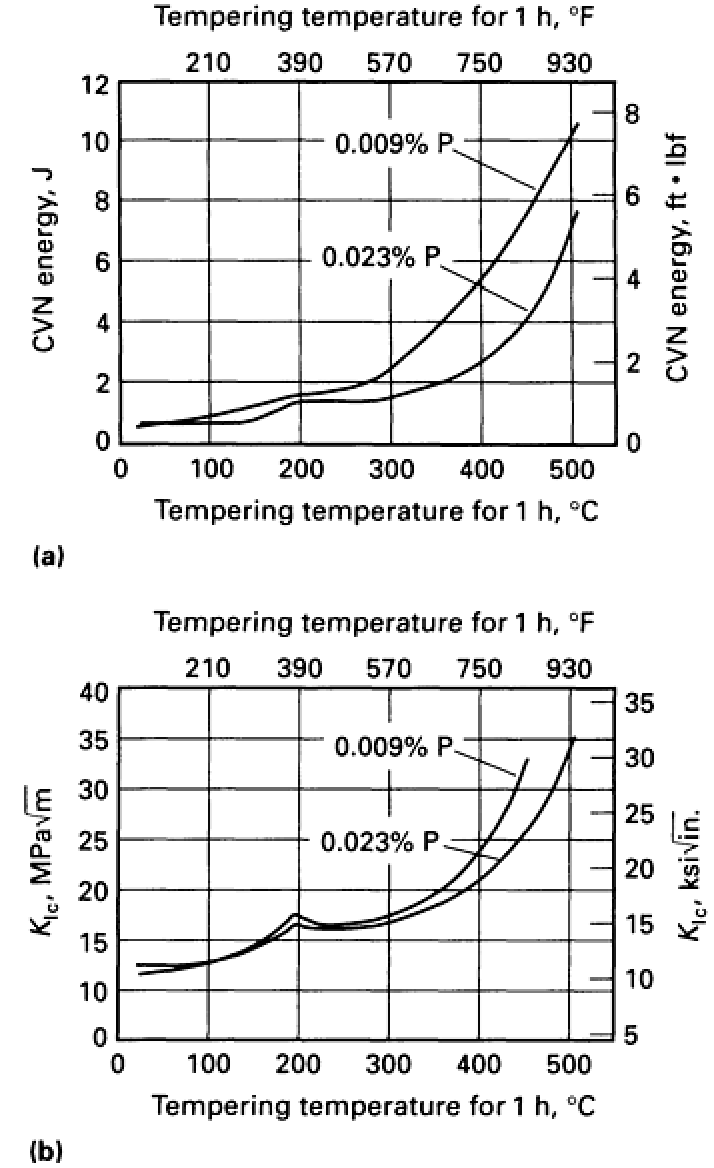

Fig. 9 Toughness of 52100 steel (oil quenched from 850 °C, or 1560 °F) with microstructures of dispersed spherical carbides in tempered martensite similar to microstructures formed in the case of carburized steels reheated below A_{cm}. (a) Charpy V-notch impact energy. (b) Plane-strain fracture toughness (K_{Ic}). Source: Ref 21

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Alloying Effects

The primary concern in alloy development and the selection of carburizing steels is hardenability. In carburizing steels, a given composition must provide adequate hardenability over a range of carbon contents because hardenability is important for both the case region and the core (see the article "Introduction to Surface Hardening of Steels" in this Volume). The objective is to produce a high-carbon martensitic case (for wear and fatigue resistance) and a low-carbon martensitic core to provide sufficient strength to resist case-core failures as described previously.

The goal of hardenability is the formation of hard martensite in preference to microstructures of lower hardness (Ref 16, 23, 24). The controlling factors may be metallurgical, such as the effects of substitutional alloying elements that retard solid-state, diffusion-controlled transformation of austenite to bainite, pearlite, or ferrite; or they may be technological, such as the selection of quenchants, or compensating for slow cooling rates in heavy sections, which provide time for diffusion-controlled transformation at the expense of martensitic transformation. The alloying elements traditionally used for improving hardenability in carburized steels are manganese, chromium, molybdenum, and nickel. Combinations of moderate amounts of several elements have been found to be more effective than large amounts of a single element. Boron is most effective in improving the hardenability of low-carbon steels but loses its effectiveness as carbon content increases. Therefore, it is not expected to improve case hardenability. However, a German carburizing steel, 20MnCr5B, uses boron to remove nitrogen from solution and thereby improve toughness (Ref 25).

Most carburizing steels are deoxidized with aluminum for grain size control. Aluminum combines with nitrogen to form aluminum nitride particles, which limit austenite grain growth during carburizing (Ref 16). Fine grain size reduces hardenability, and Cook has shown that the case hardenability of plain carbon steels is reduced because of the grain-refining effect of aluminum additions (Ref 26). This effect of aluminum on hardenability is not noted in alloy carburizing steels.

Alloy Effects on Hardenability. Hardenability is important for both the case and core regions of carburized steels, and a given steel must have adequate hardenability over a range of carbon contents. Figure 10 shows Jominy end-quench data for the core and for all carbon levels up to 0.9% for an SAE 4620 carburizing steel. The powerful, beneficial effect of increasing carbon on hardenability is shown. Nevertheless, in heavy sections, where cooling rates are low, even case regions may transform to microstructures other than martensite. Jatczak (Ref 27) has evaluated the effects of various alloying elements on the hardenability of high-carbon steels and has shown that higher austenitizing temperatures increase hardenability by dissolving alloy carbides and increasing the amount of carbon and alloying elements in solution in the austenite. Other investigators have also evaluated various aspects of the hardenability of carburized steels (Ref 28, 29, 30, 31).

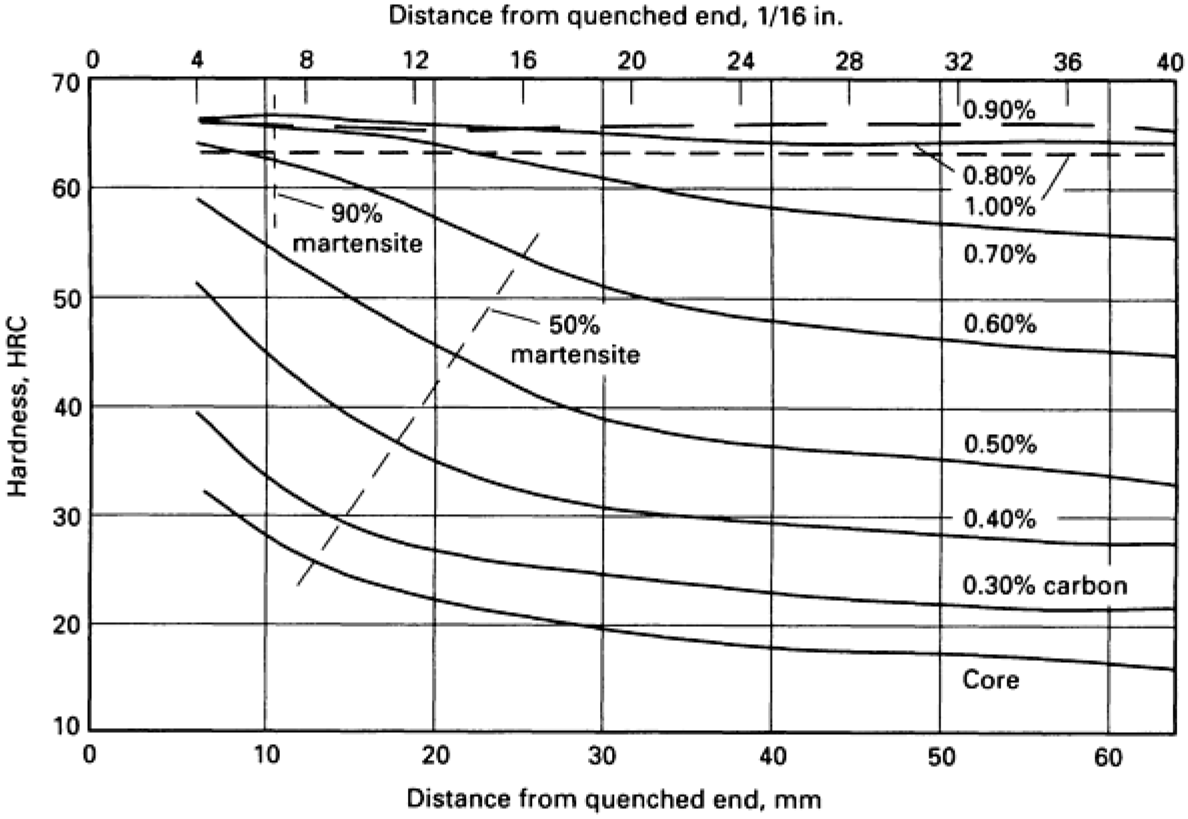

Fig. 10 Jominy end-quench curves showing hardenability differences as a function of carbon content in direct-quenched SAE 4620 steel. Source: Ref 2

Other Alloy Effects. Although hardenability is a major concern in alloying and the selection of carburizing steels, alloy elements also affect other aspects of microstructure. Many of the alloying elements, in particular chromium and molybdenum, are strong carbide and ferrite formers. Those elements shift A_{cm} temperatures (Fig. 11) and raise Ae_1 temperatures, the lowest temperatures at which austenite is stable under equilibrium conditions. The shift in A_{cm} by carbide-forming elements limits the amount of carbon that can be dissolved in austenite and increases the possibility of carbide formation in carburized steels.

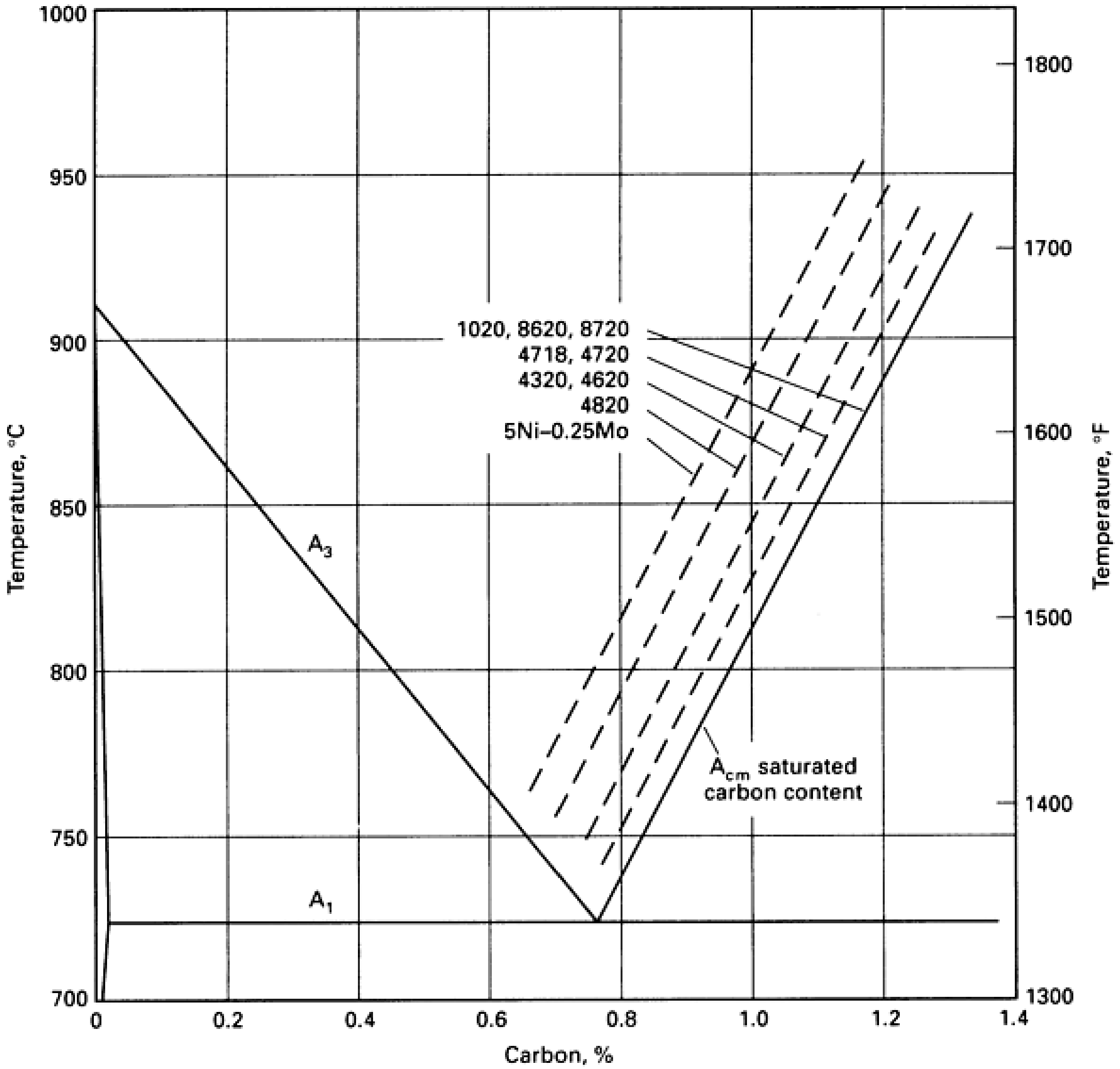

Fig. 11 The shift in A_{cm} temperatures with alloying in various carburizing steels. Source: Ref 32

Many alloying elements also lower M_s temperatures and the transformation temperature ranges for martensite formation (Ref 16, 33). Therefore increased alloying increases the amounts of austenite that are retained in carburized and hardened steels.

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Intergranular Fracture at Austenite Grain Boundaries

Figure 12 shows an example of intergranular fracture at prior austenite grain boundaries in the case overload fracture zone of a carburized 8620 steel. Such intergranular cracking is a major fracture mode of high-carbon hardened steels that have been quenched from temperatures at which the microstructure consists only of polycrystalline austenite. Thus cracking can occur in the case regions of steel directly quenched after carburizing, but rarely in carburized steels that have been reheated to produce finer-grained structures with retained carbides (Ref 17, 22). Fracture in the latter microstructures is low-toughness ductile fracture characterized by closely spaced microvoids that form around the dispersed carbide particles. Intergranular fracture occurs even in carburized steels tempered between 150 and 200 °C (300 and 400 °F), tempering temperatures that are too low to cause tempered martensite embrittlement (Ref 16).

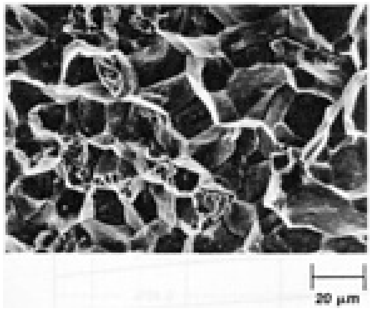

Fig. 12 Intergranular fracture from the overload fracture zone in the case of a carburized SAE 8620 steel. Scanning electron microscope (SEM) micrograph. Source: Ref 14

The reasons for the intergranular fracture of high-carbon case microstructures have been difficult to establish because no associated grain-boundary features are discernible in the light microscope. However, several studies suggest that the sensitivity to grain-boundary fracture is due to a two-step process (Ref 17, 34, 35): first, the segregation of phosphorus to austenite grain boundaries during carburizing or austenitizing for hardening and, second, the nucleation and growth of very thin cementite particles on austenite grain boundaries during quenching. The phosphorus segregation and carbide formation are largely on an atomic scale, but their combined effect is sufficient to produce interfaces that fracture at lower stresses than do the matrix martensite and austenite.

The key to the identification of microstructural features leading to intergranular fracture has been the application of Auger electron spectroscopy (AES), an analytical technique that has very high depth resolution. Auger electrons of specific energies are emitted from specific atoms on a surface that is irradiated with an electron beam in a high vacuum chamber. The Auger electrons have very low energy and originate from a depth of less than 1 nm from the surface of a specimen (Ref 36).

Figure 13 shows Auger spectra from case fracture surfaces of a carburized 8620 steel. The spectra in Fig. 13(a) is from a transgranular fracture surface, while that in Fig. 13(b) is from an intergranular fracture surface. No phosphorus peak is detectable in the spectrum produced from the transgranular fracture, and a small phosphorus peak, clearly shown by the 10× magnification, is produced from the intergranular fracture surface. These observations are consistent with other investigations that show that phosphorus segregates to austenite grain boundaries during austenitizing (Ref 35, 37). A

major difference between the two spectra is the significantly larger carbon peak in the Auger spectrum from the intergranular fracture surface. The carbon peak shape, characterized by a major peak and several auxiliary peaks, is identical to that produced by AES of cementite (Ref 35). Thus AES analysis provides evidence for cementite formation on austenite grain boundaries.

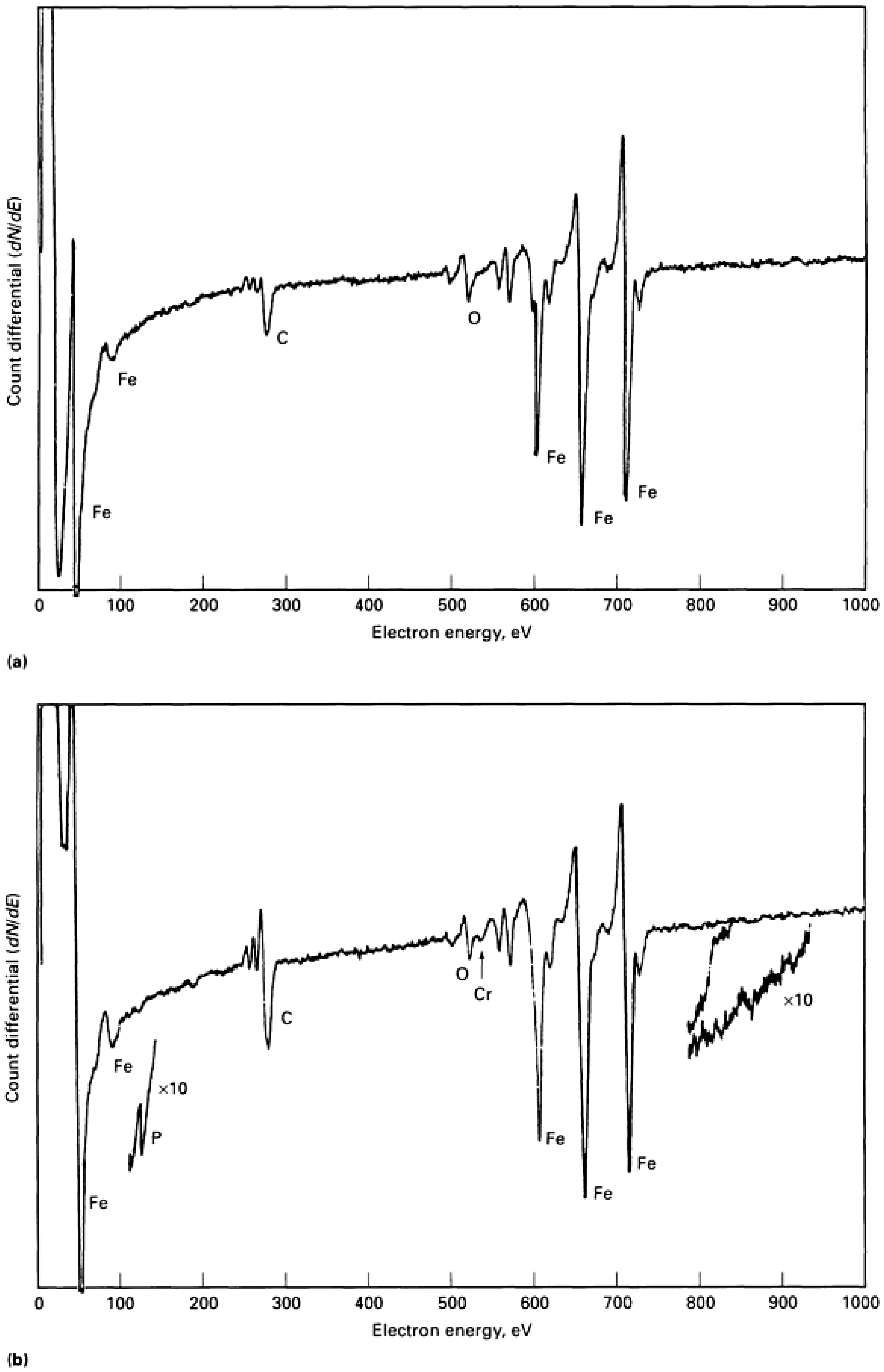

Fig. 13 Auger electron spectra from case fracture surfaces of carburized 8620 steel. (a) From transgranular fracture surface. (b) From intergranular fracture surface. Source: Ref 17

A fracture toughness study on a set of EX24-type steels (or SAE 4121) containing 0.85% C with 0.044 and 0.002% P verified the above observations (Ref 34). The high carbon content was designed to simulate the high-carbon case of carburized specimens. High phosphorus content greatly increased the amount of intergranular fracture. Intergranular fracture was significantly reduced, but not completely eliminated, in the low-phosphorus steel. Oil-quenched specimens developed more intergranular fracture than brine-quenched specimens, a result explained by increased coverage of austenite grain boundaries by cementite due to more time for diffusion during quenching at slower rates.

Ando (Ref 38, 39) has modelled the growth kinetics of cementite allotriomorphs in high-carbon, iron-chromium-carbon alloys. Figure 14 shows that growth takes place in several stages. At first, rapid thickening occurs in a stage controlled only by carbon diffusion, and no partitioning of chromium takes place. However, equilibrium considerations eventually require the diffusion of chromium to the carbide particles, and at that stage the growth of grain-boundary cementite slows significantly. Therefore, the formation of very thin cementite particles, even during the oil quenching of carburized steels, is explained by the very rapid first-stage growth, shown in Fig. 14. High phosphorus content has also been shown to accelerate the formation of cementite grain-boundary allotriomorphs (Ref 35).

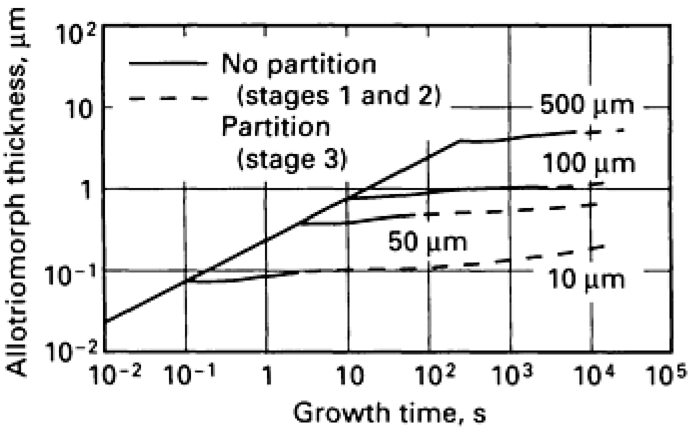

Fig. 14 Simulated growth curves for cementite allotriomorph formation on austenite grain boundaries in an iron-chromium-carbon alloy (Fe, 4.5 at.% C, 1.5 at.% Cr) at 740 °C (1365 °F). Source: Ref 38

Prevention of Intergranular Fracture. As described later in the section "Fatigue Mechanisms," intergranular fracture frequently initiates fatigue cracks in carburized steels. Lower phosphorus contents would reduce intergranular cracking, but the reduction of phosphorus to extremely low levels that might completely eliminate intergranular cracking is dependent on the economics of steelmaking. Reheating carburized specimens with nominal phosphorus contents to produce very fine austenite grain sizes eliminates intergranular cracking (Ref 18, 20), perhaps because of the dilution of phosphorus segregation by a high grain-boundary area. Finally, alloying might be used to eliminate intergranular fracture. Carburizing steels with high nickel contents have high toughness and do not seem to be sensitive to intergranular fracture (Ref 40, 41).

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Microcracking in Carburized Steels

Microcracks frequently form in martensite plates of high-carbon steels. Examples of martensite microcracks are shown in Fig. 15. Marder and Benscoter have shown by serial metallographic sectioning that the cracks form at points of contact between impinging martensite plates (Ref 43). Because the microcracks are formed by the impingement of nonparallel plates of martensite, microcracking density decreases with the transition from plate to lath martensite (Ref 44). Fine austenite grain size also limits microcracking (Ref 42, 45), apparently because smaller martensite plates do not create sufficient stresses to produce cracks.

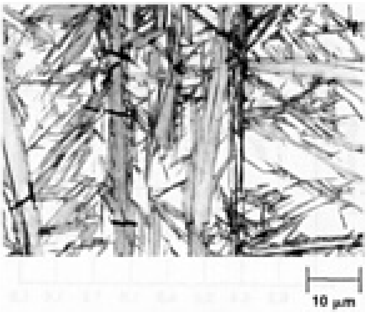

Fig. 15 Microcracks in martensite plates of an Fe-1.86C alloy. Light micrograph. Source: Ref 42

Microcracks have long been known to be present in the case microstructures of carburized steels (Ref 18, 46, 47), especially in coarse-grained microstructures with large martensite plates. The presence of microcracks may contribute to impaired fatigue performance of carburized steels. However, microcracks may have only a very secondary effect on fatigue, in light of the fact that many fatigue cracks initiate at embrittled austenite grain boundaries, as discussed in the previous section. Such grain-boundary cracks effectively bypass the microcracked martensite plates within austenite grains, and therefore the presence or absence of microcracks is immaterial to fatigue crack initiation. On the other hand, the influence of microcracks in martensite plates on transgranular crack propagation would be expected.

A study of grain size effects on microcracking in an Fe-1.22% C alloy provides a link between microcracking and grain-boundary fracture (Ref 45). In that study microcracks were found both in martensite plates and at prior austenite grain boundaries. As grain size decreased, both types of microcracks decreased, but the number of grain-boundary microcracks became a higher fraction of the total. The intergranular microcracks may have formed partly because of martensite plate impingement on embrittled grain boundaries. If such grain-boundary microcracks are present in carburized steels, intergranular fatigue crack initiation will occur at lower stresses.

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Excessive Retained Austenite and Massive Carbides

Moderate amounts of retained austenite are proper and unavoidable in the high-carbon case microstructure of carburized steels. However, excessive amounts of retained austenite, that is, greater than 50%, lower hardness significantly and reduce bending fatigue resistance. The most important cause of excessive amounts of retained austenite is too high a surface carbon content. This condition drives M_s temperatures down and shifts the balance of the temperature range for martensite transformation to well below room temperature. High alloy content also lowers M_s temperatures.

Common locations of excessive surface carbon concentration are specimen corners at which the austenite is saturated with carbon during the first part of a carburizing cycle (Ref 48, 49). The carbon has access to both surfaces of the corner during carburizing but has little physical access to the interior of the specimen during the diffusion part of a cycle. As a result, although carbon content falls to desired levels on the flat or gradually curved surfaces of a part, the carbon content at a corner remains much higher than desired. Figure 16 shows carbon contours determined at the corners of an 8620 steel specimen carburized at 1050 °C (1920 °F). Carbon contents as high as 1.20% were measured at the corner. Excessive retained austenite in the corner microstructure of a 4121 carburized specimen is shown in Fig. 17. Figure 18 shows hardness profiles from corner and plane surface regions of 8620 steel carburized at 930 °C (1700 °F). The corner surface hardness is much lower than that of the plane surface because of high retained austenite content. Reheating of direct-quenched specimens eliminates excessive retained austenite and raises surface hardness (Ref 48, 49).

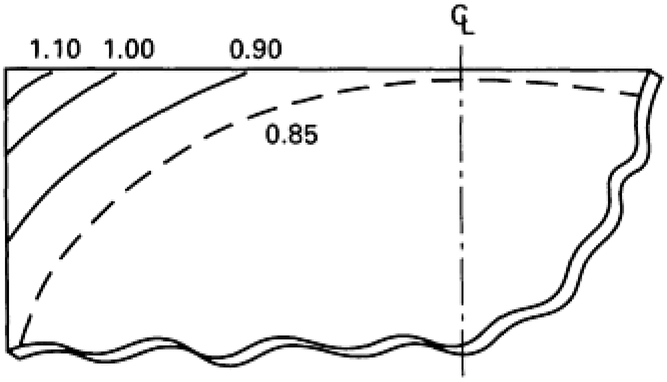

Fig. 16 Schematic of carbon concentrations at the corners of an 8620 steel specimen subjected to carburizing and diffusion at 1050 °C (1920 °F). Based on chemical analysis of chips milled from various locations of the specimen. Source: Ref 49

Fig. 17 High retained austenite content in corner of SAE 4121 steel (formerly EX24) specimen carburized at 1050 °C (1920 °F). Source: Ref 44

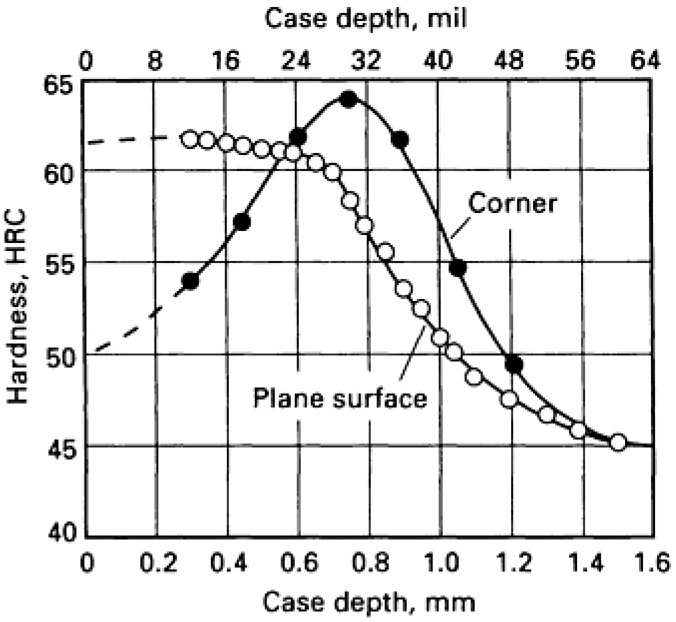

Fig. 18 Corner and plane surface microhardness profiles from 8620 steel specimen carburized at 930 °C (1700 °F). Source: Ref 48

Another consequence of too high a surface carbon content is the formation of massive carbides. The carbides form at austenite grain boundaries and may have different morphologies, depending on alloy content. As discussed relative to Fig. 14, large carbide grain-boundary allotriomorphs require considerable diffusion to grow, and therefore they form during the high-temperature stages of carburizing or when the temperature of the part is lowered to about 845 °C (1550 °F) just prior to quenching. Figure 19 shows two morphologies of massive carbides that have formed in the corners of carburized specimens. Figure 19(a) shows blocky, angular particles formed in an 8620 steel containing nominally 0.5% Cr, 0.5% Ni, and 0.2% Mo. Figure 19(b) shows long, thin carbides formed in an SAE 4121 steel containing 0.55% Cr and 0.24% Mo but no nickel.

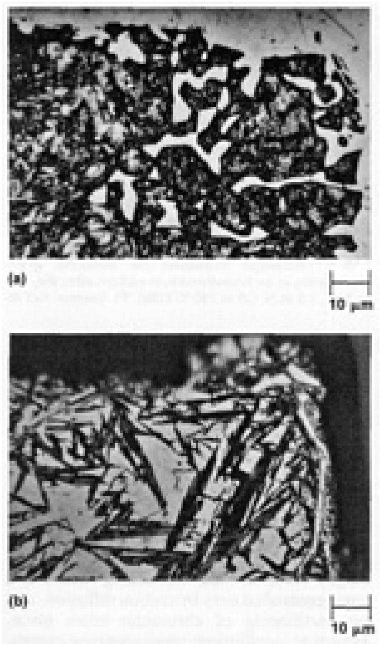

Fig. 19 Examples of massive carbides formed at the corners of carburized specimens. (a) Blocky carbides in 8620 steel. (b) Thin, continuous grain-boundary carbides in SAE 4121 steel. Light micrographs. Source: Ref 49

Effect on Fatigue Cracking. The combination of excessive retained austenite and massive carbides, together with stress concentration at sharp changes in section, causes fatigue crack initiation at specimen corners. Figure 20(a) shows

fatigue initiation at the corner of a carburized specimen of SAE 4121 steel. Details of the corner fracture along the massive carbides are shown in Fig. 20(b). Carbide grain-boundary allotriomorphs grow by ledges, which make up the interface between the carbides and the martensite-austenite matrix (Ref 39). These ledges provide preferred fracture paths, as shown in Fig. 20(b).

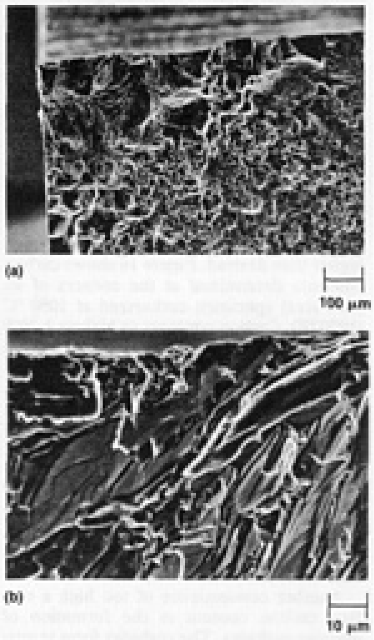

Fig. 20 Fracture surfaces of carburized SAE 4121 steel. (a) Low-magnification view of corner initiation. (b) Detail of fracture at carbide-matrix interface. SEM micrographs. source: Ref 48

Although massive network carbides are detrimental to the bending fatigue and fracture performance of carburized steels in many applications, a process referred to as super carburizing is occasionally used for special applications (Ref 50). This process supersaturates a part surface with carbon and results in the formation of large volumes of massive carbide particles. Surface carbon contents of 1.80% to greater than 3.0% are produced, and steels with large amounts of carbide-forming elements such as chromium and molybdenum respond most effectively. High volume fractions of hard alloy carbide particles significantly increase resistance to abrasive wear, but also may create problems in the grinding of the very hard surfaces.

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Residual Stresses

A major benefit of carburizing is the introduction of compressive residual stresses into the surfaces of carburized parts. These stresses counteract applied tensile stresses and therefore improve bending fatigue performance. Because of the importance of residual stresses to the performance of carburized parts, considerable effort has been devoted to modelling, measuring, and understanding their effects (Ref 1, 7, 8, 51, 52, 53, 54).

Figure 21 shows schematically the residual stress profiles that develop in properly carburized and hardened steels. The compressive stresses reach a maximum at some distance from the surface, gradually decrease, and are eventually

balanced by tensile residual stresses in the core of the carburized part. A survey of a number of carburized parts showed that measured peak compressive stresses ranged from -200 to -450 MPa (-29 to -65 ksi) (Ref 8).

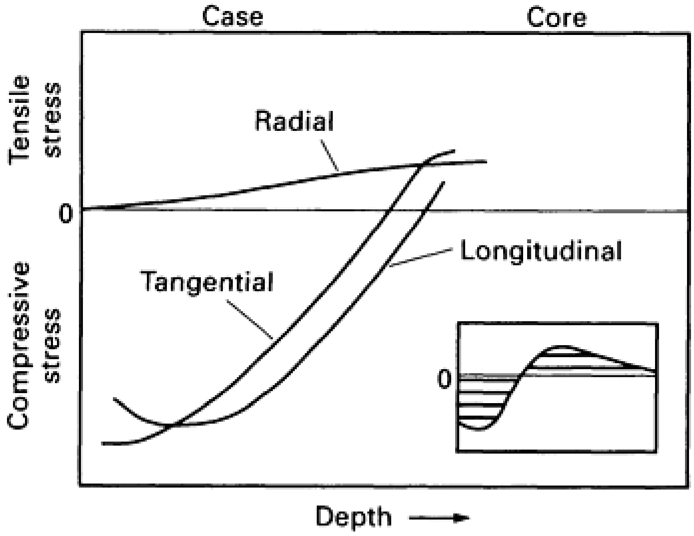

Fig. 21 Schematic diagram of residual stresses in carburized steels. Insert shows that surface compressive residual stresses are balanced by interior tensile stresses. Source: Ref 8

Surface compressive residual stresses in carburized steels arise from transformation and temperature gradients induced during cooling and the volume expansion that accompanies the transformation of austenite to martensite (Ref 55). The carbon profiles produced by carburizing introduce the M_s temperature and transformation gradients: the M_s temperature is lowest at the surface, where carbon content is the highest, and increases with increasing distance from the surface as carbon content approaches that of the core. Temperature gradients are due to heat flow and thermal-conductivity factors; at any given time during quenching, the surface temperature is lower than temperatures in the part interior.

In the early stages of cooling, martensite first forms at some distance from the surface, where the part temperature has fallen below the higher, interior M_s temperatures. The volume changes at this stage are readily accommodated by the surrounding austenite because of its low flow stresses and the high temperatures. The surface austenite does not transform because of its low M_s. The temperature continues to fall and eventually drops below the M_s in the surface regions. The expansion at this point is constrained by the interior martensite that has formed earlier, and as a result the surface microstructure is placed in compression. Many factors affect this process, including alloy and carbon levels, which set hardenability and M_s temperatures; case depths; temperature at the start of quenching; quenchant temperature; and the temperature-dependent plastic flow behavior of martensite and austenite. Despite the complexity of the interactions that affect the formation of residual stresses, hardened carburized parts with the martensite-austenite microstructures described earlier generally develop favorable compressive stresses.

Surface compressive residual stresses can be increased by shot peeping. Figure 22 shows the dramatic effect of shot peening at different velocities on the compressive residual stresses of carburized steel. These improvements in stresses translate into improved bending fatigue performance.

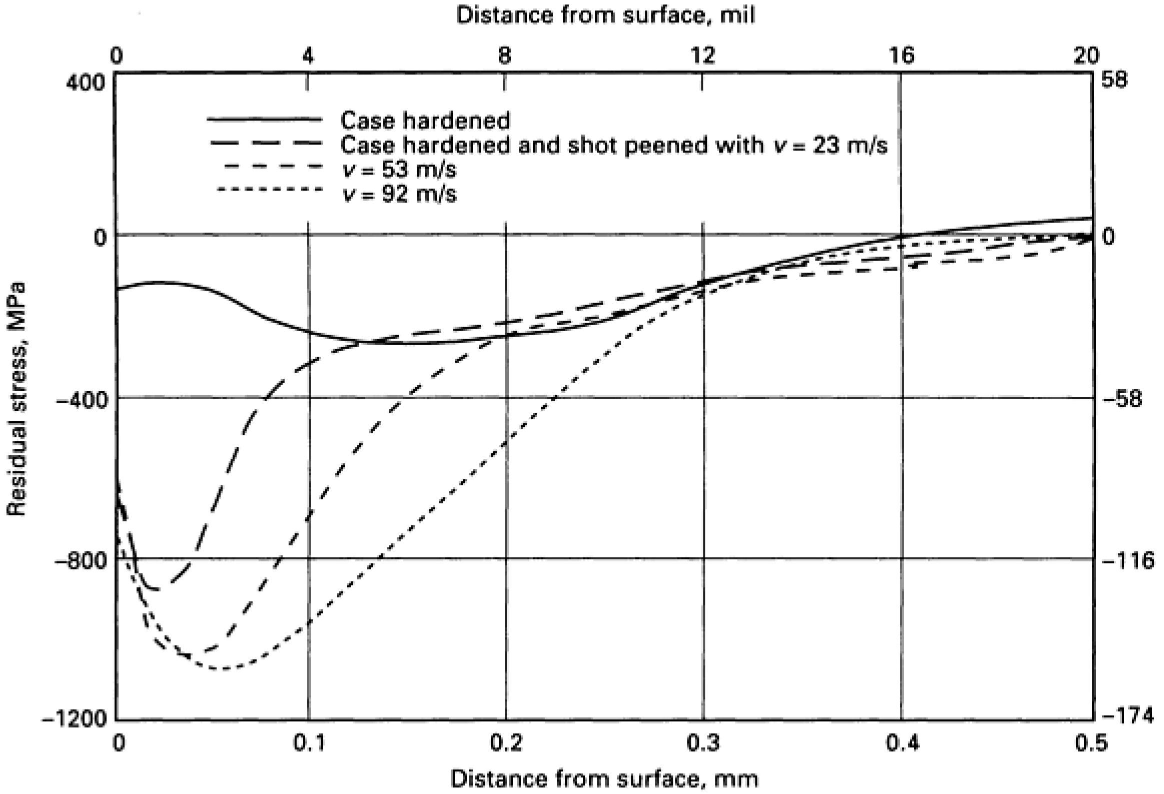

Fig. 22 Effect of shot peening at different velocities on compressive residual stresses in carburized 16MnCr5 steel (1.23% Mn, 1.08% Cr). Source: Ref 52

Residual stresses can be adversely affected by surface oxidation during gas carburizing. As discussed in the next section, certain alloying elements are preferentially oxidized and removed from solid solution in the austenite. As a result, hardenability decreases, and, in severe cases, pearlite instead of martensite forms at the surface (Ref 56). Thus the surface transformation occurs at high temperatures, and the beneficial effect of austenite-to-martensite transformation late in the quenching process is lost. Even if the oxidation is not severe enough to cause pearlite formation, surface M_s temperatures may be raised by the removal of some of the alloying element, resulting in a thin surface zone with lower compressive stresses.

Subzero, or cryogenic refrigeration is sometimes used to lower retained austenite contents (Ref 7). As a result, surface hardness increases. Also, dimensional stability in service is increased because there is less austenite available to transform to martensite by stress- or strain-controlled mechanisms. However, a number of investigations have shown that the refrigeration treatment of carburized parts lowers fatigue performance (Ref 48, 57, 58). The transformation of additional surface retained austenite would be expected to continue the process established during quenching to room temperature; that is, the volume expansion associated with the formation of new martensite would be constrained, and compressive stresses would be increased. Increased compressive stresses are in fact measured in the martensite of refrigerated specimens (Ref 7, 57, 58). However, Kim *et al.* (Ref 57) have shown that the stresses in the remaining retained austenite are tensile. Such localized tensile stresses would lower the applied stresses required to initiate and propagate fatigue cracks.

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Surface and Internal Oxidation

The H_2O/H_2 and CO_2/CO equilibria in gas carburizing atmospheres cause the internal oxidation of certain alloying elements in carburizing steels (Ref 7, 59). Figure 23 shows the oxidizing potentials for various elements in endothermic gas at 930 °C (1700 °F). Chromium, silicon, and manganese, all commonly found in carburizing steels, oxidize readily, while molybdenum, nickel, and iron are not oxidized. The oxidation is diffusion dependent, and therefore the depth and extent of oxide formation is a function of carburizing time and temperature. The oxides may form on austenite grain boundaries or within austenite grains.

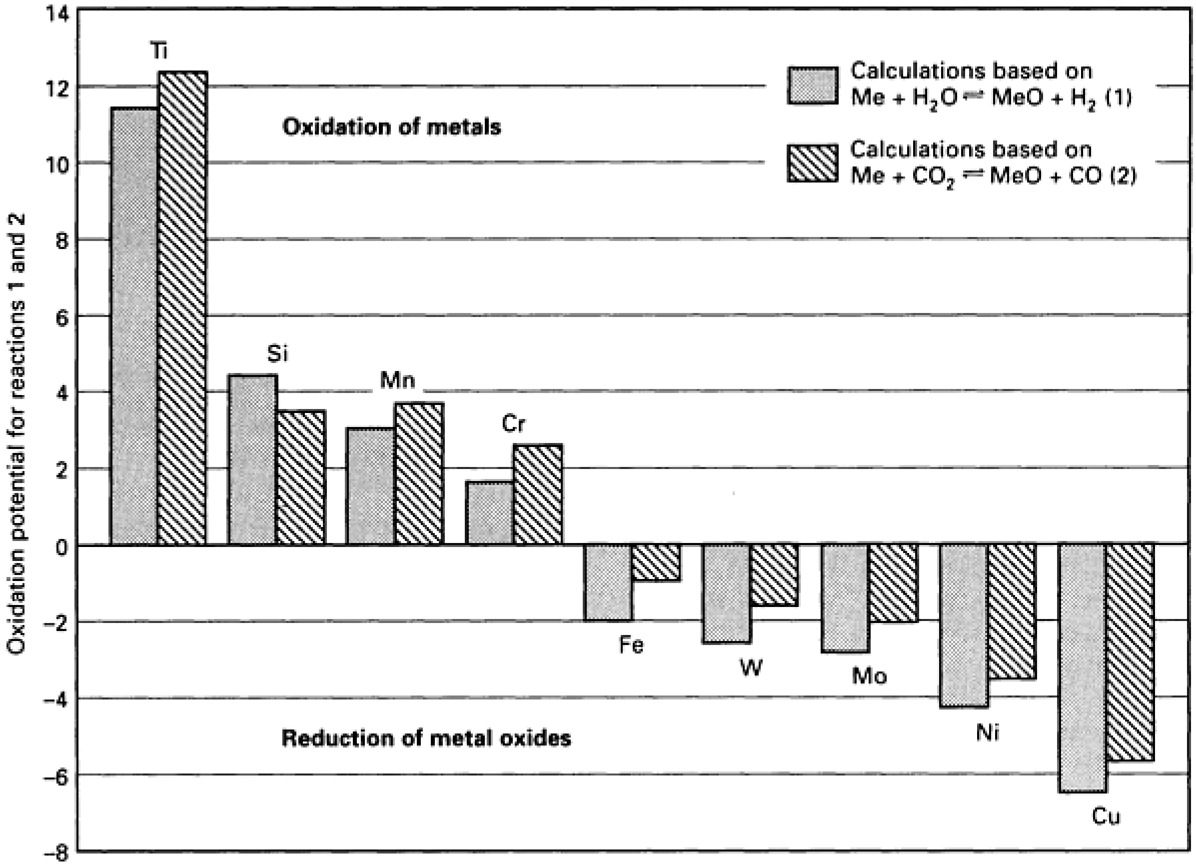

Fig. 23 Oxidation potentials of various alloying elements and iron in an endothermic gas atmosphere at 930 °C (1700 °F). Source: Ref 60

Figure 24 shows internal oxidation at the surface of a carburized specimen of a steel containing 1.06% Mn, 0.21% Si, 0.52% Cr, 0.50% Ni, and 0.17% Mo. The oxidation has followed the austenite grain boundaries to a depth on the order of

an austenite grain diameter, about 10 μm (0.4 mil). This depth of penetration is typical for steels carburized to a case depth of about 1 mm (40 mil).

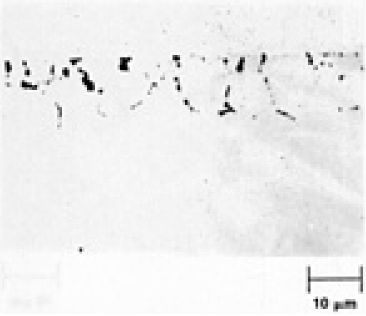

Fig. 24 Internal oxidation (dark features) at surface of gas-carburized steel containing 1.06% Mn, 0.21% Si, 0.52% Cr, 0.50% Ni, and 0.17% Mo. Light micrograph. Source: Ref 20

Figure 25 shows the surface oxidation of a carburized 20MnCr5 steel containing 1.29% Mn, 0.44% Si, 1.25% Cr, 0.25% Ni, and 0.0015% B. There are two zones of oxidation. The outer zone, about 5 μm (0.2 mil) deep, consists of chromium-rich oxides penetrating into the austenite grains. The other zone, about 30 μm (1.2 mils) deep, consists of manganese-rich and silicon-rich oxides along austenite grain boundaries. These oxide chemistries and morphologies agree with those presented by Chatterjee-Fischer (Ref 59). In addition, silicon appears to form intergranular dispersed oxide particles.

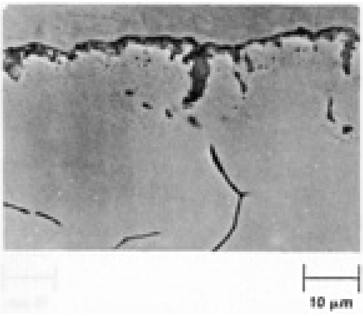

Fig. 25 Internal oxidation of gas-carburized 20MnCr5 steel containing 1.29% Mn, 0.44% Si, 1.25% Cr, 0.25% Ni, and 0.0015% B. SEM micrograph. Source: Ref 61

The grain-boundary oxides shown in Fig. 25 appear to be discontinuous. Examination of fractured specimens of the same carburized steel shown in Fig. 25 showed that the intergranular oxides grew as lamellae (Fig. 26). Thus the oxide structure appears to develop by a discontinuous or cellular transformation in which grain-boundary austenite initially containing nominal amounts of silicon and manganese decomposes to alloy oxides and austenite depleted in silicon and manganese. The discontinuous appearance of the oxides in Fig. 25 is therefore due to a sectioning effect through the oxide and austenite lamellae.

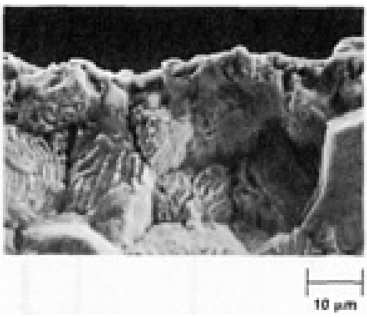

Fig. 26 Lamellar internal grain-boundary oxides on fracture surface of carburized 20MnCr5 steel containing boron. SEM micrograph. Source: Ref 61

The effect of internal oxidation on fatigue performance depends on the degree of oxidation. As noted in the section on residual stresses, if sufficient depletion of the alloying elements occurs, hardenability may decrease to the point at which pearlite and other nonmartensitic transformation products form. The latter surfaces have low hardness, tensile residual surface stresses, and reduced fatigue performance (Ref 56, 62, 63). The reduced surface hardness of some oxidized carburized steels has also been attributed to the decarburization that accompanies internal oxidation (Ref 64).

If the depth and degree of internal oxidation is limited, and if the surface structure of a carburized steel consists of martensite-austenite mixtures with surface residual compressive stresses, then there is little or no effect of intergranular oxidation on fatigue performance. Parrish (Ref 7) discussed evidence showing that oxidation less than 13 μm (0.5 mil) deep has little effect on fatigue. Pacheco and Krauss (Ref 20) showed that very good fatigue resistance could be attained in carburized specimens with the internal oxidation shown in Fig. 24, provided that the surface martensite-austenite microstructure formed in fine-grained austenite.

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Fatigue Mechanisms

Identification of the best compositions and best microstructures for the production of carburized steels with high fatigue resistance has been difficult. All of the microstructural features described in the preceding sections influence fatigue performance. Many of the earlier studies that ranked various alloy steels reported relatively modest bending fatigue strengths, between 700 and 1000 MPa (100 and 145 ksi) (Ref 65, 66). Claims for the benefits of various alloying elements have been made, but little detailed microstructural and fractographic analysis has been performed to correlate mechanisms with benefits of alloying. Nevertheless, the results of studies that show low-to-moderate fatigue strengths probably reflect the properties of commercial carburized parts that are overwhelmingly successful in service because of conservative mechanical design. However, failures do occur (Ref 13, 67), and the causes, sometimes obvious, sometimes subtle, must be identified in order to improve consistently the future performance of carburized parts.

A few studies have shown that very high bending fatigue limits (≥ 1400 MPa, or 200 ksi) can be achieved in carburized steels under conditions of tension-tension cyclic (R = 0.1) loading (Ref 18, 20, 68, 69). Moreover these studies are beginning to identify microstructures associated with various ranges of fatigue performance. Polished surfaces to eliminate machining marks and other surface flaws, as well as rounded specimen corners or specimen designs that minimize edge effects, are necessary to eliminate fatigue initiation sites which obscure the effects of microstructure.

From the standpoint of microstructures, based on experimental fatigue studies (R = 0.1), there appear to be two major mechanisms of bending fatigue crack initiation. For conciseness, these two mechanisms are defined and referred to as type 1 and type 2 in the following discussion. Type 1 is associated with intergranular fatigue initiation at austenite grain boundaries with phosphorus-carbide structures. This mechanism is typically observed in direct-quenched carburized specimens and is associated with endurance limits up to 1260 MPa (183 ksi) (Ref 12). Thus quite reasonable levels of fatigue performance can be attained in carburized steels with a sensitivity to grain-boundary fracture. The other mechanism, type 2, is associated with transgranular fatigue crack initiation and correlates with bending fatigue endurance

limits greater than 1400 MPa (200 ksi). Figure 27 shows an example of type 1 initiation, and Fig. 28 shows an example of type 2 initiation.

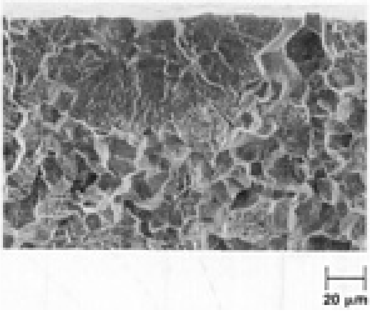

Fig. 27 Example of type 1 bending fatigue fracture initiation consisting of short intergranular crack initiation site, a region of transgranular crack propagation, and overload intergranular fracture through case. Plasma-carburized steel containing 1.06% Mn, 0.52% Cr, 0.30% Ni, and 0.1% Mo. SEM micrograph. Source: Ref 20

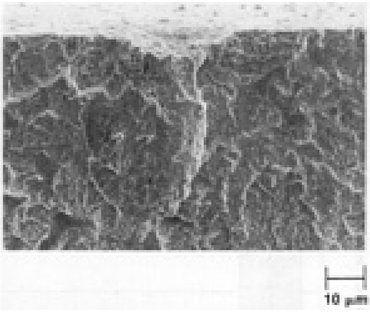

Fig. 28 Example of type 2 bending fatigue fracture initiation consisting of transgranular initiation and propagation, with gas-carburized 8719 steel. SEM micrograph. Source: Ref 20

Zaccone *et al.* (Ref 70, 71), working with simulated case microstructures, have shown that in type 1 initiation, small grain-boundary cracks form very early in the fatigue cycle, perhaps in the first cycle if the applied stresses are high enough to reach the threshold of grain-boundary cracking. This crack is arrested after traveling the length of only a few grains. The strain-induced transformation of retained austenite to martensite at the crack tip occurs and apparently creates compressive residual stresses that halt the crack (Ref 70, 71, 72). For this reason, retained austenite is beneficial for prolonging fatigue life under conditions of low-cycle, high strain fatigue. Although fatigue crack propagation rates are slowed by high retained austenite contents, fracture eventually occurs when a sufficient number of accumulated cycles cause the crack to reach the critical size for unstable overload fracture. Once the intergranular crack is arrested, propagation proceeds by transgranular cracking (Fig. 27). Overload fracture of specimens sensitive to type 1 initiation also tends to be largely intergranular until lower-carbon martensite is encountered.

Type 2, transgranular fatigue crack initiation, is dependent on slip mechanisms of crack formation during cyclic loading (Ref 73). Thus, a key feature of this mechanism, in contrast to type 1 initiation, is that a crack is not immediately generated during the first loading cycles. Cycle-dependent transgranular crack initiation develops in fine-grained case microstructures where conditions for intergranular cracking are mitigated. Low amounts of retained austenite or finely distributed retained austenite also favor type 2 initiation and therefore contribute to high performance under conditions of high-cycle fatigue because slip is more difficult in fine, largely martensitic microstructures (Ref 20, 70, 71).

Contact Fatigue Resistance of Gears and Bearings. Carburized steels in applications such as bearings and gears must also be resistant to rolling-contact fatigue (Ref 8, 13, 19, 67). The stresses that initiate failure under contact conditions are shear stresses that peak at some distance below the surface. Therefore cracks that lead to spalling develop at subsurface microstructural discontinuities such as oxide inclusion particles. Extreme cases of spalling are associated with case crushing or cracking initiated at the case-core interface. Figure 29 shows an example of a spall on a carburized SAE 4118 interface. If sliding is coupled with contact loading, surface pits develop. Very high contact loads cause microstructural changes within high-carbon martensite that are revealed by various types of etching (Ref 74, 75, 76). Generally retained austenite is regarded as a microstructural constituent that is beneficial for rolling-contact fatigue resistance (Ref 77, 78).

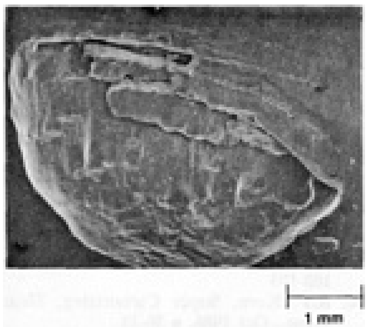

Fig. 29 An example of spalling in carburized SAE 4118 steel subjected to rolling contact loading. Courtesy of R. Miller, Colorado School of Mines, and T. Clements, Caterpillar Inc.

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Carbonitriding of Steels

Revised by Jon Dossett, Midland Metal Treating, Inc.

Introduction

CARBONITRIDING is a modified form of gas carburizing, rather than a form of nitriding. The modification consists of introducing ammonia into the gas carburizing atmosphere to add nitrogen to the carburized case as it is being produced. Nascent nitrogen forms at the work surface by the dissociation of ammonia in the furnace atmosphere; the nitrogen diffuses into the steel simultaneously with carbon. Typically, carbonitriding is carried out at a lower temperature and for a shorter time than is gas carburizing, producing a shallower case than is usual in production carburizing.

In its effects on steel, carbonitriding is similar to liquid cyaniding. Because of problems in disposing of cyanide-bearing wastes, carbonitriding is often preferred over liquid cyaniding. In terms of case characteristics, carbonitriding differs from carburizing and nitriding in that carburized cases normally do not contain nitrogen, and nitrided cases contain nitrogen primarily, whereas carbonitrided cases contain both.

Carbonitriding is used primarily to impart a hard, wear-resistant case, generally from 0.075 to 0.75 mm (0.003 to 0.030 in.) deep. A carbonitrided case has better hardenability than a carburized case (nitrogen increases the hardenability of steel; it is also an austenite stabilizer, and high nitrogen levels can result in retained austenite, particularly in alloy steels). Consequently, by carbonitriding and quenching, a hardened case can be produced at less expense within the case-depth range indicated, using either carbon or low-alloy steel. Full hardness with less distortion can be achieved with oil quenching, or, in some instances, even gas quenching, employing a protective atmosphere as the quenching medium.

Steels commonly carbonitrided include those in the 1000, 1100, 1200, 1300, 1500, 4000, 4100, 4600, 5100, 6100, 8600, and 8700 series, with carbon contents up to about 0.25%. Also, many steels in these same series with a carbon range of 0.30 to 0.50% are carbonitrided to case depths up to about 0.3 mm (0.01 in.) when a combination of a reasonably tough, through-hardened core and a hard, long-wearing surface is required (shafts and transmission gears are typical examples). Steels such as 4140, 5130, 5140, 8640, and 4340 for applications like heavy-duty gearing are treated by this method at 845 °C (1550 °F).

Often, carburizing and carbonitriding are used together to achieve much deeper case depths and better engineering performance for parts than could be obtained using only the carbonitriding process. This process is applicable particularly with steels with low case hardenability, that is, the 1000, 1100, and 1200 series steels. The process generally consists of carburizing at 900 to 955 °C (1650 to 1750 °F) to give the desired total case depth (up to 2.5 mm, or 0.100 in.), followed by carbonitriding for 2 to 6 h in the temperature range of 815 to 900 °C (1500 to 1650 °F) to add the desired carbonitrided case depth. The subject parts can then be oil quenched to obtain a deeper effective and thus harder case than would have resulted from the carburizing process alone. The addition of the carbonitrided surface increases the case residual compressive stress level and thus improves contact fatigue resistance as well as increasing the case strength gradient.

When the carburizing/carbonitriding processes are used together, the effective case depth (50 HRC) to total case depth ratio may vary from about 0.35 to 0.75 depending on the case hardenability, core hardenability, section size, and quenchant used. A more shallow effective or total case depth can be achieved with a given carbonitriding process by using fine grain steels containing higher amounts of aluminum (Ref 1) or titanium. The nitrogen from the process forms nitrides with the aluminum or titanium. The combined nitrogen does not improve case hardenability.

The fundamental problem in controlling carbonitriding processes is that the rate of nitrogen pick-up depends on the free ammonia content of the furnace atmosphere and not the percentage of ammonia in the inlet gas. Unfortunately, no state-of-the-art sensor for monitoring the free ammonia content of the furnace atmosphere has yet been developed.

Reference

1. E.R. Mantel and M.M. Shea, Hardening Response of Carbonitrided Rimmed and Aluminum-Killed SAE 1010 Steels, *J. Heat Treat.*, Vol 4 (No. 3), 1986, p 237-246

Case Composition

The composition of a carbonitrided case depends on the type of steel and on the process variables of temperature, time, and atmosphere composition. In terms of steel type, the case depth achieved during a given carbonitriding process will be lower in steels containing higher amounts of strong nitride formers such as aluminum or titanium.

The ammonia system required for carbonitriding often consists of a number of cylinders of liquid ammonia that are connected to a common manifold. In general, ammonia from only a part of the supply is employed; the remainder is held in reserve. The flow from each cylinder should be sufficiently low to prevent freezing of the valves. Only stainless steel valves and schedule 80 or stainless steel piping are recommended.

Outside bulk storage and vaporizing systems are much preferred to cylinder banks, considering the advantage of a constant, uninterrupted source on the uniformity of work quality. In general, when bulk storage is used, two-stage pressure regulation is used to ensure a constant and uniform ammonia flow. The first stage regulates the pressure for delivery to the furnace, whereas the final pressure regulation, at the furnace, controls the pressure to the process.

In terms of process variables, the higher the carbonitriding temperature, the less effective is the ammonia addition to the atmosphere as a nitrogen source, because the rate of spontaneous decomposition of ammonia to molecular nitrogen and hydrogen increases as the temperature is raised. At a given temperature, the fraction of the ammonia addition that spontaneously decomposes is dependent on the residence time of the atmosphere in the furnace: the higher the total flow of atmosphere gases, the lower the fraction of the ammonia addition that decomposes to nitrogen and hydrogen. Figure 1 shows that lower temperatures favor increased surface nitrogen concentrations. The addition of ammonia to a carburizing atmosphere has the effect of dilution by the following reaction:

$$2\ NH_3 \rightarrow N_2 + 3\ H_2$$

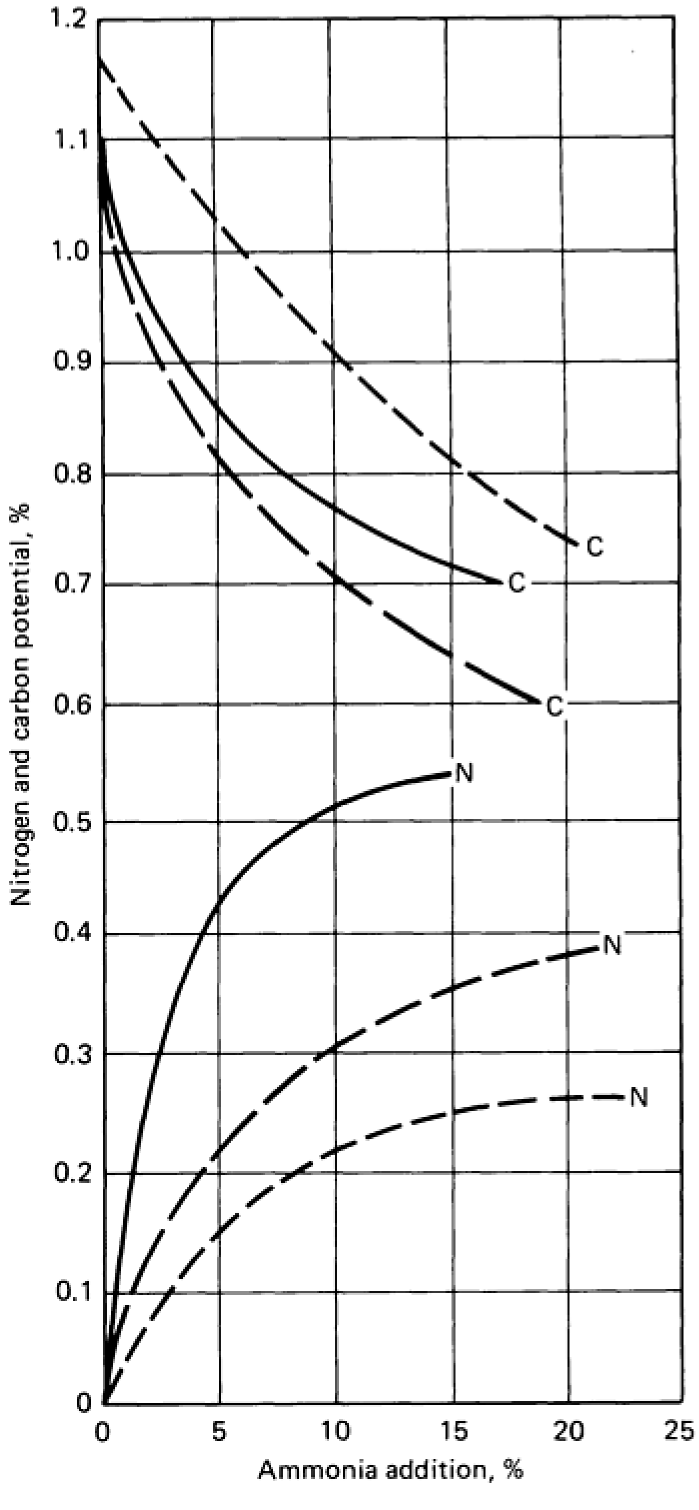

Fig. 1 Effect of ammonia additions on nitrogen and carbon potentials determined using low-carbon steel foil. For three sets of conditions: solid lines, 3 h at 850 °C (1560 °F) and 0.29% CO_2; broken lines, 1 h at 925 °C (1695 °F) and 0.13% CO_2; dashed lines, 1 h at 950 °C (1740 °F) and 0.10% CO_2. Source: Ref 2

Thus, as shown in Fig. 1, the carbon potential possible with a given carbon dioxide level is higher in a carburizing atmosphere than in a carbonitriding atmosphere. Dilution with nitrogen and hydrogen affects measurements of oxygen potential in a similar manner; the carbon potential possible with a given oxygen potential is higher in a carburizing atmosphere than in a carbonitriding atmosphere. Water vapor content, however, is much less affected by this dilution. Thus, the amount of dilution and its resulting effect on the atmosphere composition depends on the processing temperature, the amount of ammonia introduced, and the ratio of the total atmosphere gas flow rate to the volume of the furnace.

Carbonitriding can be carried out at such low temperatures as to produce a compound layer, so called because iron-carbon-nitrogen compounds are formed at the surface. In certain wear applications, this type of case structure is suitable.

To produce this layer of compound, large percentages of ammonia are required. It is usually unnecessary to liquid quench parts carbonitrided in this manner. However, because the diffusion rate of nitrogen and the rate of formation of the compound are so slow at temperatures below 705 °C (1300 °F), such practice is economically applicable only to shallow cases in applications in which dimensional tolerances would be difficult to maintain if the parts were treated at higher temperatures. When temperatures fall below the austenitic level, this process is called ferritic nitrocarburizing (Ref 3, 4).

Example 1: Effect of Atmosphere Dew Point on Case Composition from Carbonitriding.

Figure 2 shows carbon and nitrogen gradients and case hardness data for 1018 carbon steel and 8620 low-alloy steel that were carbonitrided for 4 h at 845 °C (1550 °F) in a batch-type radiant-tube furnace. These test data were obtained in a manufacturing plant under normal production conditions, employing a standard carbonitriding cycle. All test specimens were carbonitrided along with production loads of 23 kg (50 lb) of gears and shafts.

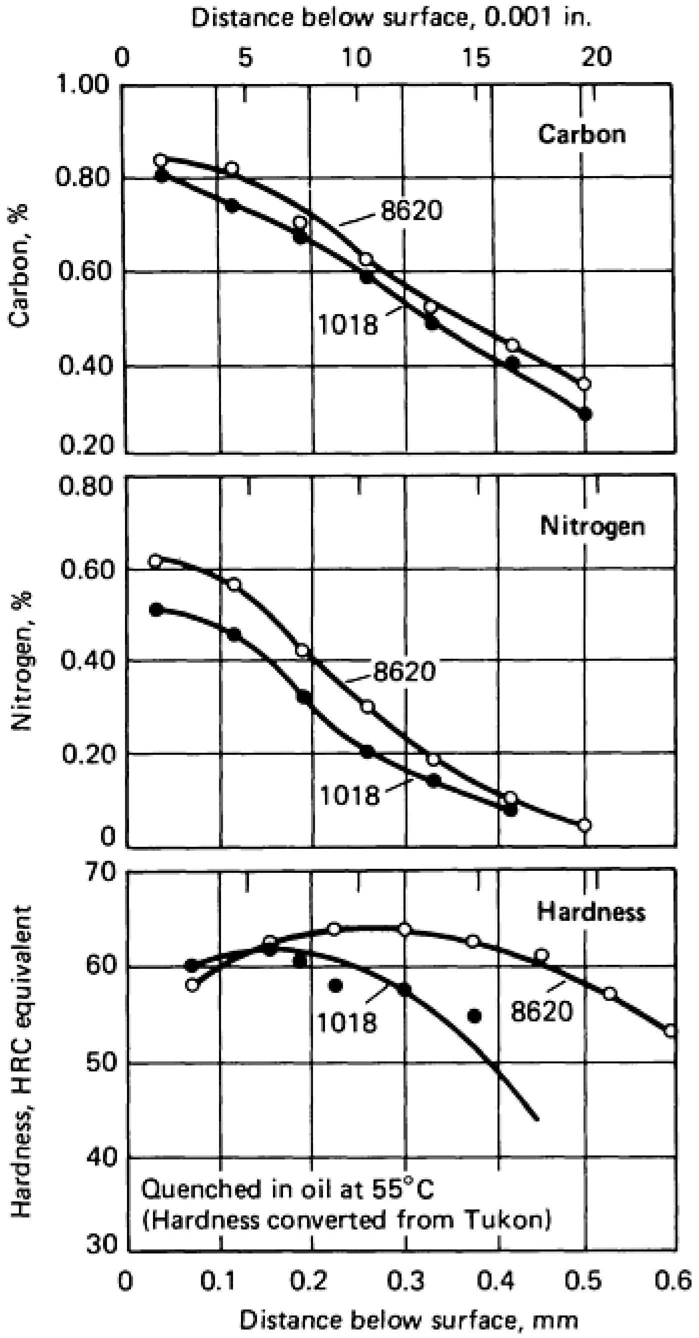

Fig. 2 Carbon, nitrogen, and hardness gradients for carburized 1018 and 8620 steels. For processing details, see text.

The carbonitriding atmosphere was controlled by an infrared control unit and consisted of an endothermic gas at 14.2 m^3/h (500 ft^3/h), ammonia at 0.7 m^3/h (24 ft^3/h), propane at 0.007 to 0.021 m^3/h (0.25 to 0.75 ft^3/h), and 0.32 to 0.34% carbon dioxide. The dew point of the atmosphere was maintained at -7 to -6 °C (19 to 21 °F) throughout the carbonitriding cycle. All specimens were quenched from the carbonitriding temperature (845 °C, or 1550 °F) into warm oil at 55 °C (130 °F); they were neither tempered nor subjected to subzero treatment.

As the dew point of a carbonitriding atmosphere is increased, carbon concentration decreases and nitrogen concentration remains fairly constant. This characteristic response is demonstrated by the data in Fig. 3 for a 1020 steel carbonitrided at 845 °C (1550 °F) for 4 h, which show that, with the ammonia content of the carbonitriding atmosphere set at high (5%) and low (1%) levels, an increase in the concentration of water vapor (decrease in atmosphere carbon potential) in the inlet gas lowered the profiles of carbon concentration but did not appreciably affect nitrogen concentrations. (Although the dew point of the atmosphere in the carbonitriding furnace, rather than the dew point of the inlet gas, is the controlling factor, data based on the inlet-gas dew point demonstrate the general effects of raising and lowering dew point on case composition.)

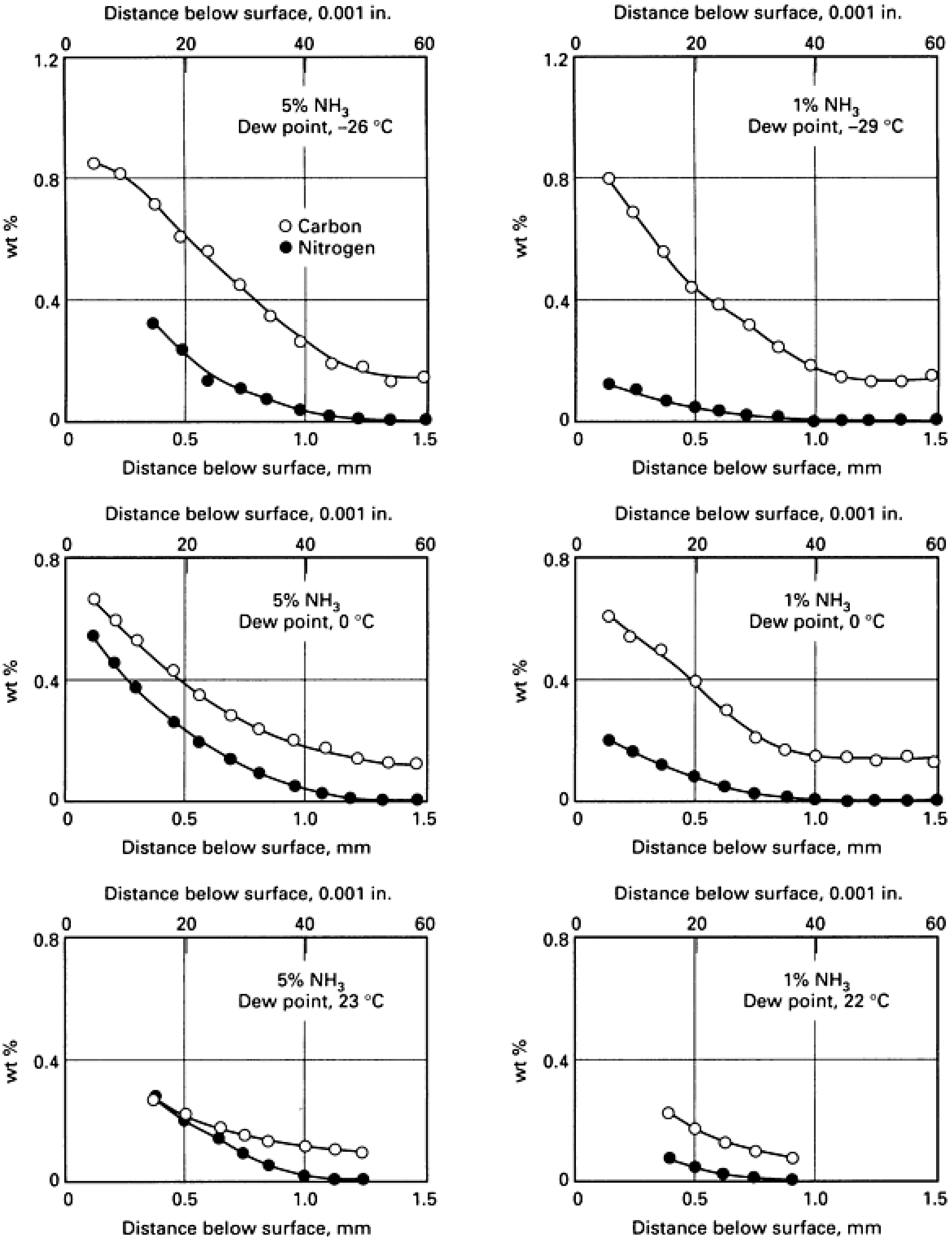

Fig. 3 Effects of ammonia concentration and inlet gas dew point on carbon and nitrogen gradients in a 1020 steel carbonitrided at 845 °C (1550 °F) for 4 h and air cooled. Inlet gas also contained 5% methane; balance, carrier gas. Source: Ref 2

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2. F.A. Clarkin and M.B. Bever, The Role of Water Vapor and Ammonia in Case Hardening Atmospheres, *Trans. ASM,* Vol 47, 1955, p 794-806
3. T. Bell, M. Kinali, and G. Munstermann, Physical Metallurgy Aspects of the Austenitic Nitrocarburizing Process, *Heat Treat. Met.,* Vol 2, 1987, p 47-51
4. F.K. Cherry, Austenitic Nitrocarburizing, *Heat Treat. Met.,* Vol 1, 1987, p 1-5

Depth of Case

Preferred case depth is governed by service application and by core hardness. Case depths of 0.025 to 0.075 mm (0.001 to 0.003 in.) are commonly applied to thin parts that require wear resistance under light loads. Case depths up to 0.75 mm (0.030 in.) may be applied to parts (such as cams) for resisting high compressive loads. Case depths of 0.63 to 0.75 mm (0.025 to 0.030 in.) may be applied to shafts and gears that are subjected to high tensile or compressive stresses caused by torsional, bending, or contact loads.

Medium-carbon steels with core hardnesses of 40 to 45 HRC normally require less case depth than steels with core hardnesses of 20 HRC or below. Low-alloy steels with medium-carbon content, such as those used in automotive transmission gears, are often assigned minimum case depths of 0.2 mm (0.008 in.).

Measurements of the case depths of carbonitrided parts may refer to effective case depth or total case depth, as with reporting case depths for carburized parts. For very thin cases, usually only the total case depth is specified. In general, it is easy to distinguish case and core microstructures in a carbonitrided piece, particularly when the case is thin and is produced at a low carbonitriding temperature; more difficulty is encountered in distinguishing case and core when high temperatures, deep cases, and medium-carbon or high-carbon steels are involved. Whether or not the core has a martensitic structure is also a contributing factor in case-depth measurements.

Effect of Time and Temperature. Based on a survey of industrial practice, Fig. 4 shows case depths for different combinations of total furnace treating time and temperature. (Note that all values given for case depth are for effective case depth unless otherwise stated.)

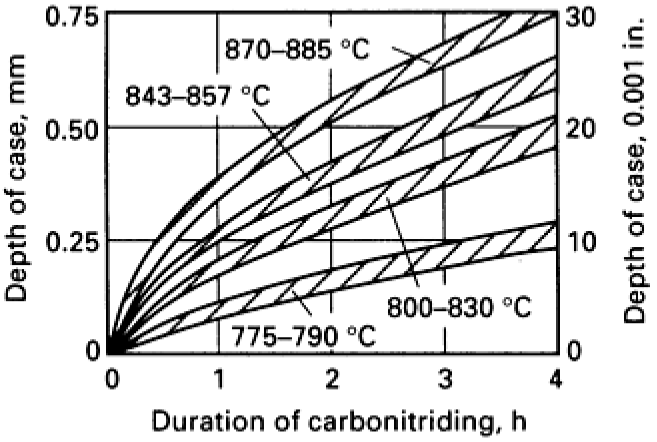

Fig. 4 Results of a survey of industrial practice regarding effects of time and temperature on effective case depth of carbonitrided cases

Figure 5(a) shows the effects of total furnace time on case depth for 1020 steel. Specimens were heated to 705, 760, 815, and 870 °C (1300, 1400, 1500, and 1600 °F) for periods of 15, 30, and 45 min. Figure 5(b) indicates the total case depths that can be obtained on a 1112 steel held for 15 min at various temperatures between about 750 and 900 °C (1380 and 1650 °F) All data in Fig. 5 were obtained in a single plant.

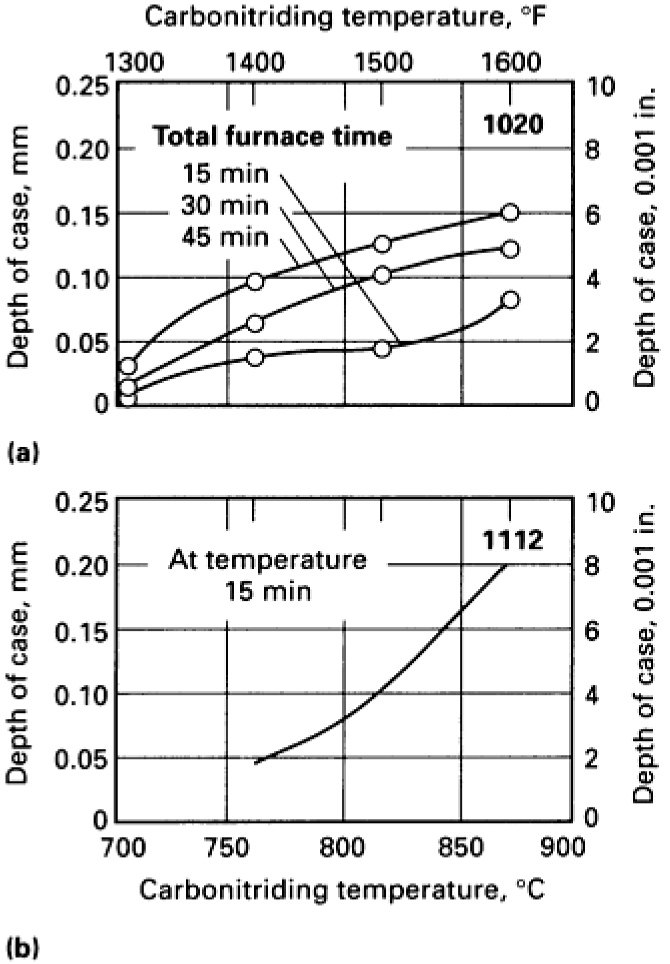

Fig. 5 Effects of temperature and of duration of carbonitriding on effective case depth. Both sets of data were obtained in the same plant. Note that upper graph (for 1020 steel) is in terms of total furnace time, whereas bottom graph (for 1112 steel) is for 15 min at temperature.

Case-depth uniformity in carbonitriding depends on temperature uniformity within the furnace chamber, adequate circulation and replenishment of atmosphere, and distribution of the furnace charge so that it is uniformly exposed to the atmosphere.

Accurate control of treatment time is also a factor in controlling case-depth uniformity. All parts in a load should be at a uniform temperature prior to exposure to the carbonitriding atmosphere in order to achieve uniform results when the processing times are short.

Example 2: Variations in Case Depth of Carbonitrided 1010 Steel.

Case-depth variations typical of carbonitriding at 775 to 800 °C (1425 to 1475 °F) are shown in Fig. 6. The data were obtained on two parts that were carbonitrided along with large production lots. One of these parts, a rack made of 1010 steel, was carbonitrided at 790 to 800 °C (1450 to 1475 °F) in a horizontal batch furnace equipped with an enclosed quench tank. Acceptable limits of case depth for these racks were 0.05 to 0.13 mm (0.002 to 0.005 in.).

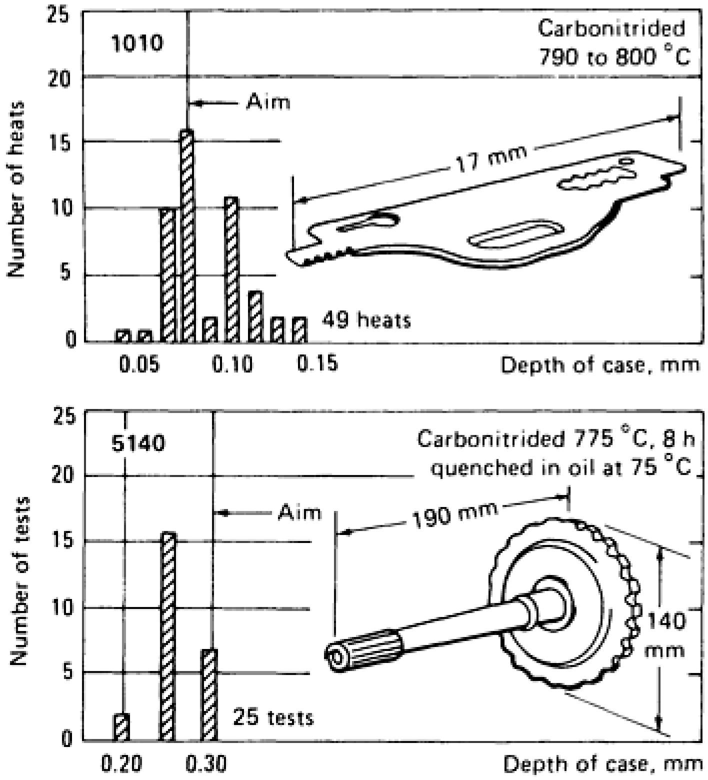

Fig. 6 Distribution of effective case depth of 1010 steel racks and 5140 steel pinion shafts

The other part, a pinion shaft of 5140 steel, was carbonitrided at 775 °C (1425 °F) for 8 h and then quenched in oil at about 75 °C (170 °F) Attainment of acceptable case depth of 0.2 to 0.3 mm (0.008 to 0.012 in.) was 100% in 25 tests.

Although the data in this example and Fig. 6 may be considered typical, they do not fully reflect the high degree of uniformity of case depth that can be achieved. For example, one plant reports total case-depth uniformity of ±0.025 mm (±0.001 in.) within a load and between loads in more than 25,000 cycles for case depths as low as 0.125 mm (0.005 in.) on small parts carbonitrided in large batch furnaces. Time, temperature, and processing variables were automatically controlled. The parts were also preheated to a uniform temperature in a neutral atmosphere prior to starting the carbonitriding process.

Hardenability of Case

One major advantage of carbonitriding is that the nitrogen absorbed during processing lowers the critical cooling rate of the steel. That is, the hardenability of the case is significantly greater when nitrogen is added by carbonitriding than when the same steel is only carburized (Fig. 7). This permits the use of steels on which uniform case hardness ordinarily could not be obtained if they were only carburized and quenched. Where core properties are not important, carbonitriding permits the use of low-carbon steels, which cost less and may have better machinability or formability.

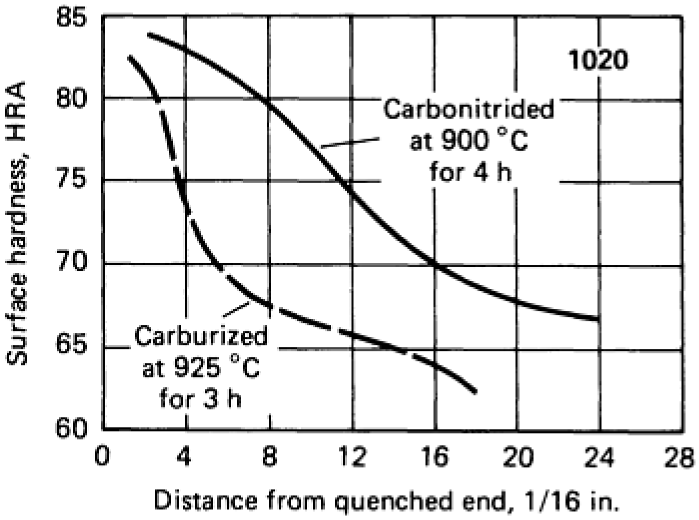

Fig. 7 End-quench hardenability curve for 1020 steel carbonitrided at 900 °C (1650 °F) compared with curve for the same steel carburized at 925 °C (1700 °F). Hardness was measured along the surface of the as-quenched hardenability specimen. Ammonia and methane contents of the inlet carbonitriding atmosphere were 5%; balance, carrier gas. Source: Ref 5

Because of the hardenability effect of nitrogen, carbonitriding makes it possible to oil quench steels such as 1010, 1020, and 1113 to obtain martensitic case structures. Because of lower processing temperatures and/or the use of less severe quenches, carbonitriding may produce less part distortion and better control of dimensions than carburizing, and thus may eliminate the need for straightening or final grinding operations.

Reference cited in this section

5. G.W. Powell, M.B. Bever, and C.F. Floe, Carbonitriding of Plain Carbon and Boron Steels, *Trans. ASM*, Vol 46, 1954, p 1359-1371

Hardness Gradients

Hardness at various levels in the case depends on the microstructure. Hardness gradients associated with the microstructures of 1117 steel are presented in Fig. 8. When the carbonitriding atmosphere was relatively high in ammonia (11% NH_3), the nitrogen content of the case was high, and enough austenite was retained after quenching to lower the hardness to 48 HRC, 500 g (1.1 lbf) load, at a depth of 0.025 mm (0.001 in.) below the surface. The amount of retained austenite was decreased, and hardness consequently was increased, either by lowering the ammonia flow rate from 0.57 to 0.14 m^3/h (20 to 5 ft^3/h), which reduced the ammonia content of the furnace atmosphere from 11 to 3%, or by introducing a 15-min diffusion period at the end of the carbonitriding operation. Either treatment increased the hardness to meet or exceed a specified minimum value of 55 HRC, 500 g (1.1 lbf) load at 0.025 mm below the surface.

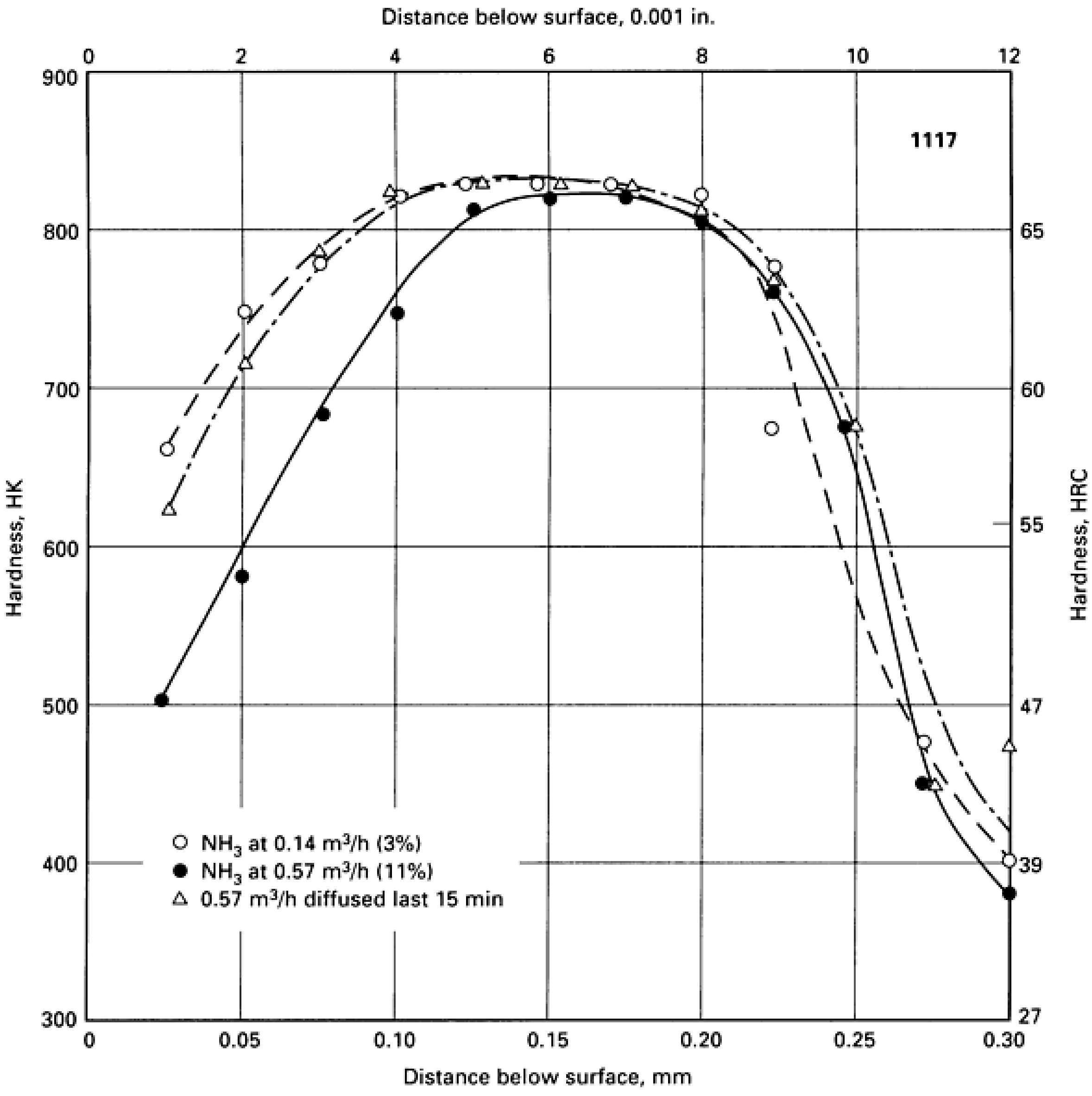

Fig. 8 Hardness gradients in 1117 steel carbonitrided at 815 °C (1500 °F) for 1 $\frac{1}{2}$ h and quenched in oil. Required minimum hardness of 630 HK (55 HRC) at 0.025 mm below the surface was met by reducing the percentage and flow rate of ammonia or by adding a diffusion period after carbonitriding, as indicated. Atmosphere consisted of endothermic carrier gas (dew point, -1 °C) at 4.25 m^3/h (150 ft^3/h), natural gas at 0.17 m^3/h (6 ft^3/h), and ammonia in the amounts indicated.

Similar data relating ammonia content to hardness for 1018 steel carbonitrided at 790 °C (1455 °F) for 2 $\frac{1}{2}$ h and at 845 °C (1550 °F) for 2 $\frac{1}{2}$ h are shown in Fig. 9.

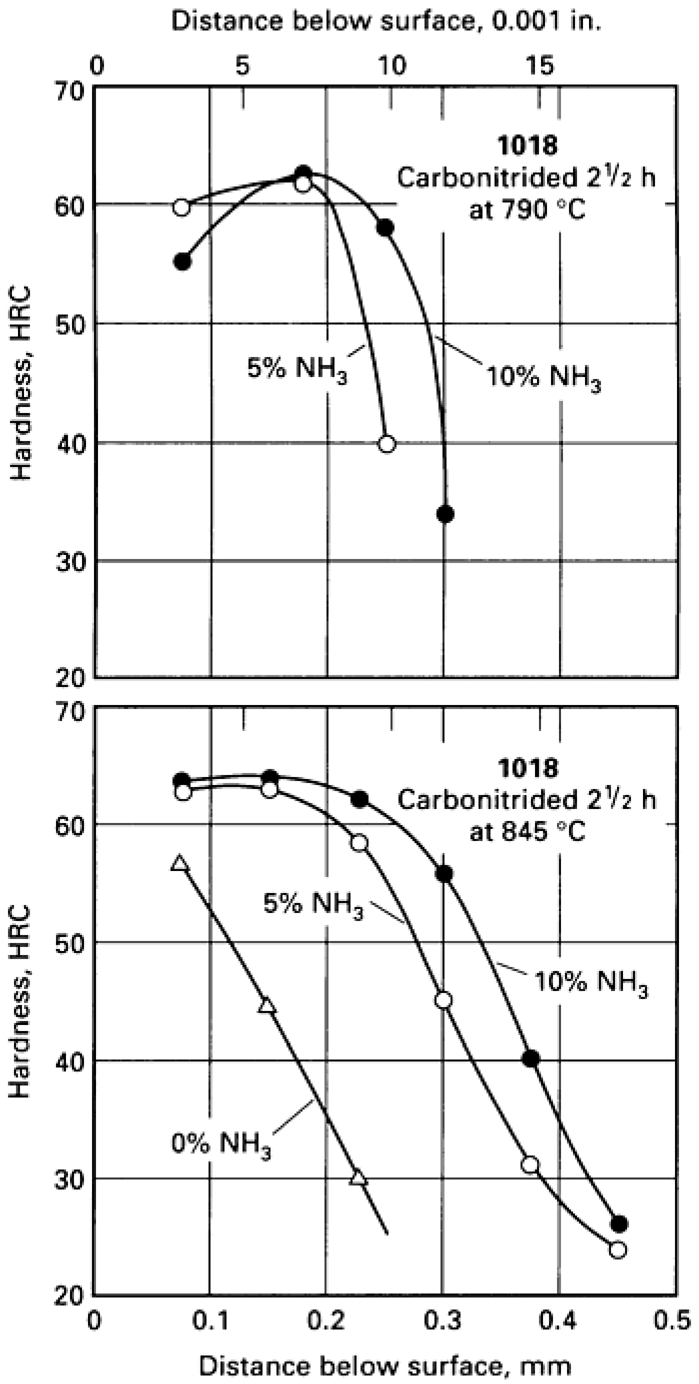

Fig. 9 Fffect of ammonia content of carbonitriding gas on hardness gradient

Void Formation

Subsurface voids or porosity in the case structure (Fig. 10) may occur in carbonitrided parts if the processing conditions are not adjusted properly. Although details of the mechanism of void formation are not completely understood, this problem has been related to excessive ammonia additions. Table 1 summarizes the factors that have been shown singly or in combination to contribute to void formation. No attempt has been made to quantify the interaction of the material and process variables presented in Table 1. Rather, this information should be used as a guide for avoiding or eliminating porosity problems. It should also be noted that the reprocessing of parts previously carbonitrided can in many instances also lead to void formation.

Table 1 Effect of material/variables on the possibility of void formation in carbonitrided cases

Material/processing variables[(a)]	Possibility of void formation

Temperature increase	Increased
Longer cycles	Increased
Higher case nitrogen levels	Increased
Higher case carbon levels	Increased
Aluminum-killed steel	Increased
Increased alloy content of steel	Decreased
Severe prior cold working of material	Increased
Ammonia addition during heat-up cycle	Increased

(a) All other variables held constant. Sources: Based on data in Fig. 10 and Ref 4 and 5

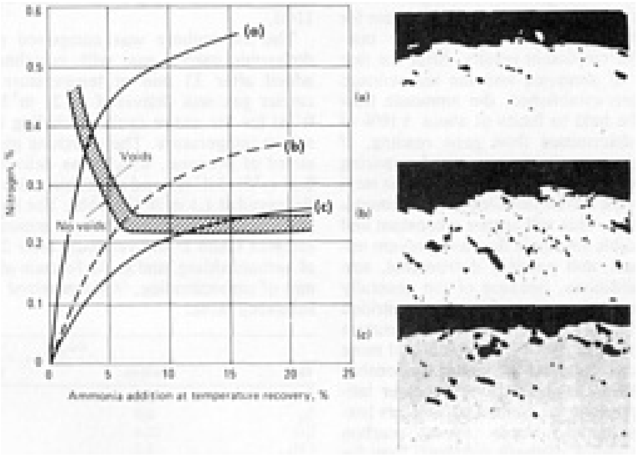

Fig. 10 Effect of ammonia additions on nitrogen content and formation of subsurface voids in foils. (a) 850 °C (1560 °F) 0.29% CO_2. (b) 925 °C (1695 °F) 0.13% CO_2. (c) 950 °C (1740 °F) 0.10% CO_2. Source: Ref 6

None of the data included in this article were obtained from parts or test pieces containing case porosity.

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4. F.K. Cherry, Austenitic Nitrocarburizing, *Heat Treat. Met.*, Vol 1, 1987, p 1-5
5. G.W. Powell, M.B. Bever, and C.F. Floe, Carbonitriding of Plain Carbon and Boron Steels, *Trans. ASM*, Vol 46, 1954, p 1359-1371
6. R. Davies and C.G. Smith, A Practical Study of the Carbonitriding Process, *Met. Prog.*, Vol 114 (No. 4), 1978, p 40-53

Applications

Although carbonitriding is a modified carburizing process, its applications are more restricted than those of carburizing. As has been stated previously, carbonitriding is largely limited to case depths of about 0.75 mm (0.03 in.) or less, while no such limitation applies to carburizing. Two reasons for this are: carbonitriding is generally done at temperatures of 870 °C (1600 °F) and below, whereas, because of the time factor involved, deeper cases are produced by processing at higher temperatures; and the nitrogen addition is less readily controlled than is the carbon addition, a condition that can lead to an excess of nitrogen, and, consequently, to high levels of retained austenite and case porosity when processing times are too long.

The resistance of a carbonitrided surface to softening during tempering is markedly superior to that of a carburized surface. Other notable differences exist in terms of residual-stress pattern, metallurgical structure, fatigue and impact strength at specific hardness levels, and effects of alloy composition on case and core characteristics.

Various production parts that have been successfully carbonitrided are listed in Table 2. A review of this list suggests the range of applications for which carbonitriding has been found to be an advantage.

Table 2 Typical applications and production cycles for carbonitriding

Part	Steel	Case depth		Furnace temperature		Total time in furnace	Quench
		mm	0.001 in.	°C	°F		
Carbon steels							
Adjusting yoke, 25 by 9.5 mm (1 by 0.37 in.)	1020	005-0.15	2-6	775 and 745	1425 and 1375	64 min	Oil
Bearing block, 64 by 32 by 3.2 mm (2.5 by 1.3 by 0.13 in.)	1010	0.05-0.15	2-6	775 and 745	1425 and 1375	64 min	Oil
Cam, 2.3 by 57 by 64 mm (0.1 by 2.25 by 2.5 in.)	1010	0.38-0.45	15-18	855	1575	$2\frac{1}{2}$ h	Oil
Cup, 13 g (0.46 oz)	1015	0.08-0.13	3-5	790	1450	$\frac{1}{2}$ h	Oil
Distributor drive shaft, 125 mm OD by 127 mm (5 by 5 in.)	1015	0.15-0.25	6-10	815 and 745	1500 and 1375	108 min	Gas[a]
Gear, 44.5 mm diam by 3.2 mm (1.75 by 0.125 in.)	1213[b]	0.30-0.38	12-15	855	1575	$1\frac{3}{4}$ h	Oil[c]
Hex nut, 60.3 by 9.5 mm (2.4 by 0.37 in.)	1030	0.15-0.25	6-10	815 and 745	1500 and 1375	64 min	Oil
Hood-latch bracket, 6.4 mm diam (0.25 in.)	1015	0.05-0.15	2-6	775 and 745	1425 and 1375	64 min	Oil
Link, 2 by 38 by 38 mm (0.079 by 1.5 by 1.5 in.)	1022	0.30-0.38	12-15	855	1575	$1\frac{1}{2}$ h	Oil
Mandrel, 40 g (1.41 oz)	1117	0.20-0.30	8-12	845	1550	$1\frac{1}{2}$ h	Oil
Paper-cutting tool, 410 mm long	1117	~0.75	~30	. . .	. . .	. . .	. . .
Segment, 2.3 by 44.5 by 44.5 mm (0.09 by 1.75 by 1.75 in.)	1010	0.38-0.45	15-18	855	1575	$2\frac{1}{2}$ h	Oil
Shaft, 4.7 mm diam by 159 mm (0.19 by 6.25 in.)	1213[b]	0.30-0.38	12-15	815	1500	$2\frac{1}{2}$ h	Gas[a][d]
Shift collar, 59 g (2.1 oz)	1118	0.30-0.36	12-14	775	1430	$5\frac{1}{2}$ h	Oil[e]
Sliding spur gear, 66.7 mm OD (2.625 in.)	1018	0.38-0.50	15-20	870	1600	2 h[f]	Oil[g]
Spring pin, 14.3 mm OD by 114 mm (0.56 by 4.5 in.)	1030	0.25-0.50	10-20	815 and 745	1500 and 1375	144 min	Oil
Spur pinion shaft, 41.3 mm OD (1.625 in.)	1018	0.38-0.50	15-20	870	1600	2 h[f]	Oil[h]
Transmission shift fork, 127 by 76 mm (5 by 3 in.)	1040	0.25-0.50	10-20	815 and 745	1500 and 1375	162 min	Gas[a]
Alloy steels							
Helical gear, 82 mm OD (3.23 in.)	8617H	0.50-0.75	20-30	845	1550	6 h[f]	Oil[g]
Input shaft, 1.2 kg (2.6 lb)	5140	0.30-0.35	12-14	775	1430	$5\frac{1}{2}$ h	Oil[e]
Pinion gear, 0.2 kg (0.44 lb)	4047	0.30-0.35	12-14	775	1430	$5\frac{1}{2}$ h	Oil[e]
Ring gear, 0.9 kg (2 lb)	4047	0.20-0.30	8-10	760	1400	9 h	Oil[i]
Segment, 1.4 by 83 mm (0.055 by 3.27 in.)	8617	0.18-0.25	7-10	815	1500	$1\frac{1}{2}$ h	Gas[a]
Spur pinion shaft, 63.5 mm OD by 203 mm (2.5 by 8 in.)	5140H	0.05-0.20	2-8	845	1550	1 h[f]	Oil[j]
Stationary gear plate, 0.32 kg (0.7 lb)	5140	0.30-0.35	12-14	775	1430	$5\frac{1}{2}$ h	Oil[e]
Transmission main shaft sleeve, 38 mm OD by 25 mm (1.5 by 2 in.)	8622	0.15-0.25	6-10	815 and 745	1500 and 1375	108 min	Gas[a]
Transmission main shaft washer, 57 mm OD by 6.4	8620	0.25-	10-20	815 and	1500 and	162 min	Gas[a]

(a) Modified carbonitriding atmosphere.

(b) Leaded.

(c) Tempered at 190 °C (375 °F).

(d) Tempered at 150 °C (300 °F).

(e) Tempered at 165 °C (325 °F).

(f) Time at temperature.

(g) Oil at 150 °C (300 °F); tempered at 150 °C (300 °F); for 1 h.

(h) Oil at 150 °C (300 °F); tempered at 260 °C (500 °F) for 1 h.

(i) Tempered at 175 °C (350 °F).

(j) Oil at 150 °C (300 °F); tempered at 230 °C (450 °F) for 2 h. OD, outside diameter

For many applications, carbonitriding the less expensive steels will provide properties equivalent to those obtained in gas carburized alloy steels. The following example illustrates choices of carbonitrided carbon steels for applications ordinarily requiring alloy steels.

Example 3:

Camshaft eccentrics stamped from 1010 aluminum-killed steel 4 mm (0.16 in.) thick were carbonitrided to a depth of 0.25 to 0.50 mm (0.01 to 0.02 in.) and a minimum surface hardness equivalent to 58 HRC. The required metallurgical properties for this application could have been attained also with carbonitrided or gas-carburized 1011 or 1016 steel. However, the 1010 steel had the advantage of facilitating the stamping operation because of its lower carbon and manganese contents and fine grain size.

Furnaces

Almost any furnace suitable for gas carburizing can be adapted to carbonitriding. Whether dense or shallow (openly spaced) work loads are to be processed, the furnace must be equipped with a fan to circulate the atmosphere. For work that is to be clean and bright after quenching, the furnace must be equipped with protective-atmosphere vestibules to the quench area.

Atmosphere Constituents

The atmospheres used in carbonitriding generally comprise a mixture of carrier gas, enriching gas, and ammonia. Basically, the atmospheres used in carbonitriding are produced by adding from about 2 to 12% ammonia to a standard gas-carburizing atmosphere.

Ammonia used for carbonitriding is anhydrous ammonia of 99.9+% purity. Grade designations such as Premium, Refrigeration, and Metallurgical are used to specify suitable materials. Grades known as Commercial and Agricultural contain appreciable amounts of carbon dioxide, water, and oils, which prohibit their use in furnace atmospheres.

Most ammonia is produced from natural gas, so costs and availability are related to natural gas supplies.

Control of Atmospheres

The three types of gases that comprise carbonitriding atmospheres usually are measured through flowmeters and may be premixed just before they enter the furnace. Large continuous furnaces require addition of the gas mixture at several points to provide the desired composition within the chamber. Control of the atmosphere usually is obtained by producing a carrier gas that is as constant in chemical composition and dew point as practical, and by varying the enriching gas and ammonia either manually or automatically to give the desired carbon and nitrogen composition in the carbonitrided case. In varying the enriching gas, care must be taken not to introduce excessive amounts of high hydrocarbons into the furnace because this will cause sooting. Heavy deposits of soot, in addition to making the work difficult to clean, have a detrimental effect on alloy furnace parts and may impede the rate of carbonitriding.

Ammonia Content. Among factors to be considered in establishing ammonia content for the influent gas are:

- *Atmosphere Turnover.* Frequently, lower ammonia percentages must be used with high rates of furnace gas change (that is, total gas flow divided by furnace chamber volume) to produce a specific microstructure for a specific furnace and load
- *Recirculation Rate.* Generally, increases in recirculation rate, and hence in atmosphere uniformity, permit the use of lower ammonia concentrations
- *Furnace-Cycle Time.* The rate of absorption of nitrogen in austenite decreases with time; hence, short furnace cycles and low case depths require higher ammonia percentages
- *Furnace Temperature.* Higher ammonia percentages often must be used with higher furnace temperatures
- *Load Size, Density, and Surface Area.* As size, density, and surface area of load increase, a higher rate of flow of ammonia is required to match the increase in nitrogen demand
- *Carbon Potential/Hydrocarbon Addition.* Lower ammonia percentages can normally be used with higher carbon potentials. However, as the load size or surface area of the load increases, hydrocarbon additions of up to 25% by volume may be necessary to adequately control the carbon potential early in the cycle or for shallow case depths
- *Type of Steel.* The minimum percentage of ammonia required for hardenability depends largely on steel composition. Austenite retention increases with an increase in ammonia content. Therefore, lower ammonia contents should be used with alloy steels, particularly those containing nickel or high manganese, and with higher-manganese carbon steels such as 1117, 1118, and 1024

Only enough ammonia should be added to sustain the carbonitriding reactions in the atmosphere; excess ammonia does not contribute to the nitrogen content of the case and can lead to void formation, as discussed above. Usually, 2.5 to 5% ammonia is sufficient to produce a satisfactory nitrogen content in the case. Ammonia contents as high as 10% or more, although relatively common, are often unnecessarily high.

Contaminants must be avoided in order to maintain an effective atmosphere in the furnace chamber. Infiltration of air and leaks in radiant tubes cause products of combustion, which are detrimental to the atmosphere, to enter the work chamber. Even the work load itself can provide a source of contamination. When significant amounts of grease, oil, cleaning agents, moisture, or quenching salts are present on surfaces of the work load, these materials can seriously contaminate the atmosphere. This source of contamination can be avoided by cleaning the work with a suitable agent before charging and by the use of purging cycles.

Influence of Furnace Type. Different types of furnaces require different percentages of entering component gases and different volumes of gases, depending on turnover (the number of gas changes per hour). Major variables include: the reactions of the gas with furnace brickwork and alloy; tightness of the furnace and number of door openings (shaker-hearth and belt furnaces will have an opening between the door and hearth at all times); and degree of circulation of gases, as related to load density and surface area of work. Data on the interrelationship of rate of gas flow, furnace volume, and number of gas changes per hour, as a function of type of furnace, are given in Table 3. From these data it is evident that:

- For brick-lined batch furnaces, fewer gas changes per hour are required as the furnace volume increases (ostensibly because relatively less gas leakage through furnace-door openings occurs as furnace volume increases)
- Shaker-hearth (or belt-type) furnaces require much higher gas flows per unit volume because of large losses of atmosphere through the fixed door opening at the charge end of the furnace

Table 3 Influence of type of furnace on mixture and flow rate of carbonitriding gases

Type of furnace	Constituents of gas, % by volume			Total gas flow,		Furnace volume,		Gas changes per hour
	Ammonia	Natural gas	Carrier gas	m^3/h	ft^3/h	m^3	ft^3	
Batch, brick-lined	10.4	20.8	68.8	6.8	240	0.29	10	23.5
Batch, brick-lined	4	6	90	14.5	510	1.42	50	10.2
Batch, brick-lined	8.3	8.3	83.3	10.2	360	2.55	90	4.0

Batch, brick-lined	5	20	75	11.3	400	8.50	300	1.3
Continuous, brick-lined	3.4	2.3[(a)]	94.3	42.0	1480	8.07	285	5.2
Continuous, brick-lined	7	7	86	28.3	1000	25.5	900	1.1
Continuous, brick-lined	5	4	91	31.1	1100	25.5	900	1.2
Shaker-hearth, metal-lined	2.5	2.5	95	6.2	220	0.06	2	110.0

(a) C_3H_8

Batch Furnace Atmospheres

For maximum uniformity of case composition and case depth, the load must be heated uniformly to the carbonitriding temperature, and an adequate supply of atmosphere maintained at constant composition must be circulated throughout the load. Processing uniformity may be significantly improved by preheating parts in an atmosphere of endothermic gas for 15 to 60 min to ensure temperature uniformity within the load before adding enriching gas and ammonia for the actual carbonitriding portion of the cycle. This is a practicable procedure for batch furnaces that have sufficient heating capacity as well as an efficient work-loading pattern, good atmosphere-circulating fans, and dependable devices for mixing and controlling the addition of gases.

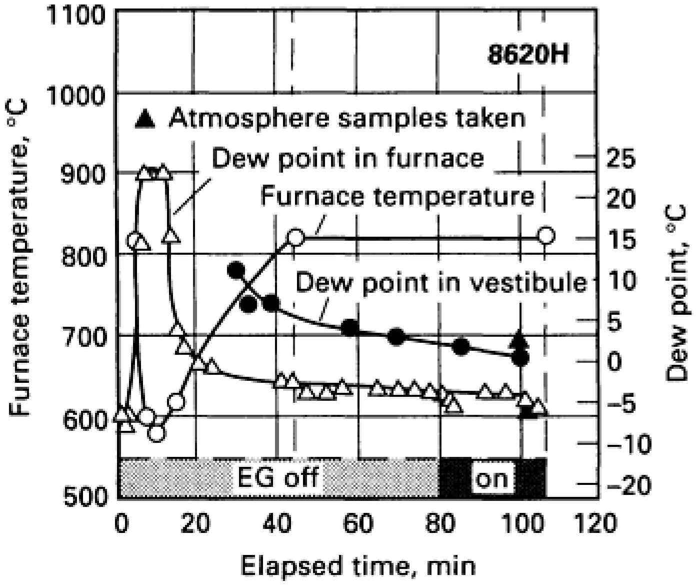
Control of Composition. As in gas carburizing, the composition of the atmosphere for carbonitriding should be carefully controlled for consistent results. After the rate of flow of ammonia and the temperature have been established, the ammonia flow should be held to limits of about ±10% of the predetermined flow gage reading. If similar parts are to be processed requiring the same ammonia addition, a stainless steel orifice plate can be installed in the ammonia supply line. This will ensure a constant and reproducible ammonia flow and prevent unintentional, and possibly detrimental, ammonia additions. Because of the generally lower carbon content of the carbonitrided case, the lower operating temperature (which permits higher dew points and more carbon dioxide), and the higher hardenability of the carbonitrided case, greater latitude is possible for control parameters (oxygen potential, water vapor, carbon dioxide, and/or methane contents) than for the same steel composition using the carburizing process.

For example, when carburizing at 925 °C (1700 °F) to obtain a case carbon content of 0.90 ± 0.05% or 0.80 ± 0.05%, it is desirable to hold the dew point within ±0.5 °C (±1 °F), and the carbon dioxide content within ±0.005%, of the control values; when carbonitriding at 815 °C (1500 °F) to obtain a case carbon content of 0.80 ± 0.05%, it is desirable to hold the dew point within ±1.5 °C (±3 °F), and the carbon dioxide content within ±0.03%, of the control values. The carbon dioxide levels corresponding to a certain carbon potential will not be the same for carbonitriding and carburizing, as discussed above.

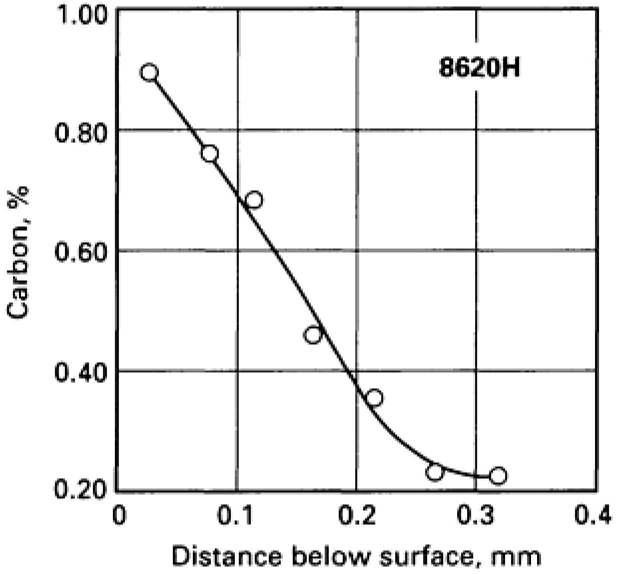
Data reported for atmospheres consisting of endothermic generator gas with additions of 5% ammonia and less than 1% propane indicate dew points in the furnace chamber of -7 °C at 845 °C (20 °F at 1550 °F) and of -4 °C at 815 °C (25 °F at 1500 °F) for a surface carbon content of 0.80 to 0.90% with 1018 and 8620 steels. Dew points ranging from -7 to 4 °C (20 to 40 °F) will cover most commercial carbonitriding applications at approximately 845 °C (1550 °F) with surface carbon content of about 0.80%.

Example 4:

Gears (Fig. 11) made of 8620H steel were carbonitrided in batches, each of which had a net weight of 340 kg (750 lb) and a gross weight of 460 kg (1010 lb). Typically, carbonitriding was done at 815 °C (1500 °F) for 30 min, after which the gears were quenched directly from the carbonitriding temperature.



(a)



(b)

Fig. 11 Effect on gears carbonitrided in a batch-type furnace. (a) Temperature and dew-point variations during carbonitriding cycle. (b) Carbon gradient produced by the cycle shown in (a). EG, enriching gas

The furnace was a batch-type furnace with a brick-lined heating chamber. It was heated by radiant tubes and had a vestibule-enclosed quench. Dimensions of the furnace chamber were 1.4 m wide by 1.7 m long by 1.1 m high (56 by 66 by 43 in.) from brick floor to center of arch. The variation of furnace temperature with time during a typical carbonitriding cycle is shown in Fig. 11(a).

The atmosphere was composed of endothermic carrier gas, with enriching gas added after 33 min at temperature. The carrier gas was delivered at 21 m^3/h (750 ft^3/h) for the entire cycle, including the 63 min at temperature. The enriching gas consisted of propane, which was delivered at 0.14 m^3/h (5 ft^3/h), and ammonia, which was delivered at 1.1 m^3/h (38 ft^3/h). The furnace-gas analysis, determined from atmosphere samples taken in the vestibule after 23 min of carbonitriding, and in the furnace after 26 min of carbonitriding, is summarized in the following table:

Gas	Gas, %	
	Vestibule	Furnace
CO_2	0.8	0.4

O_2	0.0	. . .
CO	22.4	20.4
CH_4	1.2	1.2
H_2	34.2	34.2
N_2	bal	bal

The carrier-gas dew point, measured at the generator, was maintained at -15 to -14 °C (5 to 7 °F) throughout the cycle. Figure 11(a) indicates the dew points in the furnace and in the vestibule at various elapsed times during the carbonitriding cycle.

Figure 11(b) shows a typical carbon gradient in a gear resulting from the processing described.

Control of atmosphere composition begins by accurately controlling the carrier gas. With endothermic gas generators, the air-gas ratio is usually adjusted to produce a dew point of 2 to 4 °C (35 to 40 °F), which is equivalent to about 0.25 to 0.32% carbon dioxide content. Automatic, closed-loop control based on oxygen potential, carbon dioxide, or dew point is preferred for ensuring the uniformity of endothermic generator gas output.

Dew-point instruments that contain a lithium chloride cell are not recommended for use with carbonitriding atmospheres because ammonia will cause deterioration of the lithium chloride. If an infrared instrument for CO_2 is used, it is recommended that stainless steel tubing be used instead of copper to avoid the corrosive action of the ammonia. Aluminum tubing can be used successfully if care is taken to avoid any possibility of producing water condensate in the sample lines. In general, the advice of the instrument manufacturer should be obtained before using these devices with carbonitriding atmospheres.

Because of the relatively light carbonitrided case, turnings from test bars are not frequently employed for determining carbon content. Metallographic examination and the control of case microhardness gradient are common process control methods. However, the most commonly used process control setups incorporate a regulator to control ammonia flow.

Better control of furnace atmospheres can be obtained when the parts to be carbonitrided and the work baskets are free of dirt and oil. Sintered powder metallurgy parts containing oil must be "burned out" in a tempering furnace before they are carbonitrided.

Continuous Furnace Atmospheres

Setting up a program for efficient and dependable control of a carbonitriding atmosphere in a continuous furnace is similar to that for a batch furnace. Good circulation of atmosphere and good control of temperature are of prime importance. It is advantageous to introduce ammonia only to those areas in which the temperature of the work is equal to the operating temperature for carbonitriding. If the furnace is of appreciable internal length, about $3\frac{1}{2}$ m ($11\frac{1}{2}$ ft) or more, it is important to introduce the mixture of carburizing gas and ammonia at frequent intervals over the length of the furnace where the work is at temperature and in regions where the temperatures may be decreased for metallurgical reasons near the end of the cycle.

Safety

Caution: Gaseous carbonitriding media are highly toxic, flammable, and explosive. The safety precautions that must be taken to protect equipment and personnel are essentially the same as those used in gas carburizing.

Ammonia cylinders should not be located near the furnaces, in direct sunlight, or near flammable gases or other combustibles. It is recommended that the ammonia supply be placed in a room that is well ventilated at the ceiling and separated from the work area by a fire-resistant wall.

Because ammonia is lighter than air, as well as a moderate fire hazard and a toxic material, an automatic sprinkling system is recommended. *Caution: Gas masks should be readily available, but should not be stored in the same area as the ammonia.* A sulfur stick can be used to check for ammonia leaks. Additional recommendations pertaining to safety in ammonia systems can be obtained from fire insurance companies.

Caution: Under no circumstances should combustible gas be introduced into the furnace when the furnace temperature is less than 760 °C (1400 °F). When a lower operating temperature is required, the furnace should be heated to 760 °C and purged with generator gas before the temperature is decreased. This type of operation can be very dangerous and should be done only by qualified personnel.

Temperature Selection

Choice of carbonitriding temperature is based on a number of considerations, including steel composition, dimensional control, fatigue and wear properties, hardness, microstructural constituents, cost, and equipment.

Steel Composition. Although higher temperatures permit the use of higher concentrations of ammonia, ammonia content must be decreased as the alloy content of the steel increases to minimize austenite retention. To this extent, temperature, atmosphere, and alloy content are closely interrelated.

Dimensional control is often the most important consideration in the selection of carbonitriding temperature. The following two examples illustrate the relation between carbonitriding temperature and dimensional stability.

Example 5:

A 1010 steel rack 11.75 cm long by 1 mm thick (4.63 in. long by 0.040 in. thick) could not be kept within limits of straightness tolerance (and, because of brittleness, it could not be straightened) after it was quenched from a carbonitriding temperature of 845 °C (1550 °F) into warm oil at about 65 to 70 °C (150 to 160 °F) The part had a case-depth requirement of 0.075 mm (0.003 in.) and a flatness requirement of 0.05 mm (0.002 in.) over its entire length. Lowering the temperature to the range of 790 to 800 °C (1450 to 1475 °F) significantly reduced distortion and increased ductility to within acceptable limits. Although temperatures below 790 °C (1450 °F) might have resulted in even less distortion and more ductility, they were not used because of the increase in time required to produce the desired case depth.

Example 6:

Figure 12 presents data pertaining to the effect of carbonitriding temperature on the dimensional stability of three production parts. All three parts of 1010 commercial-quality steel sheet were processed in batch-type equipment at temperatures ranging from 790 to 845 °C (1450 to 1550 °F) The atmospheres consisted of endothermic gas at 7 m^3/h (250 ft^3/h), enriching gas at 0.8 m^3/h (30 ft^3/h), and ammonia at 0.14 m^3/h (5 ft^3/h). Dew points were maintained at -1 to -4 °C (25 to 30 °F). Depending on temperature, furnace times were varied to produce specified case depths of 0.13 to 0.20 mm (0.005 to 0.008 in.).

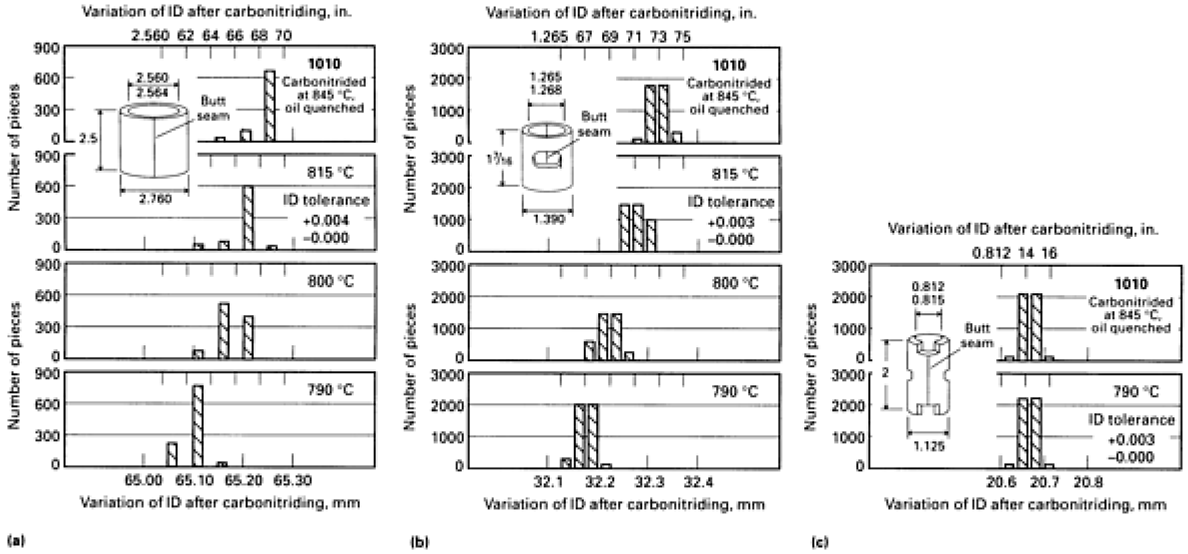


Fig. 12 Effect of carbonitriding temperature on dimensional stability of three 1010 steel production parts. Parts were carbonitrided to produce a case depth of 0.13 to 0.20 mm (0.005 to 0.008 in.) with minimum surface hardness of 89 HR15N. Gas ratios and dew points were essentially the same for all temperatures. Time at temperature was 15 to 45 min, depending on temperature. ID, inside diameter. Part dimensions and tolerances

given in inches

Equal numbers of parts were hand loaded in baskets and processed in a batch furnace. The parts shown in Fig. 12(a) and 12(b) were loaded with their axes in the vertical position; parts like those in Fig. 12(c) were randomly loaded. Baskets and parts were quenched in slightly agitated oil at 60 to 70 °C (140 to 160 °F).

Data in Fig. 12 represent eight heats for the part in Fig. 12(a) and three heats for each of the two other parts. All parts were within inside-diameter tolerance before carbonitriding.

For the parts carbonitrided at four temperatures, the least distortion resulted at the lowest temperature. Distortion is lower at lower temperatures because there is more ferrite in the structure at the lower temperature and consequently less volume expansion on quenching. However, for the part with the smallest inside diameter (Fig. 12c), dimensional variation was not affected by a reduction in temperature.

Temperature also has a direct bearing on core hardness. Steels treated at the higher carbonitriding temperatures and quenched from above the upper critical temperature of the core will produce higher core hardnesses. These high core hardnesses are usually desirable in applications involving high surface loads because a strong core is needed to support the hardened case.

Special fabrication and service requirements of a particular part may restrict the choice of carbonitriding temperature. For instance, in one application, cold headed pins used in door-catch mechanisms required both riveting quality and wear resistance. A carbonitriding temperature of 790 °C (1450 °F) satisfied both requirements by producing a soft center for riveting and a thin, file-hard case for wear resistance.

Control of Retained Austenite

Nitrogen lowers the transformation temperature of austenite. Therefore, a carbonitrided case usually contains more retained austenite than a carburized case of the same carbon content. The low indentation hardness resulting from retained austenite is undesirable in many applications. It can be extremely detrimental in components of close fitting assemblies--for example, shaft and sleeve assemblies wherein the shaft is intended to rotate or reciprocate in the sleeve. The delayed transformation of austenite to martensite at ambient temperature results in a volume increase that may cause moving parts to bind or "freeze" in service.

The amount of retained austenite can be significantly decreased by cooling the quenched parts to -40 to -100 °C (-40 to -150 °F). When close-tolerance ground parts are involved, this treatment should precede finish grinding. Subzero treatment of parts that are to be tempered should precede final tempering. Subzero treatment may cause microcracks in the case, particularly in coarse-grain steels. Because the amount of retained austenite is normally at a maximum near the steel surface, it can be removed from symmetrical contours by grinding. However, care must be exercised in grinding high retained austenite surfaces because of the increased possibility of grinding burn or checking. If grinding is not required for any reason other than to remove retained austenite, it also may be considered an expensive operation. The most economical way to minimize retained austenite is by selection of preferred steels and control of the carbonitriding process.

Minimizing retained austenite in the carbonitrided case is assisted by modification of several processing factors:

- *Furnace Temperature.* An increase in furnace temperature will reduce the nitrogen content of the outer portions of the case, thus minimizing the amount of retained austenite. It is far better to reduce ammonia flow, rather than depend upon increased temperature to lower the nitrogen content
- *Carbon Potential.* Lowering the carbon potential will also help reduce retained austenite
- *Ammonia content* of the carbonitriding atmosphere should be restricted to the minimum required to obtain the desired hardenability. A 1 to 5% ammonia content in the inlet gas is usually a satisfactory starting point; a lower content decreases the rate of penetration, but may be desirable to minimize retained austenite and to avoid case porosity

Quenching Media and Practices

Whether carbonitrided parts are quenched in water, oil, or gas depends on the allowable distortion, metallurgical requirements (such as case and core hardness), and type of furnace equipment employed.

Water Quenching. If the accompanying distortion is tolerable, parts made of low-carbon steel may be quenched in water. For example, shift-lever pins made of B1212 steel are water quenched.

Water quenching usually is restricted to those furnaces in which the work is transferred from the furnace into the air prior to quenching, thus avoiding possible contamination of the furnace atmosphere by water vapor. However, water quenching from a rotary retort furnace is feasible, provided the quench chute is equipped with gas ejectors and a water-distribution system for condensing water vapor.

It should be noted that ammonia is very soluble in water and forms a product (NH_4OH) that is extremely corrosive to copper-base materials. In continuous operations where water is exposed to an ammonia-bearing atmosphere, brass agitators, copper tube bundles in heat exchangers, and similar copper-alloy components should be avoided.

Gas Quenching. Parts that have small mass (such as thin stampings) may be quenched in a stream of cooled atmosphere gas or nitrogen. Gas or atmosphere quenching serves principally to reduce distortion, thus eliminating the high costs of straightening.

In gas quenching, parts must be loaded into furnace trays carefully so that the surfaces of the parts can be cooled rapidly enough to produce the desired hardness. Trays should be loaded and stacked so that the total mass of the load does not exceed that which can be satisfactorily quenched.

Tempering

Many shallow-case carbonitrided parts are used without tempering. The presence of nitrogen in the carbonitrided case increases its resistance to softening, and the increase varies with the amount of nitrogen in the case. Resistance to tempering may be desirable where service operating temperatures are abnormally high, or where hot straightening is employed.

Tempering data obtained on carbonitrided cases of 1018 steel are given in Fig. 13. The data relate temper-resistance to both carbonitriding temperature and the ammonia content of the atmosphere. Figure 14 presents a summary of the effects of carbonitriding temperature and ammonia content on temper-resistance, derived from the same specimens referred to in Fig. 13.

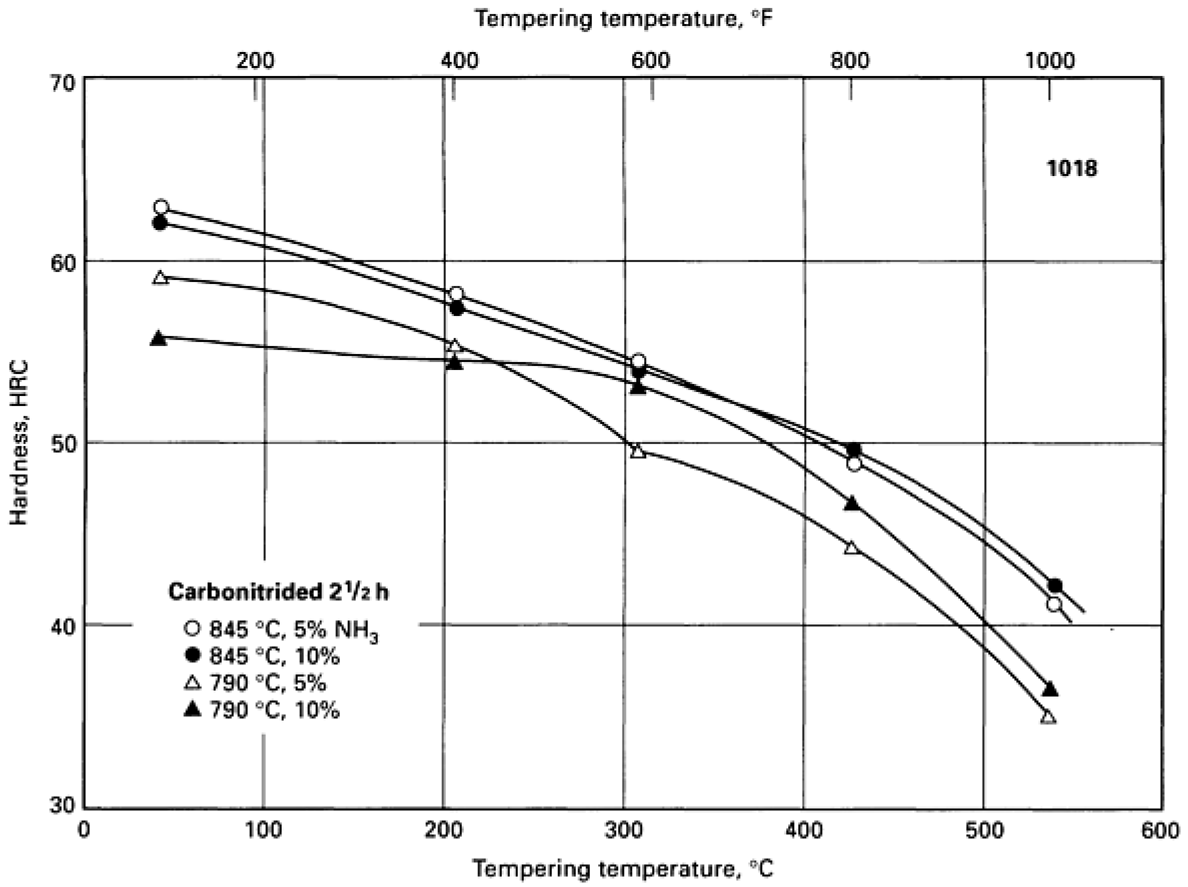


Fig. 13 Decrease of surface hardness with increasing temperature for specimens of 1018 steel carbonitrided under the conditions indicated. Rockwell C hardness converted from Rockwell 30-N. See also Fig. 14.

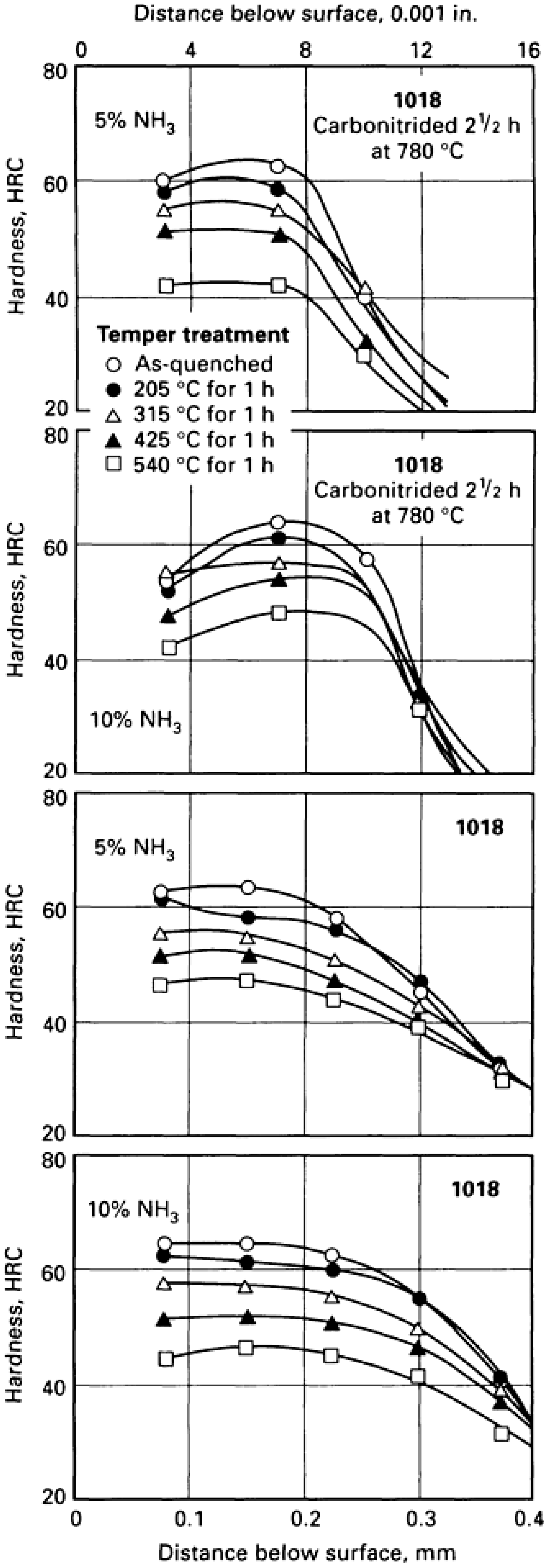


Fig. 14 Effect of tempering temperature on hardness gradients in carbonitrided cases. Rockwell C hardness

converted from Vickers. Specimens were the same as Fig. 13 and were tempered as indicated.

Because tempering a carbonitrided case at 425 °C (795 °F) and above results in a marked increase in notch toughness (see Table 4), parts that are to be subjected to repeated shock loading are invariably tempered to avoid impact and impact fatigue failures. Most carbonitrided gears are tempered at 190 to 205 °C (375 to 400 °F) to reduce surface brittleness and yet maintain a minimum case hardness of 58 HRC. Alloy steel parts that are to be surface ground are tempered to minimize grinding cracks. Low-carbon steel parts are frequently tempered at 135 to 175 °C (275 to 350 °F) to stabilize austenite and minimize dimensional variations. Tapping screws made of 1020 steel are tempered at 260 to 425 °C (500 to 795 °F) to reduce breakage in tapping holes in sheet metal. In contrast, parts that are case hardened primarily for wear resistance, such as dowel pins, brackets, and washers, need not be tempered.

Table 4 Effect of tempering on Charpy V-notch impact strength of carbonitrided 1041 steel

Specimens were carbonitrided at 845 °C (1550 °F) for 3 h in an atmosphere containing 7% ammonia, and were oil quenched from the carbonitriding temperature. Specimens were copper plated before machining of V-notch to permit exposure of the notch to the carbonitriding atmosphere.

Test	Tempering temperature		Impact strength		Hardness, HRC[(a)] Distance below surface, mm (in.)								
	°C	°F	J	ft · lb	Surface[(b)]	Core	0.075 (0.003)	0.15 (0.006)	0.25 (0.01)	0.38 (0.015)	0.64 (0.025)	1.0 (0.04)	1.4 (0.055)
1	As-quenched	As-quenched	1.4	1	60	53	63	64	64	63	61	61	58
2	370	700	2, 2	1.5, 1.5	47	46	57	57	55	54	49	50	50
3	425	800	29, 29	21.5, 21.5	42.5	43	57	57	56	55	49	47	47
4	480	900	69, 60	51, 44	38	38	54	54	52	50	42	38	38
5[(c)]	480	900	47, 52	35, 38	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
6	540	1000	78, 81	57.5, 60	35	32	49	50	50	47	36	33	32

(a) Converted from Vickers hardness.

(b) Surface hardness is less than hardness at 0.075 mm below the surface because of retained austenite.

(c) Tested at -18 °C (0 °F); all other tests at room temperature

Hardness Testing

The selection of a method of testing the surface hardness of carbonitrided steels depends primarily on the effective case depth on the parts to be tested. For effective case depths of 0.65 mm (0.025 in.) and above, accurate surface Rockwell C readings can be obtained. As the effective case depth decreases, lighter hardness testing loads must be used to obtain accurate surface hardness values. The Rockwell 15-N scale can be used in most instances for case depths of 0.25 to 0.40 mm (0.009 to 0.015 in.). On case depths of less than 0.25 mm, none of the Rockwell scales are reliable; testing may be done with files or a microhardness tester.

In file-hardness testing, parts with surface hardnesses that are less than full file hardness (64 to 68 HRC) can be tested with files that have been tempered to the desired hardness range. Surface hardness for such parts may be specified as Mfh 60, indicating that the part must be hardened to a mill file tempered to 60 HRC. However, a sample with high austenite content may indicate an indentation hardness of only 52 HRC and still resist a file hardened to 66 HRC.

Carbonitriding of Powder Metallurgy Parts

Carbonitriding is widely used as a process for case hardening parts made by powder metallurgy techniques from ferrous powders. Densities of the sintered compacts vary from approximately 6.5 g/cm^3 (0.23 lb/in.^{3}) up to those approaching that of wrought steel . Parts may or may not be copper infiltrated prior to carbonitriding.

Carbonitriding is effective in case hardening iron compacts made from electrolytic iron powders. Four characteristics of these compacts make case hardening by carburizing difficult: high martensite transformation temperature (M_s), very low hardenability, less surface oxidation, and inherent porosity, resulting in high rates of carbon penetration.

Carbonitriding at 790 to 815 °C (1450 to 1500 °F) solves these problems; lower rates of diffusion at these temperatures permit control of case depth and allow buildup of adequate carbon in the case. The effects of nitrogen in retarding the pearlite transformation result in sufficient hardenability to allow oil quenching.

File-hard cases (with microhardnesses equivalent to 60 HRC) and normal, predominantly martensitic structures can be consistently obtained. Shallow cases are obtainable, although the allowable range of case depth must be increased over that used for wrought steels. Typical ranges of case depth are 0.08 to 0.20 mm (0.003 to 0.008 in.) and 0.15 to 0.30 mm (0.006 to 0.012 in.).

The high rate of carbon and nitrogen penetration that occurs as the result of porosity is demonstrated in Fig. 15 for parts made of iron powder conforming to ASTM B 310, class A. Although the rate of penetration decreases with increasing density, case depths for the higher densities (7.20 to 7.30 g/cm^3, or 0.260 to 0.264 lb/in.^{3}) are much deeper than those obtained with a wrought steel (7.87 g/cm^3, or 0.284 lb/in.^{3}). Most commercial iron-powder compositions exhibit this type of response to carbonitriding; however, copper-infiltrated compacts are considerably more resistant to the penetration of carbon and nitrogen.

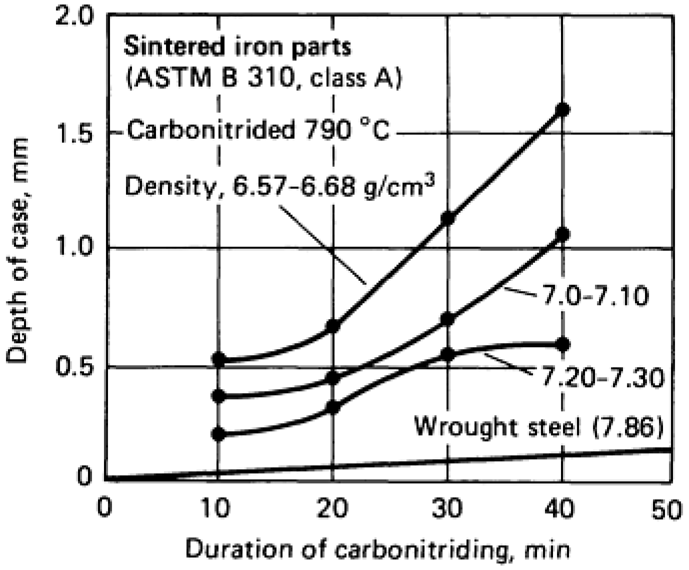


Fig. 15 Increase of case depth with decrease in density of iron powder metallurgy parts carbonitrided for various periods of time at 790 °C (1455 °F). Curve for steel is based on total furnace time and represents the average of the 775 to 790 °C (1425 to 1455 °F) band shown in Fig. 6.

Tempering. Carbonitrided iron powder metallurgy parts are usually tempered, despite the fact that there is little danger of cracking untempered pieces. Tempering accomplishes the incidental result of facilitating tumbling and deburring operations. Although tempering is potentially capable of removing oil picked up and held in the pores in the part, air tempering of oil-quenched powder metallurgy parts is normally limited to temperatures not exceeding 205 °C (400 °F) because of the fire hazard at higher temperatures. Carbonitrided iron powder metallurgy parts are usually tempered at temperatures slightly higher than the temperatures used for carbonitrided wrought steel parts. Special cleaning procedures to remove oil, thus eliminating fire hazards, are incorporated in the processing steps when the tempering temperature exceeds 205 °C.

Gas Nitriding of Steels

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Introduction

GAS NITRIDING is a case-hardening process whereby nitrogen is introduced into the surface of a solid ferrous alloy by holding the metal at a suitable temperature (below Ac_1, for ferritic steels) in contact with a nitrogenous gas, usually ammonia. Quenching is not required for the production of a hard case. The nitriding temperature for all steels is between 495 and 565 °C (925 and 1050 °F).

Application Factors

Principal reasons for nitriding are:

- To obtain high surface hardness
- To increase wear resistance and antigalling properties
- To improve fatigue life
- To improve corrosion resistance (except for stainless steels)
- To obtain a surface that is resistant to the softening effect of heat at temperatures up to the nitriding temperature

Because of the absence of a quenching requirement, with attendant volume changes, and the comparatively low temperatures employed in this process, nitriding of steels produces less distortion and deformation than either carburizing or conventional hardening. Some growth occurs as a result of nitriding, but volumetric changes are relatively small.

Nitridable Steels. Of the alloying elements commonly used in commercial steels, aluminum, chromium, vanadium, tungsten, and molybdenum are beneficial in nitriding because they form nitrides that are stable at nitriding temperatures. Molybdenum, in addition to its contribution as a nitride former, also reduces the risk of embrittlement at nitriding temperatures. Other alloying elements, such as nickel, copper, silicon, and manganese, have little, if any, effect on nitriding characteristics.

Although at suitable temperatures all steels are capable of forming iron nitrides in the presence of nascent nitrogen, the nitriding results are more favorable in those steels that contain one or more of the major nitride-forming alloying elements. Because aluminum is the strongest nitride former of the common alloying elements, aluminum-containing steels (0.85 to 1.50% Al) yield the best nitriding results in terms of total alloy content. Chromium-containing steels can approximate these results if their chromium content is high enough. Unalloyed carbon steels are not well suited to gas nitriding because they form an extremely brittle case that spalls readily, and the hardness increase in the diffusion zone is small.

The following steels can be gas nitrided for specific applications:

- Aluminum-containing low-alloy steels (Table 1)
- Medium-carbon, chromium-containing low-alloy steels of the 4100, 4300, 5100, 6100, 8600, 8700, and 9800 series
- Hot-work die steels containing 5% chromium such as H11, H12, and H13
- Low-carbon, chromium-containing low-alloy steels of the 3300, 8600, and 9300 series
- Air-hardening tool steels such as A-2, A-6, D-2, D-3, and S-7
- High-speed tool steels such as M-2 and M-4
- Nitronic stainless steels such as 30, 40, 50, and 60
- Ferritic and martensitic stainless steels of the 400 and 500 series
- Austenitic stainless steels of the 200 and 300 series
- Precipitation-hardening stainless steels such as 13-8 PH, 15-5 PH, 17-4 PH, 17-7 PH, A-286, AM350, and AM355

Table 1 Nominal composition and preliminary heat-treating cycles for aluminum-containing low-alloy steels commonly gas nitrided

Steel			Composition, %								Austenitizing temperature[a]		Tempering temperature[a]	
SAE	AMS	Nitralloy	C	Mn	Si	Cr	Ni	Mo	Al	Se	°C	°F	°C	°F
. . .	. . .	G	0.35	0.55	0.30	1.2	. . .	0.20	1.0	. . .	955	1750	565-705	1050-1300
7140	6470	135M	0.42	0.55	0.30	1.6	. . .	0.38	1.0	. . .	955	1750	565-705	1050-1300
. . .	6475	N	0.24	0.55	0.30	1.15	3.5	0.25	1.0	. . .	900	1650	650-675	1200-1250
. . .	. . .	EZ	0.35	0.80	0.30	1.25	. . .	0.20	1.0	0.20	955	1750	565-705	1050-1300

(a) Sections up to 50 mm (2 in.) in diameter, quenched is oil; larger sections may be water quenched.

Aluminum-containing steels produce a nitrided case of very high hardness and excellent wear resistance. However, the nitrided case also has low ductility, and this limitation should be carefully considered in the selection of aluminum-containing steels. In contrast, low-alloy chromium-containing steels provide a nitrided case with considerably more ductility but with lower hardness. Nevertheless, these steels offer substantial wear resistance and good antigalling properties. Tool steels, such as H11 and D2, yield consistently high case hardness with exceptionally high core strength.

Prior Heat Treatment. All hardenable steels *must* be hardened and tempered before being nitrided. The tempering temperature must be high enough to guarantee structural stability at the nitriding temperature; the minimum tempering temperature is usually at least 30 °C (50 °F) higher than the maximum temperature to be used in nitriding.

In certain alloys, such as series 4100 and 4300 steels, hardness of the nitrided case is modified appreciably by core hardness; that is, a decrease in core hardness results in a decrease in case hardness. Consequently, in order to obtain maximum case hardness, these steels are usually provided with maximum core hardness by being tempered at the minimum allowable tempering temperature.

Applications. Examples of typical gas nitriding applications and procedures are presented in Table 2. Table 3 lists examples of parts for which nitriding eliminated production or service problems that arose when the parts were case hardened by other methods.

Table 2 Nitriding applications and procedures

Part	Dimensions or weight of part	Steel	Nitriding time, h
Single-stage nitriding			
Hydraulic barrel	50 mm (2 in.) OD, 19 mm ($\frac{3}{4}$ in.) ID, 150 mm (6 in.) long	AMS 6470	48
Trigger for pneumatic hammer	. . .	AMS 6470	40
Governor push button	6 mm ($\frac{1}{4}$ in.) diam	AMS 6470	30
Tachometer shaft	380 mm (15 in.) long	AMS 6475	25
Helical timing gear	205 mm (8 in.) OD (4.5 kg or 10 lb)	4140	24
Gear	50 mm (2 in.) OD, 6 mm ($\frac{1}{4}$ in.) thick	4140	24
Generator shaft	25 mm (1 in.) OD, 355 mm (14 in.) long	4140	24
Rotor and pinion for pneumatic drill	22 mm ($\frac{7}{8}$ in.) diam	4140	9
Sleeve for pneumatic tool clutch	38 mm (1 $\frac{1}{2}$ in.) diam	4140	9
Marine helical transmission gear	635 mm (25 in.) OD (227 kg or 500 lb)	4142	32
Oil-pump gear	50 mm (2 in.) OD, 180 mm (7 in.) long	4340	25
Loom shuttle	150 mm by 25 mm by 25 mm (6 in. by 1 in. by 1 in.)	410 stainless	8
Double-stage nitriding			
Ring gear for helicopter main transmission	380 mm (15 in.) OD, 350 mm (13.8 in.) ID, 64 mm (2.5 in.) long	AMS 6470[a]	60[b]
Aircraft cylinder barrel	180 mm (7 in.) OD, 305 mm (12 in.) long	AMS 6470	35[c]
Bushing	10 kg (23 lb)	AMS 6470	90
Cutter spindle	3 kg (7 lb)	AMS 6470	45
Plunger	75 mm (3 in.) OD, 1525 mm (60 in.) long	AMS 6475	72
Crankshaft	205 mm (8 in.) OD (journals), 4 m (13 ft) long	4130	65
Piston ring	150 mm (6 in.) OD, 4.25 m (14 ft) long	4130	65
Clutch	1 kg (2 lb)	4140	45
Double helical gear	50 kg (108 lb)	4140	97
Feed screw	4 kg (9 lb)	4140	45
Pumper plunger	0.5 kg (1 lb)	4140	127
Seal ring	9.5 kg (21 lb)	4140	90
Stop pin	3 kg (7 lb)	4140	90
Thrust collar	3.6 kg (8 lb)	4140	90

Wear ring	40 kg (87 lb)	4140	90
Clamp	7 kg (15 lb)	4150	90
Die	21 kg (47 lb)	4340	90
Gib	10 kg (23 lb)	4340	49
Spindle	122 kg (270 lb)	4340	90
Torque gear	62.5 kg (138 lb)	4340	90
Wedge	1.8 kg (4 lb)	4340	42
Pumper plunger	1.4 kg (3 lb)	420 stainless	127

Note: OD, outer diameter; ID, inner diameter.

(a) Vacuum melted.

(b) 9 h at 525 °C (975 °F), 51 h at 545 to 550 °C (1015 to 1025 °F).

(c) 6 h at 525 °C (975 °F), 29 h at 565 °C (1050 °F)

Table 3 Examples of parts for which nitriding proved superior to other case-hardening processes for meeting requirements

Part	Requirement	Material and process originally used	Resultant problem	Solution
Gear	Good wear surface and fatigue properties	Carburized 3310 steel 0.4 to 0.6 mm (0.017 to 0.025 in.) case	Difficulty in obtaining satisfactory case to meet a reliability requirement	AMS 6470 substituted for 3310 and double-stage nitrided for 25 h
High-speed pinion (on gear motor)	Provide teeth with minimum (equivalent) hardness of 50 HRC	8620 steel gas carburized at 900 °C (1650 °F) to 0.5 mm (0.02 in.) case, direct quenched from 845 °C (1550 °F) and tempered at 205 °C (400 °F)	Distortion in teeth and bore caused high rejection rate	4140 steel, substituted for 8620, was heat treated to 255 HB; parts were rough machined, finish machined, nitrided[(a)]
Bushings (for conveyor rollers handling abrasive alkaline material)	High surface hardness for abrasion resistance; resistance to alkaline corrosion	Carburized bushings	Service life of bushings was short because of scoring	Substitution of Nitralloy 135 type G (resulfurized) heat treated to 269 HB and nitrided[(b)]
Spur gears (in train of power gears; 10-pitch, tip modified)	Sustain continuous Hertz stress of 1035 MPa (150 ksi) (overload of 1550 MPa, or 225 ksi), continuous Lewis stress of 275 MPa (40 ksi) (overload of 725 MPa, or 105 ksi)[(c)]	Carburized AMS 6260	Gears failed because of inadequate scuff resistance, also suffered property losses at high operating temperatures	Substitution of material of H11 type, hardened and multiple tempered (3 h + 3 h) to 48 to 52 HRC, then double-stage nitrided[(d)]

(a) Single-stage nitrided at 510 °C (950 °F) for 38 h. Cost increased 5%, but rejection rate dropped to zero.

(b) Single-stage nitrided at 510 °C (950 °F) for 38 h. Case depth was 0.46 mm (0.018 in.), and hardness was 94 HR15-N; parts had three times the service life of carburized parts.

(c) Must withstand operating temperatures to 290 °C (550 °F).

(d) 15 h at 515 °C (960 °F) (15 to 25% dissociation); then 525 °C (980 °F) (80 to 83% dissociation). Effective case depth (to 60 HRC), 0.25 to 0.4 mm (0.010 to 0.015 in.); case hardness, 67 to 72 HRC (converted from Rockwell 15-N scale)

Single-Stage and Double-Stage Nitriding

Either a single- or a double-stage process may be employed when nitriding with anhydrous ammonia. In the single-stage process, a temperature in the range of about 495 to 525 °C (925 to 975 °F) is used, and the dissociation rate ranges from 15 to 30%. This process produces a brittle, nitrogen-rich layer known as the white nitride layer at the surface of the nitrided case.

The double-stage process, known also as the Floe process (U.S. Patent 2,437,249), has the advantage of reducing the thickness of the white nitrided layer.

The first stage of the double-stage process is, except for time, a duplication of the single-stage process. The second stage may proceed at the nitriding temperature employed for the first stage, or the temperature may be increased to from 550 to 565 °C (1025 to 1050 °F); however, at either temperature, the rate of dissociation in the second stage is increased to 65 to

80% (preferably, 75 to 80%). Generally, an external ammonia dissociator is necessary for obtaining the required higher second-stage dissociation.

The principal purpose of double-stage nitriding is to reduce the depth of the white layer produced on the surface of the case. Except for a reduction in the amount of ammonia consumed per hour, there is no advantage in using the double-stage process, unless the amount of white layer produced in single-stage nitriding cannot be tolerated on the finished part or unless the amount of finishing required after nitriding is substantially reduced. In Fig. 1, the amount of white layer formed during a 25-h double-stage nitriding treatment is compared to that formed during a 24-h single-stage nitriding of the same material.

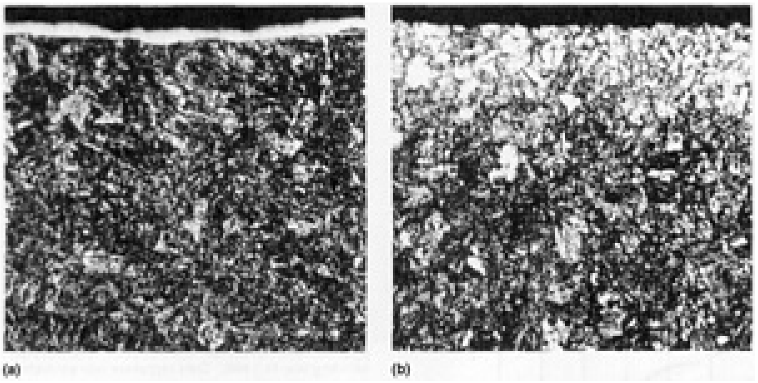


Fig. 1 Microstructure of quenched and tempered 4140 steel after (a) gas nitriding for 24 h at 525 °C (975 °F) with 20 to 30% dissociation and (b) gas nitriding for 5 h at 525 °C (975 °F) with 20 to 30% dissociation followed by a second stage of 20 h at 565 °C (1050 °F) with 75 to 80% dissociation. Both specimens were oil quenched from 845 °C (1550 °F) tempered for 2 h at 620 °C (1150 °F), and surface activated with manganese phosphate before nitriding. (a) Structure after single-stage nitriding 0.005 to 0.0075 mm (0.0002 to 0.0003 in.) white surface layer (Fe_2N), iron nitride, and tempered martensite. (b) The high second-stage dissociation caused absence of white layer, and the final structure had a diffused nitride layer on a matrix of tempered martensite. Both 2% nital. 400×

Figure 2 shows the effect of nitriding time on the depth of case developed on 4140 steel during double-stage nitriding at 525 °C (975 °F) for both stages. Use of a higher temperature during the second stage would have produced a deeper case of slightly lower hardness.

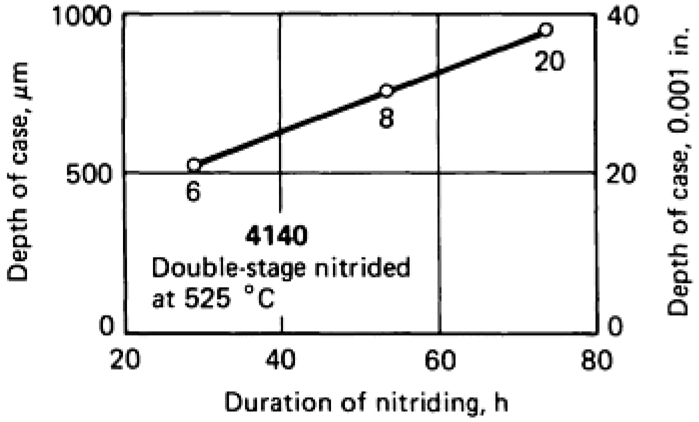


Fig. 2 Depth of case developed on 4140 steel during double-stage nitriding. Numbers indicate hours of nitriding at 15 to 25% dissociation. Remainder of cycle at 83 to 85% dissociation

Hardness gradients obtained in double-stage nitriding of SAE 7140 (AMS 6470) are shown in Fig. 3. The hardness results shown in Fig. 3(a), 3(b), and 3(c) were obtained by grinding off progressively increasing amounts of case to form steps on which HR-15N readings were made. Data for Fig. 3(d), 3(e), and 3(f) were obtained from microhardness measurements, converted to HRC equivalents. Similar data, for double-stage nitriding of AMS 6475, are shown in Fig. 4.

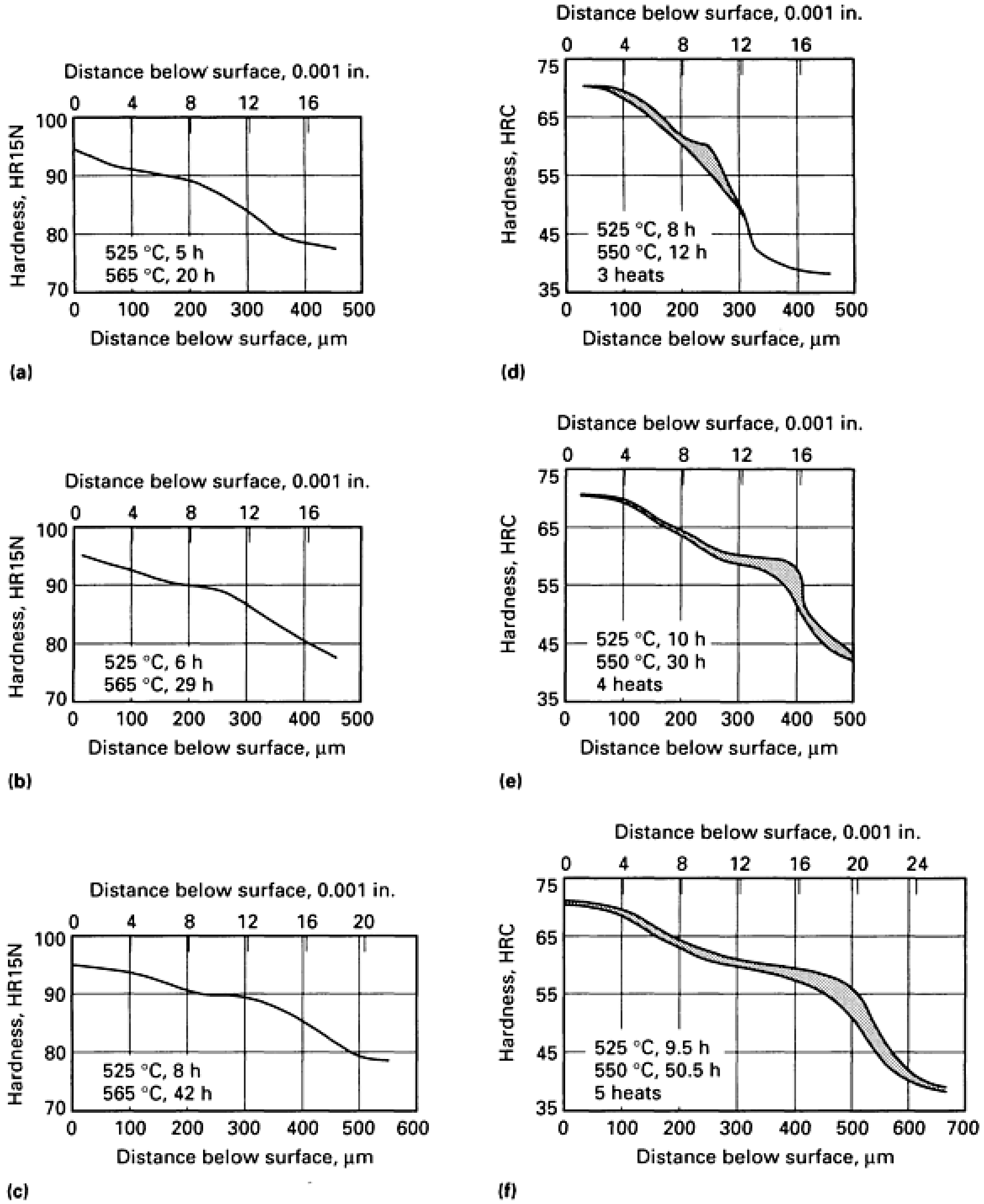


Fig. 3 Hardness gradients for double-stage nitrided SAE 7140 (AMS 6470) steel. (a)-(c) Material nitrided with dissociation rates of 15 to 20% during first stage and 60 to 70% during second stage. (d)-(f) Material nitrided with dissociation rates of 25 to 28% during first stage and 75 to 80% in second stage. Material produced by consumable-electrode vacuum-arc-remelting method

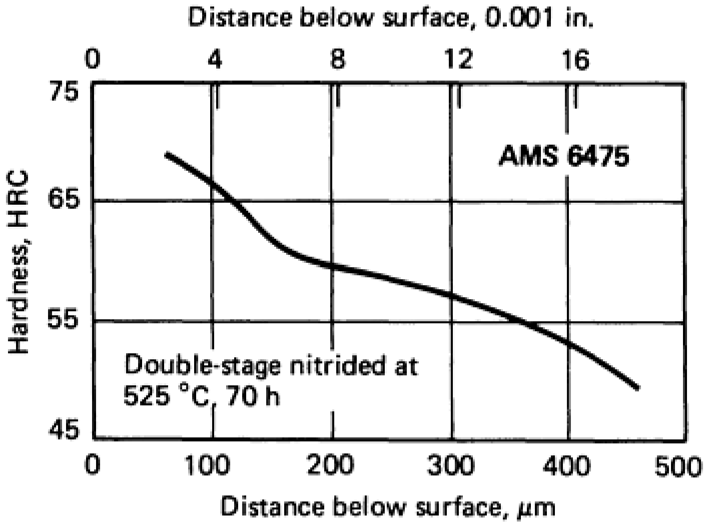


Fig. 4 Hardness gradient obtained for double-stage nitrided AMS 6475 steel. HRC hardness numbers were obtained by conversion from diamond pyramid hardness measurements. Core hardness after nitriding was 41.5 HRC. Data represent one air-melted heat of AMS 6475.

To summarize, the use of a higher temperature during the second stage:

- Lowers the case hardness
- Increases the case depth
- May lower the core hardness depending on the prior tempering temperature and the total nitriding cycle time
- May lower the apparent effective case depth because of the loss of core hardness, depending on how effective case depth is defined

Operating Procedures

After hardening and tempering, and before nitriding, parts should be thoroughly cleaned. Most parts can be successfully nitrided immediately after vapor degreasing. However, some machine-finishing processes such as buffing, finish grinding, lapping, and burnishing may produce surfaces that retard nitriding and result in uneven case depth and distortion. There are several methods by which the surfaces of parts finished by such methods may be successfully conditioned before nitriding.

One method consists of vapor degreasing parts and then abrasive cleaning them with aluminum oxide grit or other abrasives such as garnet, or silicon carbide, immediately prior to nitriding. Any residual grit must be brushed off before parts are loaded into the furnace. Parts should be handled with clean gloves.

A second method consists of preoxidizing the parts in an air atmosphere at approximately 330 °C (625 °F). This may be done as a separate operation, or it may be incorporated as part of the heating portion of the nitriding cycle if suitable precautions are taken.

Furnace Purging

After loading and sealing the furnace at the start of the nitriding cycle, it is necessary to purge the air from the retort before the furnace is heated to a temperature above 150 °C (300 °F). This prevents oxidation of parts and furnace components, and, when ammonia is used as the purging atmosphere, avoids production of a potentially explosive mixture. Nitrogen is preferred in place of ammonia for purging, but the same precautions should be taken to avoid oxidation of parts, except when preoxidation is intentionally included as part of the cycle.

A typical purging cycle using anhydrous ammonia follows:

- Close furnace and start flow of anhydrous ammonia gas at as fast a flow rate as is practical with first

step

- Set furnace temperature control at 150 °C (300 °F) simultaneously. Heat furnace to this temperature but do not exceed
- When the furnace has been purged to the degree that 10% or less air and 90% or more ammonia are present in the retort, the furnace may be heated to the nitriding temperature

It is not feasible to incorporate preoxidation as part of the cycle unless nitrogen is available as a purging medium at the end of the 320 °C (625 °F) oxidizing stage. *Caution: Under no circumstances should ammonia be introduced into a furnace containing air at 330 °C (625 °F) because of the explosion hazard.*

Purging is employed also at the conclusion of the nitriding cycle when the furnace is cooled from the nitriding temperature. It is common practice to remove the ammonia remaining in the retort with nitrogen to reduce the amount of ammonia that would otherwise be released into the immediate area when the load is removed. Dilution of the ammonia lessens the discomfort to employees working near the furnace. The introduction of nitrogen into the retort can be delayed until the nitrided parts have cooled to below 150 °C (300 °F).

Emergency Purging. If the supply of ammonia is cut off during the nitriding cycle, or if a break occurs in the supply line, there is great danger that air will be sucked into the furnace by the contraction of gases within the furnace. This danger is greatest during the cooling cycle. To guarantee a positive pressure within the furnace, it is general practice to provide an emergency purging system that will pump dry nitrogen or an oxygen-free generated gas into the furnace and maintain a safe pressure. If a generated gas is used, it should be as moisture-free as possible. These purge gases are released directly into the ammonia line by a special system of valves.

If emergency purging facilities are not available, further cooling of the furnace should be prevented. Exhaust and inlet lines should be closed, and if no air has entered the retort, the temperature of the furnace and load should be increased slightly to maintain a positive pressure within the retort. Temperature should be maintained until the break is repaired and the flow of ammonia is restored.

Nitrogen versus Ammonia for Purging. Advantages of nitrogen as a purging gas include its safety, ease of handling, and ease of control. The use of nitrogen, however, requires additional equipment, including piping.

Ammonia requires no additional equipment and is relatively safe when properly handled; *Caution: mixtures of 15 to 25% ammonia in air, however, are explosive if ignited by a spark.*

Dissociation Rates. The nitriding process is based on the affinity of nascent nitrogen for iron and certain other metallic elements. Nascent nitrogen is produced by the dissociation of gaseous ammonia when it contacts hot steel parts. Although various rates of dissociation can be used successfully in nitriding, it is important that the nitriding cycle begin with a dissociation rate of about 15 to 35% and that this rate be maintained for 4 to 10 h, depending on the duration of the total cycle; temperature should be maintained at about 525 °C (975 °F). Typically ammonia is supplied at a flow rate to achieve a minimum of four (4) atmosphere changes in the retort per hour. This initial cycle develops a shallow white layer from which diffusion of nitrogen into the main case structure proceeds.

In most nitriding cycles, dissociation rates vary somewhat, even though the controlling factors--ammonia flow rate, surface area, and nitriding temperature--remain constant. Characteristically, the dissociation rate gradually increases as the cycle proceeds at a constant ammonia flow rate. This increase, however, usually is not enough to affect nitrided case characteristics significantly.

When nitriding with a dissociation rate of 15 to 35%, it is normal to control this rate entirely by the flow rate of ammonia. At a dissociation rate of 75 to 80%, however, it is necessary to introduce completely dissociated ammonia from an external dissociator or nitrogen to ensure adequate positive flow within the furnace.

Furnace Heating and Cooling

For reasons of economy, it is generally desirable to keep the total cycle time as short as possible by heating and cooling as rapidly as the equipment will permit and allowing for the following considerations. It may be an advantage to:

- Limit the heating rate, for example to 55 °C/h (100 °F/h) or slower, to allow time for any residual contaminants on the work and from stop-off paint to be completely expelled before reaching the nitriding temperature
- Both heat and cool at limited rates to minimize temperature gradients throughout large loads or in large and complex parts, and thus to minimize distortion

Many pit-type nitriding furnaces are equipped with a heat exchanger that will accelerate cooling of the furnace and work load at the conclusion of the nitriding cycle. When an external water-cooled heat exchanger is used, the furnace heating elements are turned off when the nitriding cycle is completed, and the furnace temperature is allowed to drop approximately 55 °C (100 °F). At this point, the ammonia flow is approximately doubled, and the cooling water is turned on in the heat exchanger. The circulating blower of the heat exchanger also is turned on, and a gate valve is opened to permit circulation of the furnace atmosphere through the heat exchanger. Extreme care must be exercised to ensure a positive gas flow through the furnace as evidenced by the exit gas bubbles. When gas flow through the furnace has been stabilized, the flow may be reduced to the minimum required for positive pressure. After cooling to 150 °C (300 °F) or below, the furnace may be opened.

Bell-type furnaces may be cooled with a cooling bell that is placed over the sealed nitriding retort after the heating bell has been removed. The following is a typical procedure for cooling a bell-type furnace with either raw ammonia or dissociated ammonia:

- Place cooling bell in position on base
- Insert plug of cooling bell into receptacle
- Turn on bell cooling fan
- Cool furnace and load to not less than 315 °C (600 °F), as indicated on base recorder. Turn off flow of dissociated ammonia, and increase flow of raw ammonia to approximately 1.4 m^3/h (50 ft^3/h)
- When burette reading indicates a dissociation rate of 5% or less and temperature is 120 °C (250 °F) or below, shut off flow of ammonia to furnace and open air valve to furnace. If dissociation rate is 5% or less before temperature falls to 120 °C (250 °F), flow of raw ammonia can be reduced to 1.1 m^3/h (40 ft^3/h) for remainder of cooling time
- Remove cooling bell
- Open air valve to meter; allow 4.2 m^3/h (150 ft^3/h) of air into furnace, and open exhaust valve wide. (Level on manometer will drop nearly to zero)
- Turn off base fan when burette reading increases to 65% dissociation. (*Caution: A mixture of 16 to 25% ammonia in air is explosive. Therefore, fan must be shut off when ammonia level reaches 35%, or 65% burette reading.*) This eliminates hazard from sparks that may be generated by a moving fan
- Continue to purge furnace until burette reading is 95% or higher. (This is not a safety precaution but is done to minimize discomfort to personnel nearby when furnace is opened)
- Close air valve
- Drain oil seal
- Raise retort about 0.3 m (1 ft) and wipe off seal from retort lip before removing retort completely
- Remove the charge from the furnace

Control of Case Depth

Case depth and case hardness, the two criteria most commonly referred to in the control of case properties, vary not only with the duration and other conditions of nitriding, but also with steel composition, prior structure, and core hardness.

Aluminum-Containing Steels. Of the aluminum-containing nitriding steels, the most widely used is SAE 7140 (AMS 6470). Figure 5 indicates the hardness gradients and case depths obtained with this steel, as a function of cycle time and nitriding conditions. Results were obtained in single-stage nitriding for various lengths of time up to 800 h and at temperatures ranging from 510 to 540 °C (950 to 1000 °F); several different dissociation rates are represented. The 800-h specimens were nitrided in 11 consecutive 72-h periods. It is apparent that the rate of nitriding decreases over extended periods of time; the case depth obtained after 800 h is only about three times that obtained in 100 h.

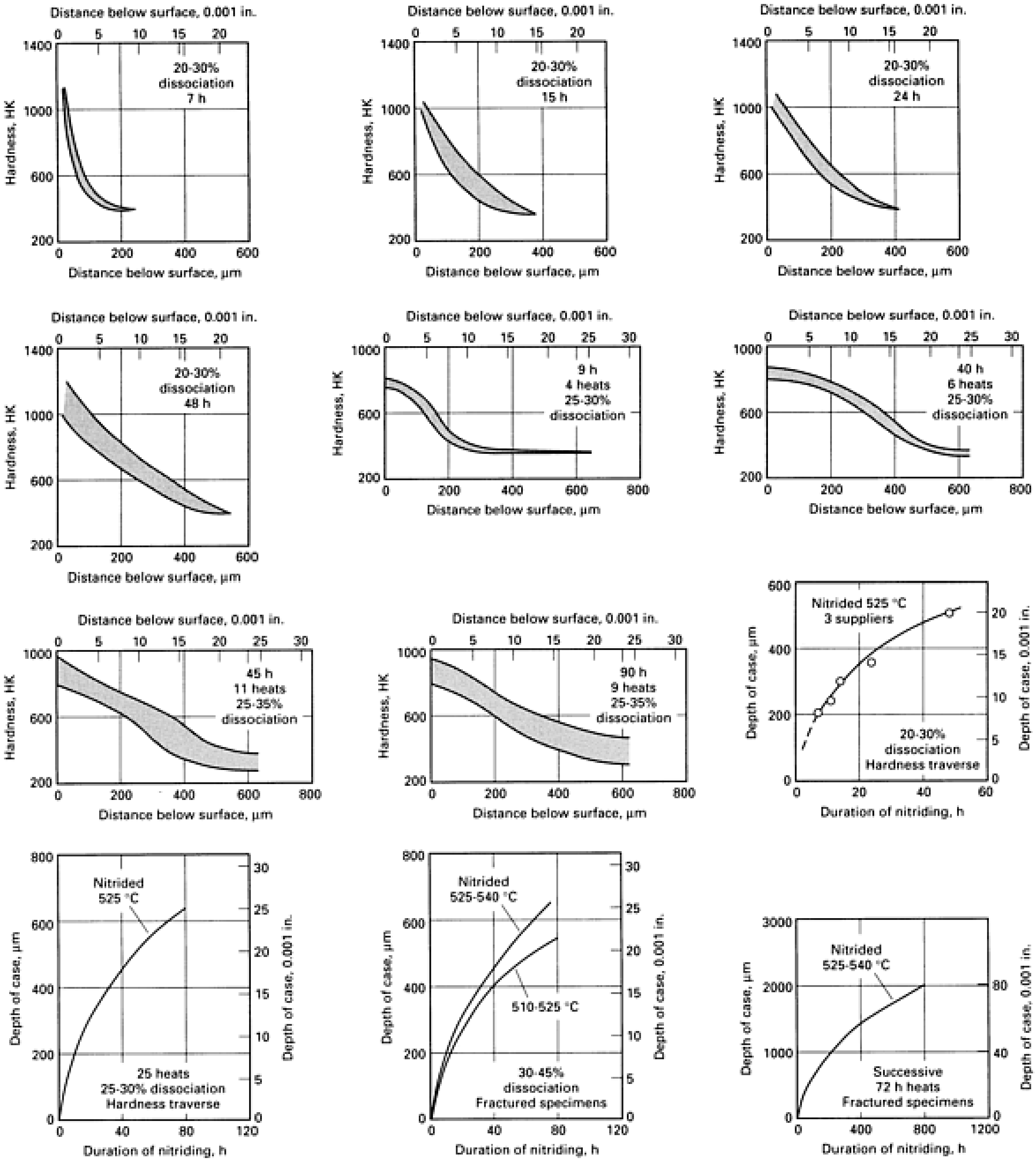
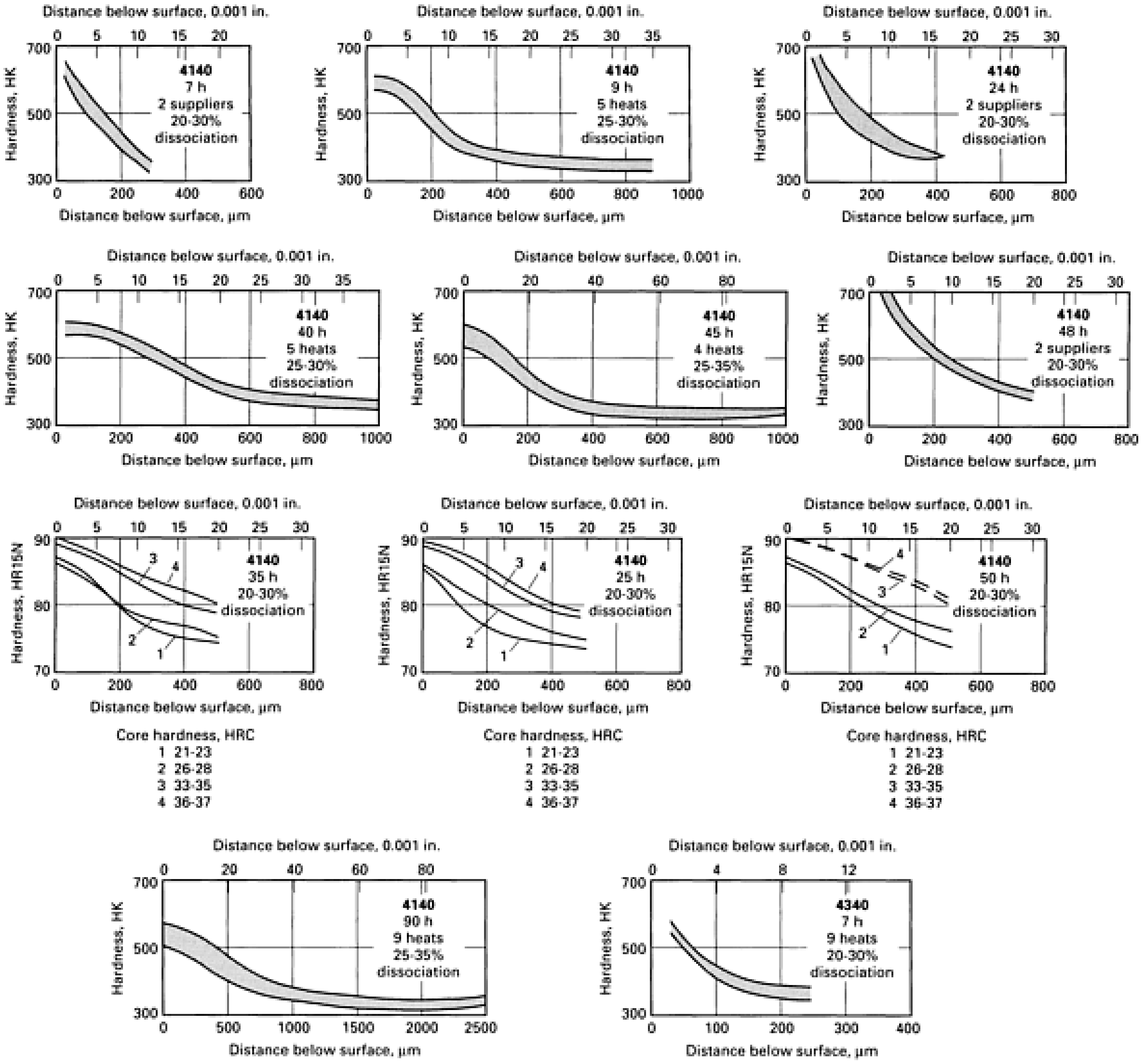


Fig. 5 Hardness gradients and case depth relations for single-stage nitrided aluminum-containing SAE 7140 steel

Chromium-Containing Low-Alloy Steels. Data relating case depth to nitriding time and conditions for chromium-containing low-alloy steels (principally 4140, 4337, 4340, and 8640) are given in Fig. 6 and 7. Of these steels, 4140 exhibits the best nitriding characteristics because of its higher chromium content and nickel-free composition. Although 4340 develops a heavier case than 8640 in the first 24 h of nitriding, this difference begins to decrease at the end of a 48-h cycle (Fig. 7).


Distance below surface, 0.001 in.
Hardness, HK
Distance below surface, μm
4140
7 h
2 suppliers
20-30%
dissociation
4140
9 h
5 heats
25-30%
dissociation
4140
24 h
2 suppliers
20-30%
dissociation
4140
40 h
5 heats
25-30%
dissociation
4140
45 h
4 heats
25-35%
dissociation
4140
48 h
2 suppliers
20-30%
dissociation
Hardness, HR15N
4140
35 h
20-30%
dissociation
Core hardness, HRC
1 21-23
2 26-28
3 33-35
4 36-37
4140
25 h
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Core hardness, HRC
1 21-23
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Core hardness, HRC
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2 26-28
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7 h
9 heats
20-30%
dissociation

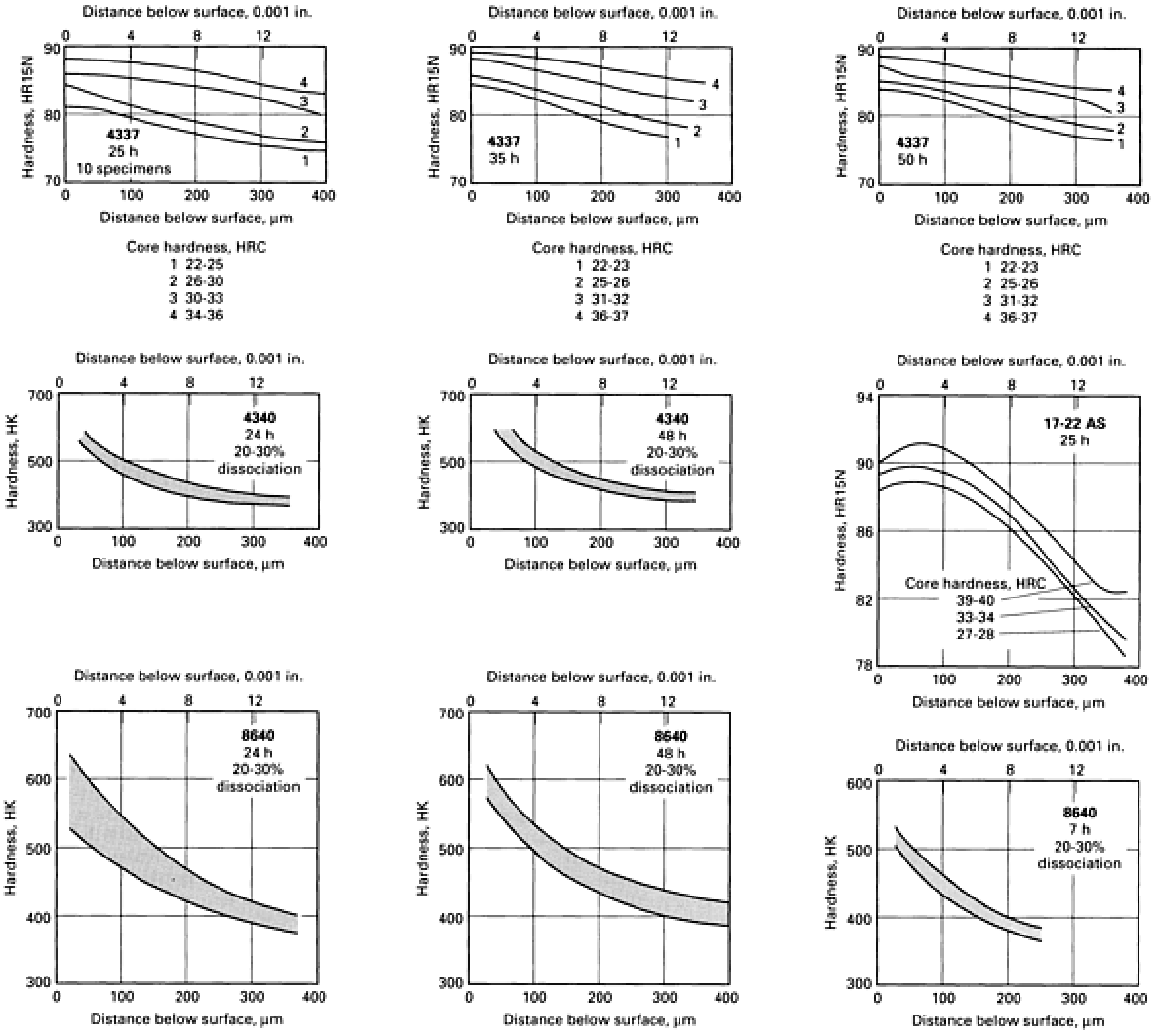


Fig. 6 Hardness gradients for nitrided chromium-containing low-alloy steels

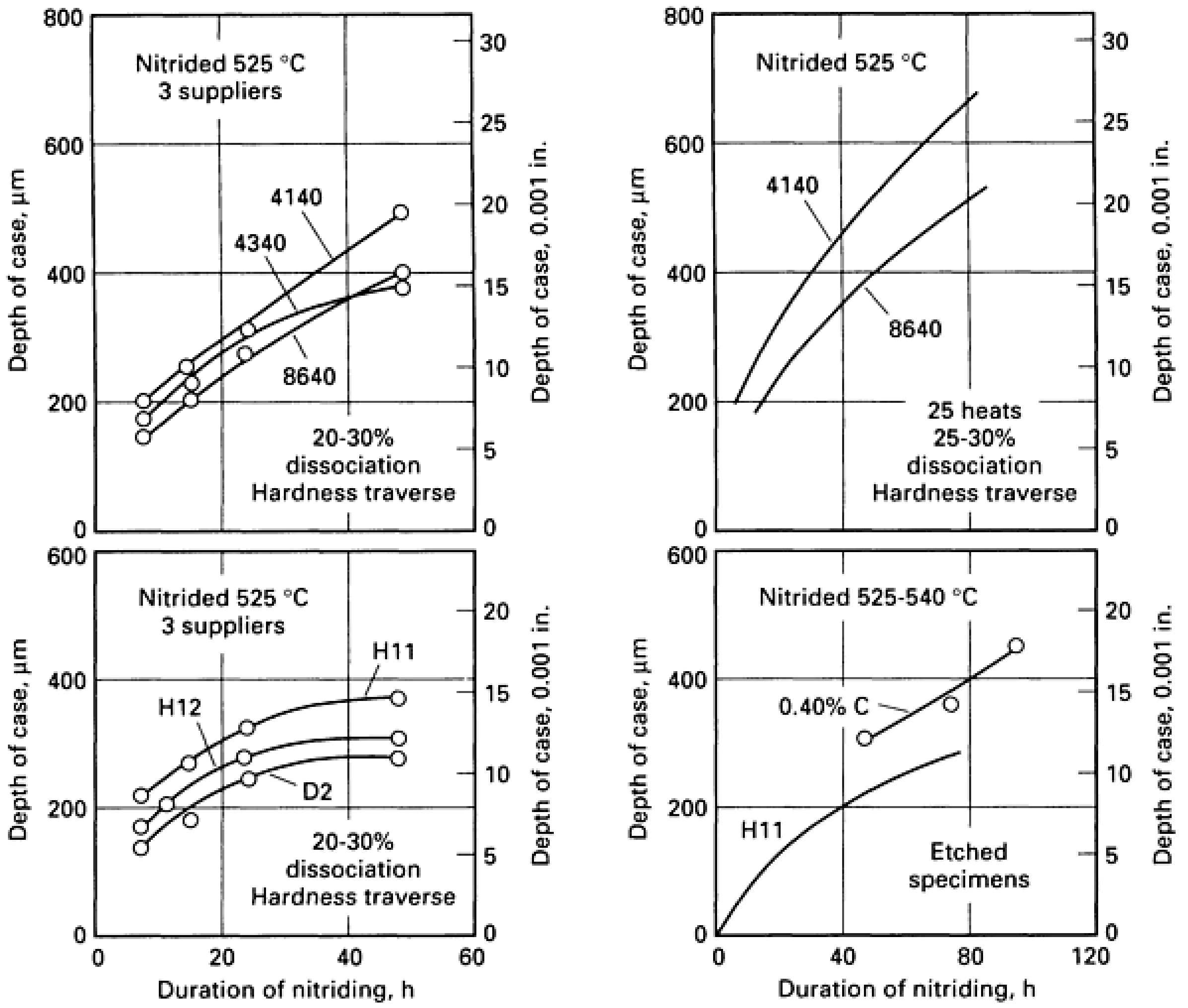


Fig. 7 Depth of case as a function of duration of nitriding for chromium-containing low-alloy and tool steels

Data for the AMS equivalents of 4337 and 4140 (AMS 6412 and 6382, respectively) in Fig. 6 are of particular interest because they demonstrate the effect of core hardness on the hardness of the nitrided case. Core hardnesses as low as 21 to 23 HRC, and as high as 36 to 37 HRC, are considered.

Chromium-containing tool steels such as H11, H12, H13, and D2 provide high core strength with high case hardness, an excellent combination for applications involving severe impact or very high unit loading. Use of these steels is limited primarily by high cost and fabricating difficulties. Case depth results for these steels in single-stage nitriding at 525 °C (975 °F) and at 525 to 540 °C (975 to 1000 °F) are given in Fig. 7. The relatively shallow case depths obtained reflect the retarding effect of increased chromium content on the penetration of nitrogen. Hardness gradients for the same steels are shown in Fig. 8.

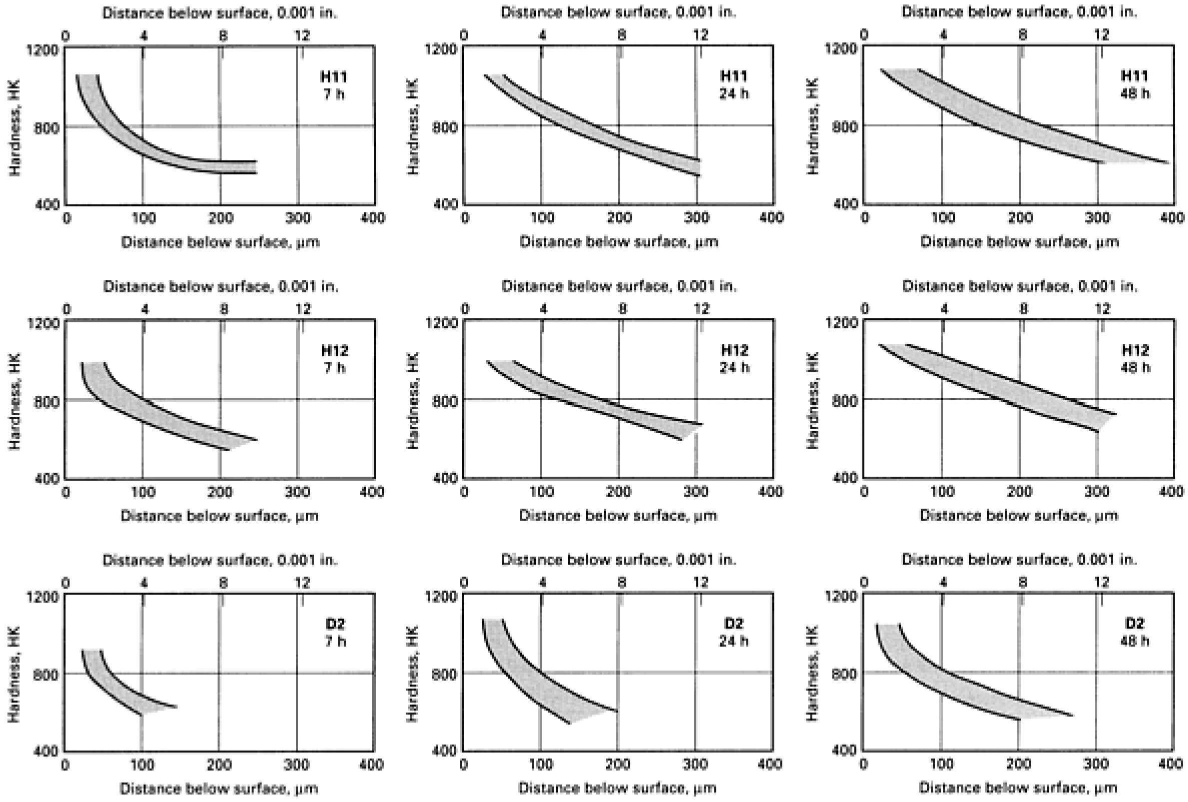


Fig. 8 Hardness gradients for chromium-containing tool steels

Distortion and Dimensional Changes

Distortion in nitriding may result from:

- Relief of residual stresses from prior operations such as welding, hardening, machining, and so forth
- Stress introduced during nitriding due to inadequate support in the furnace, or too rapid or nonuniform heating or cooling
- Stress introduced by the increase in volume that occurs in the case. This change causes a stretching of the core, which results in tensile stresses that are balanced by compressive stresses in the case after the parts have cooled to room temperature. The magnitude of the permanent set in the core and case is affected by yield strength of the material, thickness of the case, and by the amount and nature of the nitrides formed

When the prior manufacturing practice and the mechanics of the nitriding cycle are properly controlled, growth becomes the primary cause of distortion. This is governed largely by composition, tempering temperature, time and temperature of nitriding, relative thickness of case and core, and shape of the part. Growth also is affected when some areas of the part are masked to prevent nitriding.

The amount of growth is usually constant for identical parts nitrided in different batches by a fixed processing cycle. Thus, after the amount of growth for a particular part has been determined experimentally, allowance for it can be made during final machining prior to nitriding. Before experiments are conducted to determine growth, parts must be thoroughly stress relieved.

An example of growth as a function of the wall thickness of hollow cylinders made of Nitralloy 135 is shown in Fig. 9. These data may be used as an approximation in estimating growth when nitriding by the double-stage process. They should be used as a guide for determining size changes only with respect to parts of this design, however; the growth that occurs in solid rounds of bars is of the order of a 0.4 mm (0.0015 in.) increase in diameter.

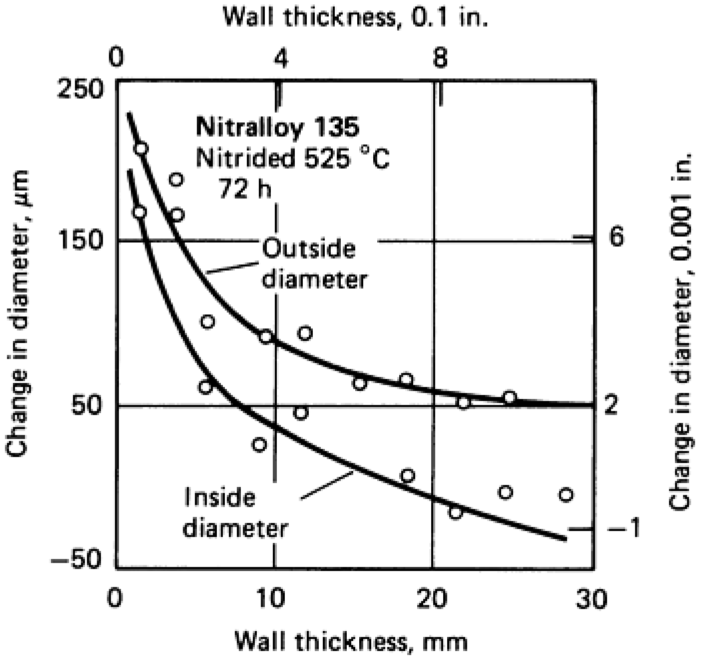


Fig. 9 Growth as a function of the wall thickness of 70 mm (2 $\frac{3}{4}$ in.) diam hollow cylinders double-stage nitrided for 72 h

In some parts, the dimensional changes during nitriding involve both internal and external surfaces. For example, the bore diameter of a 300 mm (12 in.) diam spur gear decreased as much as 0.025 mm (0.001 in.), whereas the overall gear dimension increased up to 0.1 mm (0.004 in.).

Sharp corners or edges should be avoided on parts to be nitrided because the projections formed at sharp corners, as a result of the growth that takes place, are high in nitrogen content and susceptible to chipping. Similarly, sharp edges nitride throughout the section and have no supporting core. When sharp corners are unavoidable, brittleness may be reduced by nitriding one side only, if the other side is not a wearing surface. Frequently, the problems of growth are eliminated by nitriding only those surfaces that will be subject to wear in service.

Stabilizing Treatment. In nitrided parts, there is a balance between compressive stresses in the case and tensile stresses in the core. If this balance is upset by grinding off a part of the case, slow dimensional changes may occur as the stresses approach equilibrium. (In some instances, slow dimensional changes resulting from stress redistribution during grinding have been erroneously attributed to wear.) To prevent these changes, nitrided parts are first ground almost to the final dimensions, then heated to 565 °C (1050 °F) for 1 h, and finally finish ground or lapped. Parts nitrided and not ground after nitriding have excellent dimensional stability.

Changes in Helix Angle. A sensitive indicator of dimensional changes resulting from heat treating helical gears is the change in helix angle. Accurate and reproducible measurement of helix angle can be made with electronic measuring instruments.

In general, the change in helix angle is greatest on gears with few teeth and negligible on gears with many teeth. For example, the lead of a 13-tooth 5-pitch pinion gear might change as much as 0.0005 mm/mm (0.0005 in./in.) of face in nitriding whereas the lead of the mating 67-tooth gear would not change. Consequently, when gears with few teeth are to be nitrided, the amount of helix angle change should be compensated for in machining the gear teeth.

Example 1: Lead Changes of Helical Gear after Nitriding.

The amount of lead change encountered with a nitrided 13-tooth 5-pitch helical pinion gear made of 4142 steel varied from batch to batch; the depth of case also varied. It was determined that these variations resulted from the use of different nitriding time cycles from batch to batch in an attempt to accommodate different nitriding specifications in the same furnace load. These variations were sufficient to throw the lead dimension of the gears out of tolerance and necessitated reworking of the gears by a costly lapping operation.

Subsequently, when the nitriding cycle was held constant, the gears were produced regularly within the required tolerance. Figure 10 shows the effect of case depth on the lead change of these gears.

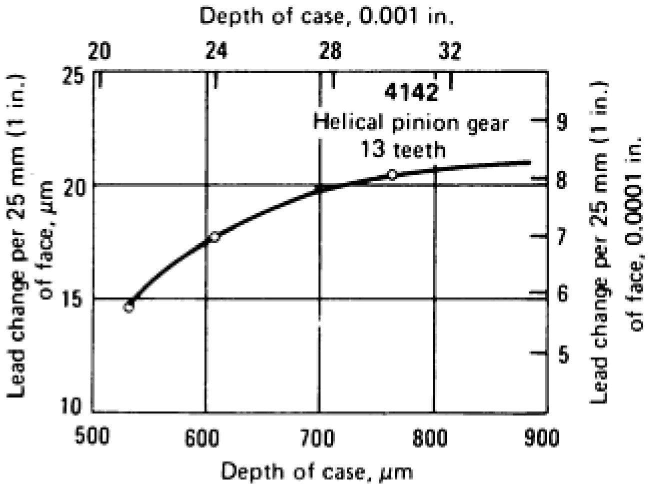


Fig. 10 Increase in lead change with depth of nitrided case for 13-tooth, 5-pitch helical pinion gear. Gears were hardened, tempered at 565 °C (1050 °F), and nitrided in two stages at 525 °C (975 °F) using ammonia dissociation rates of 15 to 25% for the first stage and 83 to 85% for the second stage.

Lead measurements also can be used to determine whether distortion in nitrided gears has been caused by residual stress in the raw material. When there is a sharp increase in the standard deviation, or scatter, of lead measurements after nitriding, the difficulty usually can be attributed to stress relief during the nitriding cycle.

Example 2: Effect of Previous Heat Treatments on Lead Changes after Nitriding.

Shaft pinions made of mill-heat-treated 4150 bar stock were scrapped because of a pronounced increase in deviation of lead measurements after nitriding. An investigation of this problem consisted of machining gears from one third of a lot of material in the as-received condition, stress relieving another third of the material at a temperature 30 °C (50 °F) higher than the nitriding temperature before machining it into gears, and oil quenching from 845 °C (1550 °F), and tempering the last portion before machining; gears of all three prior conditions were then nitrided. Figure 11(a) shows the improvement obtained by proper heat treatment prior to machining and nitriding.

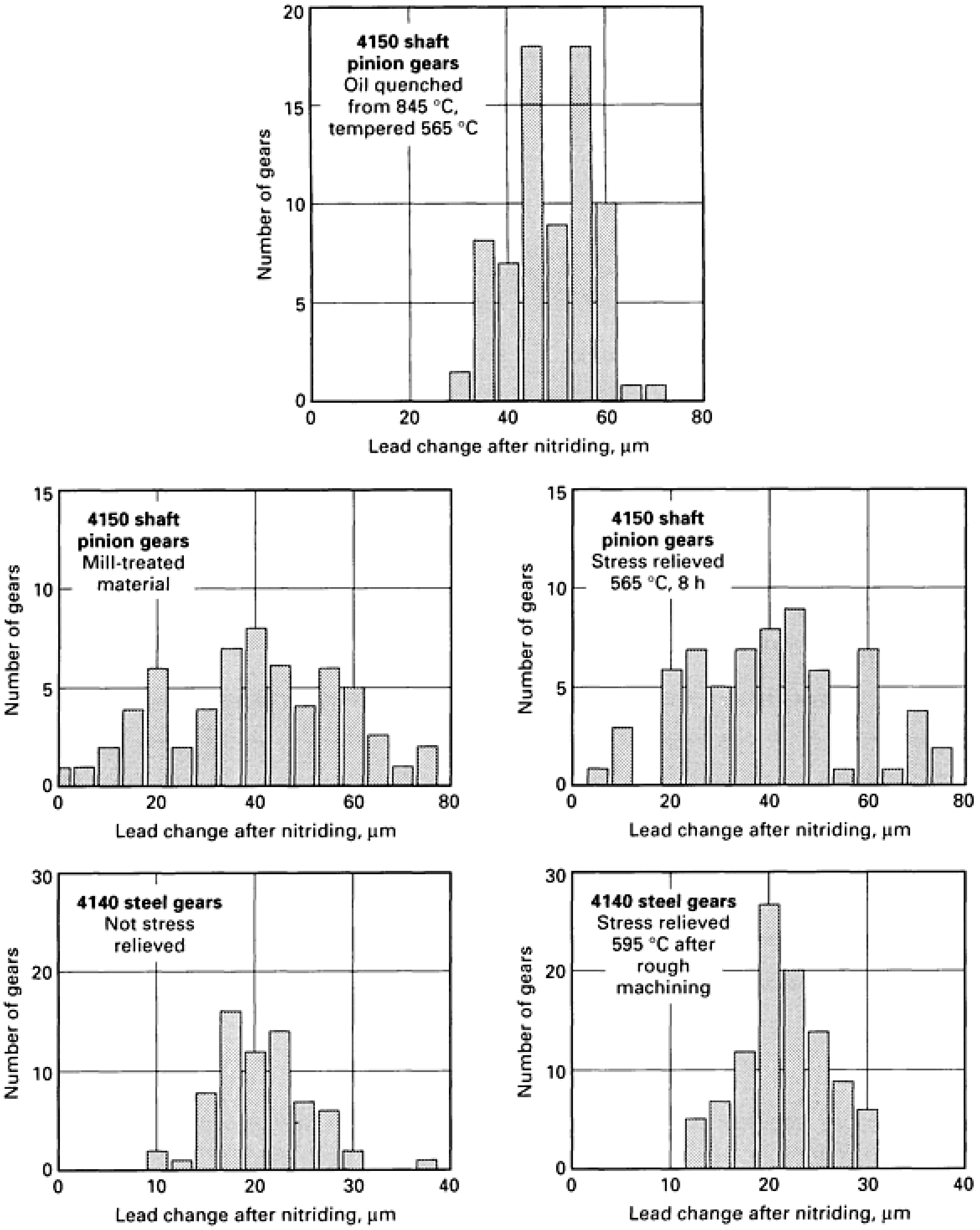


Fig. 11 Effect of stress-relieving treatments on lead change of nitrided gears

Stress Relieving. Many standard procedures require that parts be rough machined, stress relieved, and finish machined before being nitrided. For many parts, this lengthy procedure may not be required.

Figure 11(b), which presents data relating to the lead change in 4140 steel gears after nitriding, illustrates one instance in which little benefit was obtained by the stress relief of rough-machining stresses before nitriding. In general, it has been found that stress relieving after rough machining is required only for slender parts or parts with thin wall sections or large or complex sections, such as large welded gear assemblies. When distortion is caused by the removal of induced machining stresses during nitriding, stress relieving at 620 °C (1150 °F) for 4 h prior to nitriding will lessen or eliminate this problem.

Design Changes. Sometimes components that have been fully stress relieved distort during nitriding. This is usually the result of the high compressive stresses induced by the volume change occurring from the nitriding action itself. Minor

design changes or modification of the production planning of the part to improve the stress balance may prove helpful, as indicated for the parts illustrated in Fig. 12.

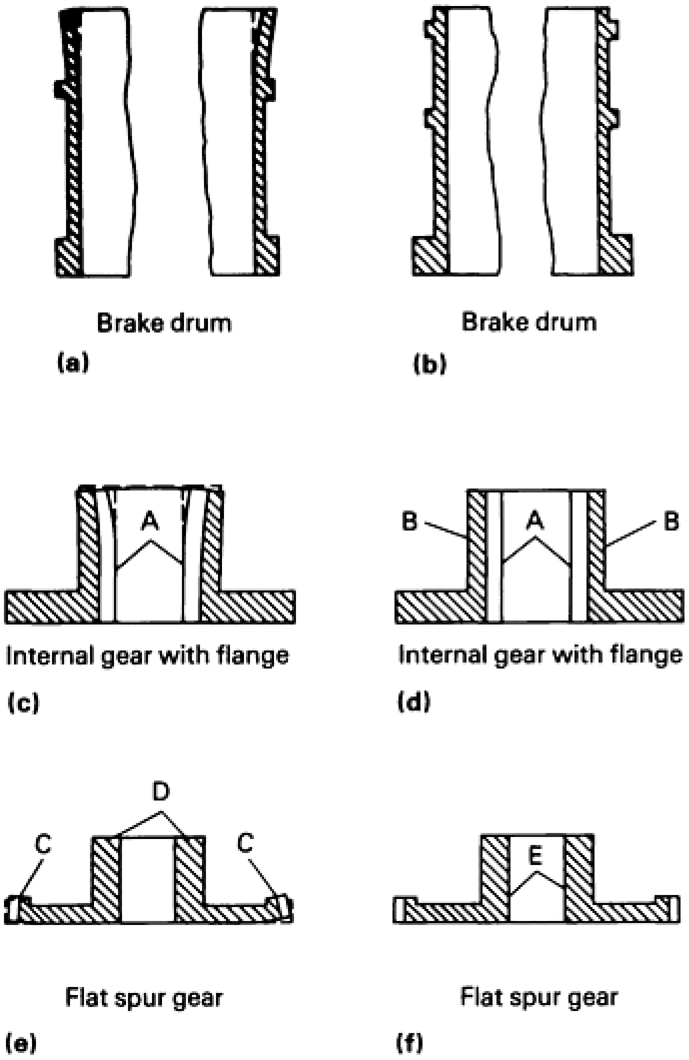


Fig. 12 Minor design changes and modifications of production planning to eliminate distortion during nitriding. (a) Nitriding of ID caused excessive taper past shoulder. (b) Location of original shoulder was changed, and second shoulder was added. (c) Compressive stresses caused gear teeth A to taper during nitriding. (d) Gear teeth A and external surface B were nitrided. (e) Nitriding of gear teeth C and surface D caused warpage. (f) Entire part was nitrided except surface E, which was finished after nitriding.

Finishing Costs. The amount of distortion resulting from nitriding is small compared to that resulting from other case-hardening processes, which involve quenching to form martensite. Consequently, the increased cost of the nitriding operation and of steels suitable for nitriding often can be offset by the savings resulting from finishing to size prior to nitriding.

Example 3: Reduction of Gear Finishing Costs with Nitriding.

One manufacturer realized considerable savings in the cost of producing gears by changing from 4130 steel to AMS 6475 (Nitralloy N). Gears made of 4130 steel were carburized in salt and marquenched in salt at 260 °C (500 °F), and had to be lapped after being treated to eliminate distortion; the Nitralloy gears were nitrided, and lapping was not required. Although the 4130 steel cost less than the Nitralloy, the cost of lapping required for the 4130 gears substantially offset the lower cost of this material. See Table 4 for distortion data for carburized and for nitrided gears of five sizes.

Table 4 Distortion data for carburized and for nitrided gears of five sizes

Gear dimensions						Diametral pitch	Helix error				Material required per gear	
L		F_c		OD			Carburizing 4130		Nitriding AMS 6475			
mm	in.	mm	in.	mm	in.		mm	10^{-4} in.	mm	10^{-4} in.	kg	lb

76	3.0	30	1.2	30	1.2	20	0.08	32	0.025	10	0.5	1.2
84	3.3	33	1.3	36	1.4	16	0.09	37	0.030	12	1.0	2.2
95	3.8	41	1.6	41	1.6	14	0.12	48	0.033	13	1.3	2.8
138	5.5	58	2.3	66	2.6	9	0.16	62	0.046	18	4.7	10.3
160	6.3	71	2.8	76	3.0	7	0.20	78	0.066	26	7.0	15.4

Equipment

Furnaces of several designs are in common use in gas-nitriding installations. Most of these are batch furnaces, which incorporate certain essential features:

- A means of sealing the charge to exclude air and other contaminants while containing the controlled atmosphere
- An inlet line for introducing atmosphere and an outlet line for exhausting used atmosphere
- A means of heating and appropriate temperature controls
- A means, such as a fan, for circulating atmosphere and equalizing temperature throughout the work load

The vertical retort furnace (Fig. 13) is stationary; parts to be nitrided are loaded into a work basket, which is lowered into the heating chamber. The lid rests on an asbestos gasket and dips into an oil-filled trough, thus effecting the seal. Atmosphere enters at the top and leaves at the bottom of the furnace. Cooling is achieved by starting a fan and opening a valve in a water-jacketed cooling manifold. Furnaces of similar design, but without the water-jacketed manifold, are used when rapid cooling as a means of increasing furnace output is not required; the quality of nitriding achieved is equivalent to that of manifolded furnaces.

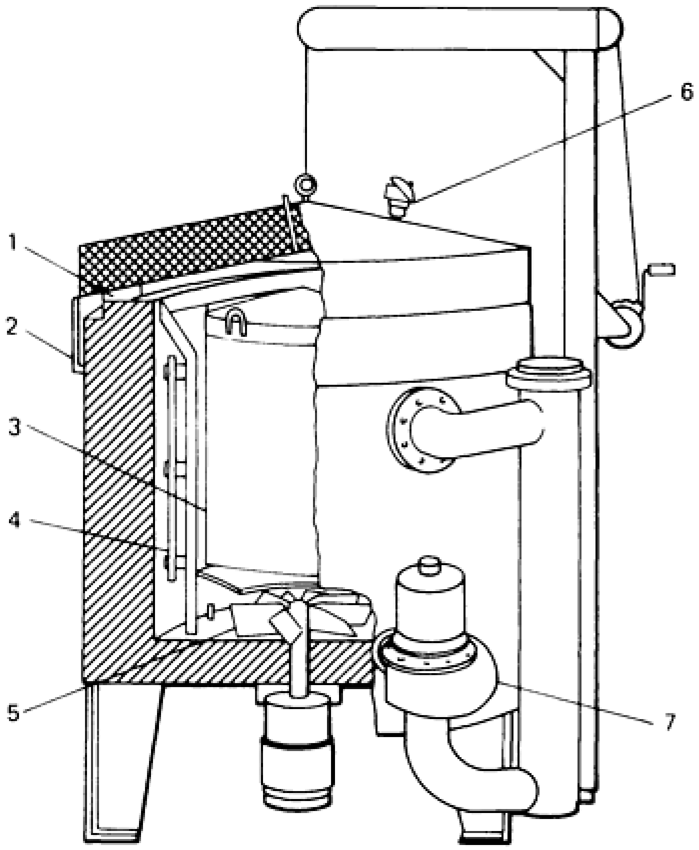


Fig. 13 Vertical retort nitriding furnace. 1, gasket; 2, oil seal; 3, work basket; 4, heating elements; 5, circulating fan; 6, thermocouple; and 7, cooling assembly. At end of cycle, a valve is opened and fan (not shown) incorporated in the external cooler circulates atmosphere through the water-jacketed cooling manifold.

Nitriding has also been successful in sealed vertical retorts without fans. Proper flows and exhaust line pressures are critical to provide sufficient ammonia. Not using the retort fan eliminates a common area of gas leakage and/or air entry.

The bell-type movable furnace (Fig. 14) has a stationary base and is equipped with atmosphere inlet and outlet, control thermocouple, circulating fan, and outlets for electric power and controls. Parts to be nitrided are loaded into work baskets, which are placed on a work support at the furnace base. A retort is lowered over the base and dips into an oil-filled trough, effecting the seal. Heat is provided by a heating bell, which is lowered over the retort and rests at the bottom on a flat portion of the retort. Heat passes through the retort walls and is transferred to the work load by radiation and convection as the atmosphere is circulated. Cooling is achieved by replacing the heating bell with a cooling bell, which draws air up around the retort walls and out at the top of the bell. This air movement is accomplished by a fan in the top of the cooling bell.

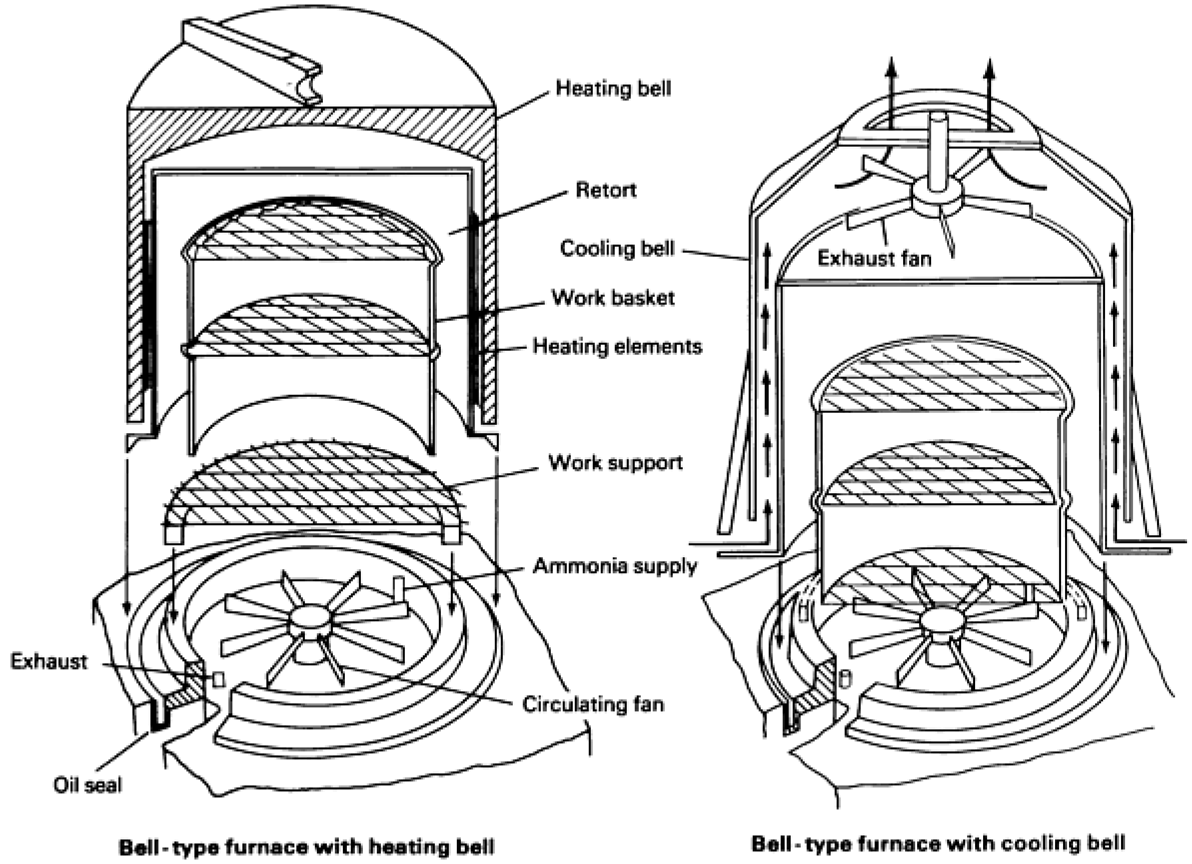


Fig. 14 Schematic of bell-type furnace showing stationary base surmounted by bell

It is customary to provide more bases than heating and cooling bells. This permits more efficient utilization of the bells. A cooling bell is not essential where there is no demand for rapid cooling as a means of increasing output of the base; the quality of nitriding achieved is equivalent to that achieved using a cooling bell, but the heat radiated from the retort can be a source of discomfort to persons working in the immediate area.

Box Furnaces. A box-type movable furnace with two stationary locations for work baskets also has been used for nitriding. Each location is equipped with atmosphere inlet and outlet, control thermocouple, circulating fan, and separate controls. Parts to be nitrided are loaded into baskets, which are placed on a heavy metal plate at each location. A cover is placed over the charge and settles into a groove in the plate that is filled with fine chrome ore, thus effecting the seal. Lugs on the cover fit into a U-shaped holder through which pins are driven to secure the cover to the plate.

The furnace then is moved into position over the charge on rails, after which sliding doors at each end of the furnace are lowered. Heat passes through the walls of the cover and is transferred to the load by radiation and convection as the atmosphere is circulated. When the box furnace has been rolled into position over the work in the basket on the second plate, cooling is achieved for the work on the first plate by transfer of heat to the surroundings, either by natural or forced circulation of air. Usually, natural air circulation is rapid enough to permit cooling and recharging before the box furnace is again available.

Box furnaces of similar design are in use in which the furnace is stationary and the locations for the work loads are movable. The cover that closes over the load is similar to the retort used with the bell-type furnace.

Tube Retorts. In nitriding the inside diameters of tubes, the tube itself may act as the retort after it has been sealed (usually by welded-on covers) at both ends. A calculated volume of ammonia is sealed in the tube (after the tube has been purged of air), and the tube is heated in a suitable furnace. After the heating cycle, the tube is cooled in still or recirculated air, and the covers are removed. Individual parts may be sealed in tube retorts and processed in this same manner (see the section of this article on pressure nitriding).

Temperature Control. Close control of nitriding temperatures is essential to prevent uneven heating and distortion of parts, many of which are finish machined prior to nitriding. Nitriding furnaces are equipped with two thermocouples: one to control and indicate temperature within the load, and another to control the heat source so that it does not exceed a maximum temperature--usually 5 to 15 °C (10 to 25 °F) above the nitriding temperature. These two thermocouples, in conjunction with fan circulation, normally result in control of furnace and load temperature to within ±3 to ±6 °C (±5 to ±10 °F). The override thermocouple arrangement also reduces the likelihood of overheating if the control couple or recorder fails.

Fixtures for nitriding are similar in design to those used in gas carburizing. Under nitriding conditions, ammonia and dissociation products can react chemically with materials in retorts, fans, work baskets, and fixtures. This reaction contributes to further dissociation of ammonia, robs the work of atomic nitrogen, and produces an excess of hydrogen. To reduce this reaction to a minimum, furnace parts and fixtures usually are made of alloys containing high percentages of nickel and chromium (see Table 5). Under certain conditions or after extended use, even these alloys develop a surface that interferes with normal processing; their usefulness can be restored, however, by heating them in an air atmosphere and holding them for a period of time at elevated temperature, followed by sandblasting to remove scale.

Table 5 Recommended materials for parts and fixtures in nitriding furnaces

Materials are recommended on the basis of maximum operating temperature of 565 °C (1050 °F).

Part	Material	
	Wrought	Cast
Retorts[a]	Type 330; Inconel 600	Not usually cast
Fans	Type 330; Inconel 600	35-15 or equivalent
Trays, baskets, fixtures	Types 310, 330; Inconel 600	35-15 or equivalent

(a) Periodic inspection of austenitic stainless steel retorts is mandatory because of embrittlement after long exposures to nitriding. Retorts of 18-8 stainless steel lined with high-temperature glass have been used successfully.

Enamel-coated carbon steel containers are satisfactory as long as the coating remains intact. Some alloys have been coated with high-temperature glass to extend their usefulness.

Low-carbon steel is unsatisfactory as a container material because it absorbs nitrogen, and the nitrided inside surface of the container becomes embrittled. Besides embrittling the container, the nitrided surface also catalyzes the decomposition of the ammonia in contact with it and thereby interferes with the proper nitriding of workpieces.

Equipment Requirements. Typical relations between production requirements and equipment requirements for gas nitriding loads of parts weighing less than 0.5 kg (1 lb) each and parts weighing from 0.5 to 5 kg (1 to 10 lb) each are given in Table 6. These data apply to single-stage nitriding at 525 °C (975 °F) for periods of 24 and 48 h, respectively.

Table 6 Typical equipment requirements for single-stage gas nitriding

Item	Parts less than 0.5 kg (1 lb) each	Parts from 0.5 to 4.5 kg (1 to 10 lb) each
Production requirements		
Pieces per cycle	800	300
Weight of pieces, kg (lb)	170 (375)	910 (2000)
Purging time, h	2	$2\frac{1}{2}$
Heating time, h	1	$1\frac{1}{4}$
Nitriding time, h	24	48
Cooling time, h	2	$2\frac{1}{2}$

Total cycle, h	29	$54\frac{1}{4}$
Equipment requirements		
Size of furnace	0.2 m^3 (6.7 ft^3)	0.5 m^3 (17 ft^3)
Retort dimensions	610 mm (24 in.) diam by 660 mm (26 in.) deep	710 mm (28 in.) diam by 1220 mm (48 in.) deep
Temperature	525 °C (975 °F)	525 °C (975 °F)
Electric supply:		
Elements	30 kW	48 kW
Motor, hp	1	3

Table 7 lists processing details and correlates production and equipment requirements for the single-stage nitriding of 5.3 kg (11.7 lb) transmission ring gears to a depth of 0.2 mm (0.008 in.).

Table 7 Requirements for nitriding transmission ring gears to a depth of 0.2 mm (0.008 in.)

Cycle	
Purge with raw ammonia	1.5 h
Heat to 525 °C (980 °F)	3.0 h
Nitride at 525 °C (980 °F) (40% dissociation)	32.0 h
Purge with ammonia and cool	2.0 h
Purge with air and continue cooling	1.5 h
Total cycle time	**40.0 h**
Production requirements	
Load weight	1340 kg (2950 lb)
Weight of each piece	5.3 kg (11.7 lb)
Total fixture weight	670 kg (1470 lb)
Pieces processed per hour	$7\frac{1}{2}$ (avg)
Furnace requirements	
Furnace	Electric bell-type batch
Hearth size	1525 mm (60 in.) diam, 1800 mm (71 in.) height
Heat input rate	360,000 kJ/h (340,000 Btu/h) (360 MJ/h, or 100 kW)
Temperature	530 °C (980 °F) (650 °C, or 1200 °F max)
Atmosphere equipment	
Ammonia dissociator capacity	2.8 m^3/h (100 ft^3/h)
Source: 3785 1 (1000 gal) tank for liquid NH_3 vaporizer	
Average ammonia consumption	
Purging	4.2 m^3/h (150 ft^3/h)
Nitriding	1.75 m^3/h (62 ft^3/h)

Ammonia Supply

Gas nitriding makes use of anhydrous liquid ammonia (refrigeration grade, 99.98% NH_3 by weight), which is available either in cylinders or in bulk (tank truck, trailer transport, and tank car). A typical, storage-tank installation with 1050 kg (2300 lb) capacity is shown in Fig. 15. Such a tank is replenished directly from a tank truck or tank car. Layouts for ammonia installation and engineering data pertaining to their operation and maintenance may be obtained from suppliers of ammonia.

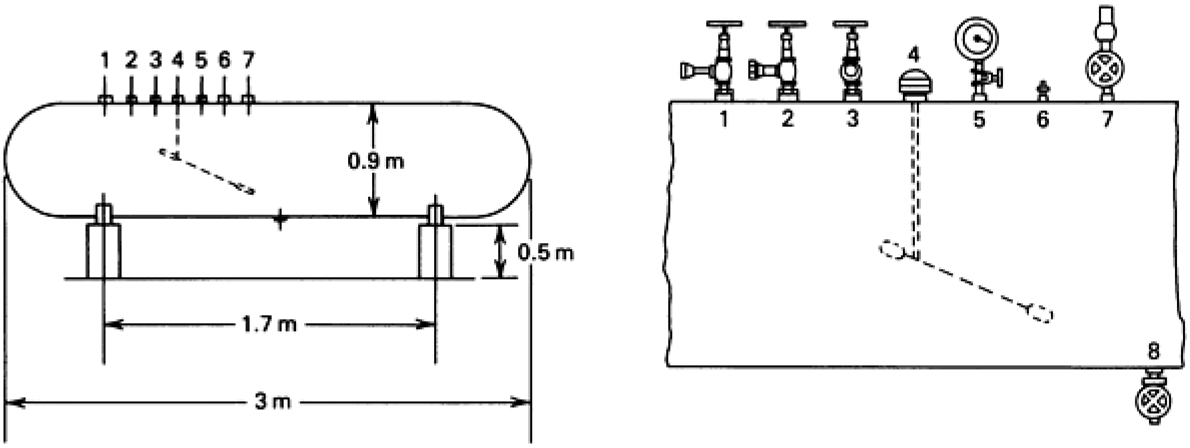


Fig. 15 Typical anhydrous ammonia storage-tank installation of 1045 kg (2300 lb) capacity. 1, pressure-equalizing valve; 2, liquid inlet valve; 3, gas outlet valve; 4, liquid level float gage; 5, pressure gage; 6, fixed level gage; 7, pressure-relief valves (2); and 8, liquid outlet valve

Usually a storage tank is situated outside the building in which the nitriding equipment is located. At moderate outdoor temperatures, the liquid ammonia will absorb enough heat from the atmosphere to vaporize and fulfill gas requirements. On very hot days, the pressure of the gas may build up enough to actuate the pressure-relief valves. On the other hand, when temperatures are below -7 °C (20 °F) or when very large volumes of gas are being used, an additional heat source is needed. This heat may be supplied by an electric immersion heater automatically actuated by gas pressures. Such a heater is started when gas pressure falls below 690 kPa (100 psi) and is stopped when a pressure of 1035 kPa (150 psi) is attained.

Special Precautions. To avoid leaks, exceptionally good pipe-fitting practice must be followed. Specific pipe-joint compounds must be used. One type of compound contains fine powdered lead, which is mixed in an insoluble, nonsetting lubricant; another type is an oxychloride mixture with graphite, which in setting, expands to form a very hard seal. When properly applied, certain high-strength, corrosion-resistant tapes also are satisfactory, as are welded joints.

Materials used for valves, piping, gages, regulators, and flow-measuring devices are similar for all installations; only iron, steel, stainless steel, and aluminum can be used because ammonia corrodes zinc, brass, and bronze. Piping should be made of extra-heavy black iron (except for vent lines, which may be made of standard-weight black iron or galvanized iron). Fittings should be made of extra-heavy malleable iron or forged steel. Valves should be made of steel and should be of the high-pressure, back-seating type.

Pressure Regulation. Ammonia gas from the supply tank or cylinder bank is under pressures up to 1380 kPa (200 psi), depending on the temperature of the gas. This pressure is reduced to about 14 to 105 kPa (2 to 15 psi) by means of pressure regulators.

Another reduction may be made just ahead of each furnace or dissociator to about 255 to 1015 mm (10 to 40 in.) water column, or an adequate pressure to supply from 1 m^3/h (approximately 35 ft^3/h) or more in small furnaces, to 40 m^3/h (1500 ft^3/h) on very large furnaces. Such supply lines are arranged to feed from a common line operating in manifold fashion at pressures not exceeding about 10 kPa (1.5 psi). Equipment to obtain this last reduction may be furnished with the dissociator or furnace.

The flow of gas into furnaces or dissociators is regulated by a suitable needle valve and is measured by a device such as a flowmeter. This device also serves to permit a visible check that gas is moving through the lines. Flow and pressure may be monitored by contact points that close and sound an alarm at predetermined settings. On very large furnaces where high gas flows may be required, it is desirable to manifold the gas downstream of the flowmeter and introduce it into the furnace at several locations, so as to prevent a local cool spot at a single point of entry.

Exhaust Gas. Depending on the stage of the cycle, the exhaust gas may contain air, air and ammonia, or ammonia plus hydrogen and nitrogen. Because of the variable composition of exhaust gas and the customary use of only a single exhaust line, the exhaust gas should be conducted to the outside atmosphere and released at as high an elevation as is practical. Terminating the exhaust line inside a building may be considered when all of the following conditions can be met:

- Nitrogen is used as the purge gas during heating and cooling
- The exhaust gas is flared (burned) at the terminal during the nitriding cycle
- The building is well ventilated so that nitrogen does not accumulate

Note that environmental considerations may dictate a more sophisticated approach to handling exhaust gas.

To provide a slight back pressure within the furnace, an oil-containing bubble bottle or water bubbler may be installed in the exhaust line. As an alternative, a throttle valve installed in the exhaust line may be used to restrict the flow of exhaust gases and maintain a slight back pressure in the furnace. This pressure is indicated on a manometer (water type) and maintained at about 25 to 50 mm (1 to 2 in.) water column.

Suitable piping and valves should be installed in the exhaust line to permit gas flow through a dissociation burette. See the "Appendix" of this article for analysis of exhaust gas procedures. Because water absorbs ammonia, dissociation checks must be made before the gas enters a water bubbler. If a throttle valve is used, gas can be sampled ahead of the valve and returned to the exhaust line past the valve.

Safety Precautions

Anhydrous ammonia is flammable with a narrow range; *Caution: concentrations of 15 to 25% ammonia in air produce explosive mixtures.* Ammonia is classified as a nonflammable compressed or liquefied gas by the Interstate Commerce Commission and is shipped under a green label. Because of the high coefficient of expansion of liquid ammonia, all containers must be filled in accordance with Department of Transportation (DOT) regulations to allow for this expansion in the event of temperature rise.

Dry ammonia is not corrosive to iron or steel and therefore entails no problems of internal corrosion in storage containers or piping. Moist ammonia in contact with air, however, is corrosive, and leaks in any portion of the system must be avoided. All storage containers, valves, and piping should be examined periodically for signs of external corrosion. Corrosion-preventive coatings should be applied to all parts of an ammonia storage or distribution system.

Ammonia gas is not harmful at low concentrations, and because of its pungent odor, leaks are readily noticed. Leak detection, using sulfur dioxide or sensitized papers, is simple and positive.

Ammonia constitutes a potential panic hazard. Because of the discomfort resulting from traces of ammonia in air, adequate ventilation and exhaust facilities should always be employed, particularly in enclosed areas. A gas mask approved for use in ammonia atmospheres should always be available for use in the event of bad leaks. Protective clothing, such as gloves, hats, and goggles, also should be provided for emergencies.

Ammonia is highly soluble in water. In case of severe leaks, spraying equipment is effective in carrying away the fumes. The gas is lighter than air and will rise; in emergencies, it should be remembered that the area closest to the floor will be lowest in ammonia content.

Hydrogen Hazard. *Caution: Although anhydrous ammonia is classed as a nonflammable gas, it produces considerable amounts of hydrogen (which is flammable) upon cracking. Cracking, or complete dissociation, does not occur in the nitriding furnace, but there is enough hydrogen contained in the exhaust gases to constitute a potential hazard.* Because of the concentrations of hydrogen and ammonia in exhaust gases, these gases must be vented to the outside atmosphere and not into an enclosed area. The exhaust line should never be terminated in a container of water, and it is not good practice to attempt to burn the exhaust gases indoors or outdoors, unless adequate precautions are taken.

Caution: Because of the presence of hydrogen in the nitriding furnace, the furnace should never be opened while it is heated up to nitriding temperature. If it is necessary to remove the work before the furnace has cooled to below 150 °C (300 °F),the furnace must be thoroughly purged with an inert gas, such as nitrogen. Even at 150 °C (300 °F)or below, the furnace should be thoroughly purged with air before it is opened.

Common Nitriding Problems

Some of the problems commonly encountered in nitriding are:

- Low case hardness or shallow case
- Discoloration of workpieces
- Excessive dimensional changes
- Cracking and spalling of nitrided surfaces
- Variations in percentage of ammonia dissociation
- White layer deeper than permitted
- Plugging of exhaust lines and pipette lines

A knowledge of the causes of these problems should be of assistance in avoiding, preventing, or correcting them. A number of possible causes are indicated below.

Low case hardness or shallow case may be caused by the characteristics of the steel or faulty processing. The steel characteristics affecting case hardness and depth include:

- Composition unsuitable for nitriding
- Improper microstructure
- Failure to quench and temper prior to nitriding
- Low core hardness
- Surface passivation, from machining, inadequate cleaning, or foreign matter

In terms of processing, a shallow case or low case hardness may be affected by:

- Excessively low or high nitriding temperature
- Insufficient ammonia flow
- Nonuniform circulation or temperature in furnace
- Prolonged exposure of furnace parts and work baskets to nitriding conditions such as ammonia (burnout required); see section on fixtures
- Insufficient time at temperature

Finally, low case hardness or shallow case may only be apparent--occurring as the result of inaccuracies in testing due to faulty adjustment of equipment, improper preparation or positioning of the test specimen, or the use of a test load excessive for the case depth.

Discoloration of workpieces may be caused by:

- Improper or inadequate prior surface treatment including etching, washing, degreasing, and phosphate coating
- Oil, air, or moisture in the retort

Oil in the retort can occur because of:

- Inadequate cleaning of parts, especially those with deep holes and recesses
- Loss of pressure at seal, or overheating of seal
- Leakage at the base, or other parts, of the furnace

Moisture in the retort can occur because of:

- Leakage from the cooling chamber

- Water being sucked in from water bottle during rapid cooling with inadequate gas flow

Air in the retort can occur because of:

- Inadequate seal
- Leakage due to inadequate sealing around pipes or thermocouple
- Introduction of air to purge ammonia while charge is at or above 175 °C (350 °F)

Excessive dimensional changes may be caused by:

- Inadequate stress relieving prior to nitriding
- Inadequate support of parts during nitriding
- Inappropriate design of parts, including nonsymmetry of design, wide variations in section thickness
- Unequal cases on various surfaces of parts, resulting from *nonuniform conditions* (created by furnace design or manner in which parts are arranged in load) or *variations in absorptive power of surfaces* (resulting from stop-off practices or from variations in surface metal removed, surface finishing technique, or in degree of cleanliness)

Cracking and spalling of nitrided surfaces may be caused by dissociation in excess of 85% and also (especially for aluminum-containing steels) by:

- Design (particularly sharp corners)
- Excessively thick white layer
- Decarburization of surface in prior heat treatment
- Improper heat treatment

Variations in percentage of ammonia dissociation may be caused by:

- Charge being too small for furnace area
- Overactive surface of furnace parts and fixtures
- Leakage or loss of sample from burette
- Change in gas flow caused by buildup of pressure in furnace
- Variations in furnace temperature

White layer deeper than permitted may be caused by:

- Nitriding temperature being too low
- Percentage of dissociation below the recommended minimum (15%) during the first stage
- First stage held too long
- Percentage of dissociation too low during the second stage
- Fast purging with raw ammonia instead of cracked ammonia or nitrogen, above 480 °C (900 °F) during slow cooling

Plugging of exhaust lines and pipette lines is caused by precipitates that are formed by the reaction of ammonia with many of the various chemical compounds commonly present in ordinary domestic water. These precipitates may plug lines and prevent proper sampling, or cause pressure to build up in the furnace by plugging exhaust lines or restricting valve openings.

Enlarging lines or treating them periodically with a dilute acid solution will correct this, especially if the solution is trapped in a low spot and drained. (The use of distilled water, or water of similarly low impurity, also will eliminate this difficulty.)

In some installations, water from pipettes can leak down into exhaust lines, flushing scale and other foreign material into low spots or restrictions and thus plugging the lines. A drop leg to trap such products will reduce trouble from this source, as will reduction of right-angle bends and elimination of pipes smaller than 19 mm ($\frac{3}{4}$ in.) in diameter, where possible.

Selective Nitriding

Many coatings are available as stopoffs to prevent gas nitriding of selected areas. The success of a coating depends on such variables as density and thickness of the coating, adhesion of coating to steel, surface finish of the part, and degree of leakage permitted.

Proprietary paints are effectively used in commercial heat-treating operations. They are also used to touch up other coatings that have been inadvertently removed or damaged during processing. These paints usually consist of a tin base suspended in a vehicle of lacquer, aromatic hydrocarbon, or a water glass. It is important that the constituents be mixed in the proper proportions (thick coatings may run, and thin coatings are not completely effective) and that the paints be applied to uniform thickness. The surface to be painted must be very clean. Ground or polished surfaces may be difficult to wet uniformly with paint.

Plated deposits of bronze or copper are the most common stopoff coatings. Nickel (including electroless nickel), chrome, and silver are effective also, but their higher cost restricts their use to special applications.

Thickness and density of plated coatings are important in determining their effectiveness as stopoffs. Minimum thickness of bronze or copper plate should be 18 μm (0.7 mil) for ground surface finishes of 1.6 μm (64 μin.) or smoother, 25 μm (1.0 mil) for finishes between 1.6 and 3.2 μm (64 and 125 μin.), and 38 μm (1.5 mil) for finishes of 3.2 μm (125 μin.) and rougher. Compared to copper and bronze, nickel is a more effective stopoff; therefore, a thinner coating is permitted.

Electroplated silver is 100% effective when the plate thickness is a minimum of 38 μm (1.5 mil); it is 95% effective even during long nitriding cycles, when as little as 25 μm (1.0 mil) of plate is used.

Surface finish of the base metal also influences the thickness of the coating. A finish of 3 μm (120 μin.) will require a thicker coating than a finish of 1.5 μm (60 μin.). Usually, a finish of 1.5 μm (60 μin.) or smoother is recommended.

Processing Procedures. Several processing procedures are employed to accomplish selective nitriding. One of the most widely used consists of rough machining, plating, machining, or grinding areas to be nitrided, nitriding, then finish machining or grinding wherever required. In another procedure, the areas to be nitrided are masked to prevent plating. When masking is difficult, the plating material is applied to all surfaces and then selectively stripped from the areas to be nitrided.

Fine threads (external or internal) on precision parts can be protected by a tin-lead solder. The threads should be cleaned and coated with a flux containing a tinning compound, then heated slowly until both solder and flux are melted. The excess solder and flux are blown out with compressed air, leaving a coating thin enough so that it does not run during nitriding and does not require cleaning or stripping after nitriding.

When the application does not permit the retention of any protective plate on the finished part after nitriding, selection of the coating is important from the standpoint of subsequent stripping. Copper and silver are the easiest to strip; bronze is more difficult. Nickel is very difficult to remove without detrimentally affecting the part. Stopoff paint residues may be reduced by brushing or washing, or may be removed by lightly blasting with fine abrasives.

Nitriding of Stainless Steels

Because of their chromium content, all stainless steels can be nitrided to some degree. Although nitriding adversely affects corrosion resistance, it increases surface hardness and provides a lower coefficient of friction, thus improving abrasion resistance.

Austenitic and Ferritic Alloys. Austenitic stainless steels of the 300 series are the most difficult to nitride; nevertheless, types 301, 302, 303, 304, 308, 309, 316, 321, and 347 have been successfully nitrided. These nonmagnetic alloys cannot be hardened by heat treating; consequently, core material remains relatively soft, and the nitrided surface is limited as to the loads it can support. This is equally true of the nonhardenable ferritic stainless steels. Alloys in this group that have been satisfactorily nitrided include types 430 and 446. With proper prior treatment, these alloys are somewhat easier to nitride than the 300 series alloys.

Hardenable Alloys. The hardenable martensitic alloys are capable of providing high core strength to support the nitrided case. Hardening, followed by tempering at a temperature that is at least 15 °C (25 °F) higher than the nitriding temperature, should precede the nitriding operation. Precipitation-hardening alloys, such as 17-4 PH, 17-7 PH, and A-286, also have been successfully nitrided.

Prior Condition. Before being gas nitrided, 300 series steels and nonhardenable ferritic steels should be annealed and relieved of machining stresses. The normal annealing treatments generally employed to obtain maximum corrosion resistance are usually adequate. Microstructure should be as nearly uniform as possible. Observance of these prior conditions will prevent flaking or blistering of the nitrided case. Martensitic steels, as previously noted, should be in the quenched and tempered condition.

A special pretreatment for 410 stainless is hardening from a lower-than-normal temperature; this results in a very uniform nitrided case with reduced internal stresses. Cracking or spalling of the case is avoided; formation of brittle grain-boundary carbonitrides is suppressed. Austenitizing at 860 °C (1580 °F), followed by tempering at 595 °C (1100 °F) uniformly distributes carbides and provides low residual stress. Case growth is accommodated by a hardness of about 25 HRC.

Surface Preparation. The nitriding of stainless steels requires certain surface preparations that are not required for nitriding low-alloy steels. Primarily, the film of chromium oxide that protects stainless alloys from oxidation and corrosion must be removed. This may be accomplished by dry honing, wet blasting, pickling, chemical reduction in a reducing atmosphere, or submersion in molten salts, or by one of several proprietary processes. Surface treatment must precede placement of the parts in the nitriding furnace. If there is any doubt of the complete and uniform depassivation of the surface, further reduction of the oxide may be accomplished in the furnace by means of a reducing hydrogen atmosphere or halogen-based proprietary agents. Of course, hydrogen must be dry (free of water and oxygen).

Before being nitrided, all stainless parts must be perfectly clean and free of embedded foreign particles. After depassivation, care should be exercised to avoid contaminating stainless surfaces with fingerprints. Sharp corners should be replaced with radii of not less than 1.6 mm ($\frac{1}{16}$ in.).

Nitriding Cycles. In general, stainless steels are nitrided in single-stage cycles at temperatures from about 495 to 595 °C (925 to 1100 °F) for periods ranging from 20 to 48 h, depending on the depth of case required. Dissociation rates for the single-stage cycle range from 20 to 35%; a two-stage cycle using 15 to 30% in first phase and 35 to 45% in the second phase is also used. Thus, except for the prior depassivation of the metal surface, the nitriding of stainless steels is similar to the single-stage nitriding of low-alloy steels.

Nitriding Results. Hardness gradients are given in Fig. 16 for types 302, 321, 430, and 446. These data are based on a 48-h nitriding cycle at 525 °C (975 °F), preceded by suitable annealing treatments. A general comparison of the nitriding characteristics of series 300 and 400 steels is presented in Fig. 17; the comparison reflects the superior results that we obtained with series 400 steels, as well as the effects of nitriding temperature on depth of case. Data are plotted for single-stage nitriding at temperatures of 525 and 550 °C (975 and 1025 °F). For steels of both series, greater case depths were obtained at the higher nitriding temperature.

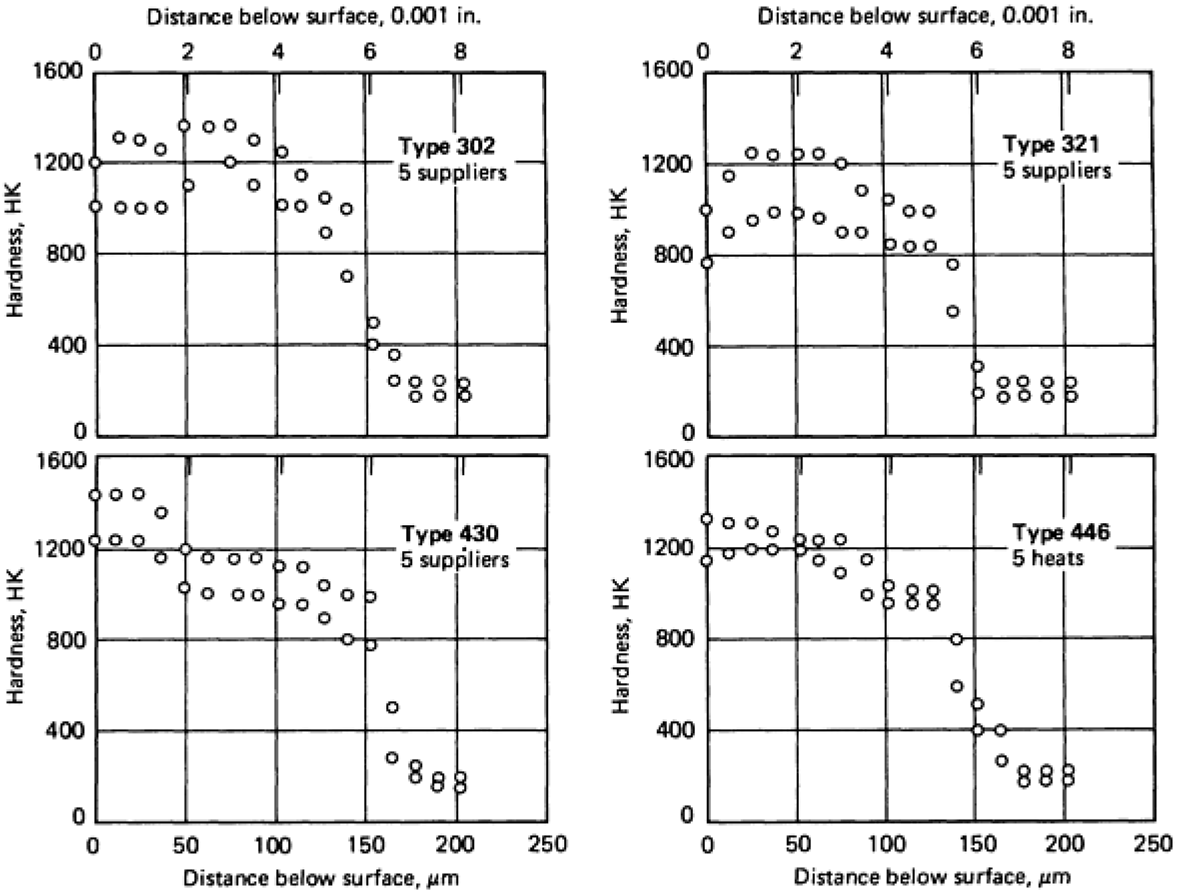


Fig. 16 Hardness range as a function of depth of case for four stainless steels that were annealed prior to nitriding. Annealing temperatures: type 302 and type 321, at 1065 °C (1950 °F); type 430, at 980 °C (1800 °F); and type 446, at 900 °C (1650 °F)

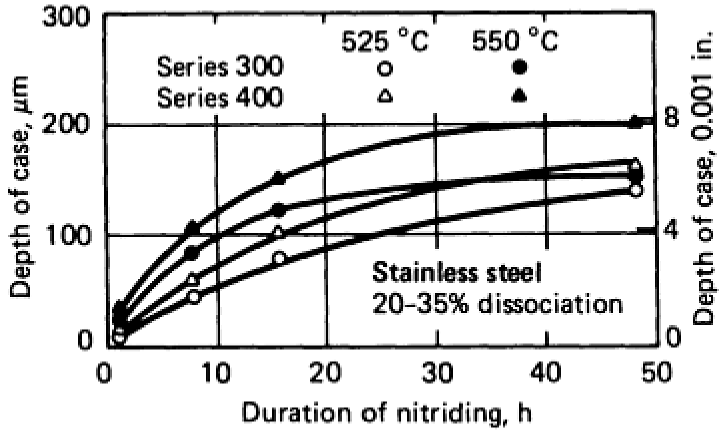


Fig. 17 Comparison of nitriding characteristics of series 300 and 400 stainless, single-stage nitrided at 525 and 550 °C (975 and 1025 °F)

Applications. Although nitriding increases the surface hardness and wear resistance of stainless steels, it decreases general corrosion resistance by combining surface chromium with nitrogen to form chromium nitride. Consequently, nitriding is not recommended for applications in which the corrosion resistance of stainless steel is of major importance. For example, a hot-air valve made of cast type 347 and used in the cabin-heating system of a jet plane was nitrided to improve its resistance to wear by the abrading action of a sliding butterfly. When the valve remained in the closed position for an extended period, the corrosive effects of salt air froze the valve into position so that it could not be opened.

In contrast, a manufacturer of steam-turbine power-generating equipment has successfully used nitriding to increase the wear resistance of types 422 and 410 stainless steel valve stems and bushings that operate in a high-temperature steam atmosphere. Large quantities of these parts have operated for 20 years or more without difficulty. In a few instances, a

light-blue oxide film has formed on the valve stem diameter, causing it to "grow" and thus reduce the clearance between stem and bushing; the growth condition, however, was not accompanied by corrosive attack.

Nitrided stainless is also being used in the food-processing industry. In one application, nitrided type 321 was used to replace type 302 for a motor shaft used in the aeration of orange juice. Because the unhardened 302 shaft wore at the rubber-sealed junction of the motor and the juice, leaks developed within three days. The nitrided 321 shaft ran for 27 days before wear at the seal resulted in leakage. In machinery used in the preparation of dog foods, nitrided type 420 gears have replaced gears made of an unhardened stainless and have exhibited a considerable increase in life.

Modern synthetic fibers, several of which are highly abrasive, have increased the wear of textile machinery. Mechanical parts in textile machines are subjected to high humidity, absence of lubrication, high-speed movements with repeated cycling, and the abrasive action of fibers traveling at high speeds. A shear blade made of hardened, 62 to 64 HRC, 1095 steel experienced a normal life of about one million cuts (four weeks of service) in cutting synthetic fibers at the rate of 90 cuts per minute. In contrast, a nitrided type 410 blade with 0.04 mm (0.0015 in.) case depth showed less wear after completion of five million cuts.

With nitrided stainless steels, the case almost always has lower corrosion resistance than the base material; nevertheless, the corrosion resistance of the case can be adequate for certain applications. For example, nitrided types 302 and 410 stainless steel resist attack from warp conditioner and size in the textile industry but do not resist attack from the acetic acid used in dyeing liquors.

Nitrided stainless is not resistant to mineral acids and is subject to rapid corrosion when exposed to halogen compounds. However, a nitrided type 302 piston lasted for more than five years in a liquid-ammonia pump; it replaced a piston made of an unnitrided 300 series alloy that lasted approximately six months. Nitrided 17-4 PH impellers have performed satisfactorily and without corrosion in various types of hydraulic pumps.

Pressure Nitriding

Pressure nitriding (U.S. Patents 2,596,981, 2,779,697, and 2,986,484) differs from conventional gas nitriding in that it requires the use of a sealed retort capable of withstanding high pressures to contain the parts being nitrided. Nevertheless, it has been determined that within practical limits, depth and quality of case obtained in pressure nitriding depend less on pressure than on the ratio of the available mass of ammonia to the area of the surface presented for reaction with the gas.

Procedure. Surfaces to be nitrided are cleaned and placed in a carbon steel retort that is first evacuated of air and then filled with ammonia to a predetermined pressure. The pressure chosen depends on the total surface area of parts to be nitrided and the volume of the retort. Approximately 50 to 100 g (1.8 to 3.5 oz) of ammonia are supplied per square meter of surface to be nitrided. When only the inside surface of a part is to be hardened, as with carbon steel tubing for bottom-hole oil-well pumps, the tube can act as its own retort. The retort is then heated in any furnace in which temperature can be controlled for the required time cycle, after which the retort can be air cooled, vented, and opened. Precise temperature control is not highly critical.

Advantages. Pressure nitriding provides a convenient method for nitriding part shapes that are difficult to handle by other methods. By varying the amount of ammonia added initially, the thickness of the white layer can be controlled.

Disadvantages include the following:

- Retort sealing is not always convenient
- After 45 h of operation, the ammonia content is about 50% expended, and further development of the case proceeds at a very slow rate
- To restrict the depth of the white layer to 0.00025 to 0.00050 mm (9.8 to 20 μin.), case depth must not exceed 0.50 to 0.63 mm (0.02 to 0.025 in.)
- In filling the welded retort with ammonia, dangerous pressures can develop if a sufficient quantity of ammonia is allowed to condense. This hazard can be avoided by keeping the retort warmer than the ammonia supply tank; however, a safety disk should be provided

Bright Nitriding

Bright nitriding (U.S. Patents 3,399,085 and 3,684,590) is a modified form of gas nitriding employing ammonia and hydrogen gases. Atmosphere gas is continually withdrawn from the nitriding furnace and passed through a temperature-controlled scrubber containing a water solution of sodium hydroxide (NaOH). Trace amounts of hydrogen cyanide (HCN) formed in the nitriding furnaces are removed in the scrubber, thus improving the rate of nitriding. The scrubber also establishes a predetermined moisture content in the nitriding atmosphere, reducing the rate of cyanide formation and inhibiting the cracking of ammonia to molecular nitrogen and hydrogen. By this technique, control over the nitrogen activity of the furnace atmosphere is enhanced, and nitrided parts can be produced with little or no white layer at the surface. If present, the white layer will be composed of only the more ductile Fe_4N (gamma prime) phase.

Pack Nitriding

Pack nitriding (U.S. Patent 4,119,444), which is a process analogous to pack carburizing, employs certain nitrogen-bearing organic compounds as a source of nitrogen. Upon heating, the compounds used in the process form reaction products that are relatively stable at temperatures up to 570 °C (1060 °F). Slow decomposition of the reaction products at the nitriding temperature provides a source of nitrogen. Nitriding times of 2 to 16 h can be employed. Parts are packed in glass, ceramic, or aluminum containers with the nitriding compound, which is often dispersed in an inert packing media. Containers are covered with aluminum foil and heated by any convenient means to the nitriding temperature.

Ion (or Plasma) Nitriding

Since the mid-1960s, nitriding equipment utilizing the glow-discharge phenomenon has been commercially available. Initially termed glow-discharge nitriding, the process is now generally known as ion, or plasma, nitriding. The term plasma nitriding is gaining acceptance.

Ion nitriding is an extension of conventional nitriding processes using plasma-discharge physics. In vacuum, high-voltage electrical energy is used to form a plasma, through which nitrogen ions are accelerated to impinge on the workpiece. This ion bombardment heats the workpiece, cleans the surface, and provides active nitrogen.

Metallurgically versatile, the process provides excellent dimensional control and retention of surface finish. Ion nitriding can be conducted at temperatures lower than those conventionally employed. Control of white-layer composition and thickness enhances fatigue properties. The span of ion-nitriding applications includes conventional ammonia-gas nitriding, short-cycle nitriding in salt bath or gas, and the nitriding of stainless steels.

Ion nitriding lends itself to total process automation, ensuring repetitive metallurgical results. The absence of pollution and insignificant gas consumption are important economic and public policy factors. Moreover, selective nitriding accomplished by simple masking techniques may yield significant economies. For further information on ion nitriding, see the article "Plasma (Ion) Nitriding" in this Volume.

Structure and Properties of Ion-Nitrided Steel. Ion nitriding, like other nitriding processes, produces several distinct structural zones as shown in Fig. 18, which include a light etching layer of iron-nitride compounds at the surface; a gradient zone of fine iron/alloy nitrides, Fe_4N, that constitutes the bulk of the case depth; and a gradient zone of interstitial nitrogen that extends to the parent material.

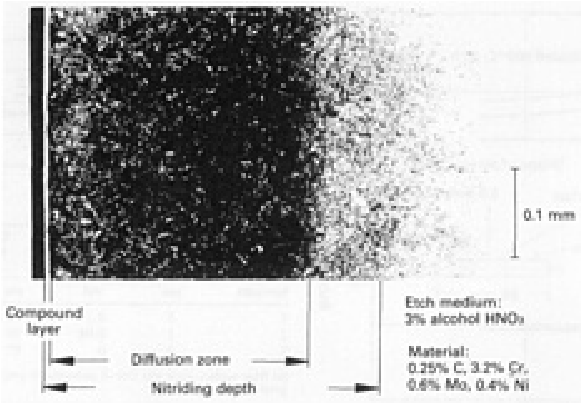


Fig. 18 Microstructure of ion-nitrided steel

The light etching surface layer, commonly termed white layer, has more recently been appropriately named compound zone. The ion-nitriding process offers the possibility of forming a single-phase compound zone with the structure Fe_4N, the gammaprime phase shown in Fig. 19(a). Depth of the gamma-prime compound zone is inherently process limited to about 10 μm (0.0004 in.) maximum. Steels with alloy contents greater than 6 to 8% inherently form compound zones with only thickness.

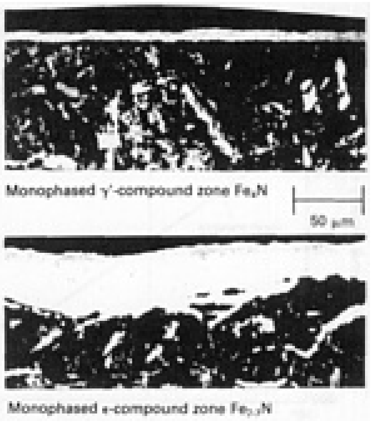


Fig. 19 Photomicrographs showing γ' and ε compound layers. (a) Single-phase γ' compound zone Fe_4N. (b) Single-phase ε compound zone Fe_2N-Fe_3N

Process-gas mixtures free of carbonaceous material are required to form compound zones having the gamma-prime structure. In the limiting condition, a diffusion zone is formed without an overlying compound zone. Gas compositions with less than the commonly used 25% nitrogen can completely suppress compound zone formation.

A shallow gamma-prime compound zone with an underlying diffusion zone is the desired structure for the majority of ion-nitriding applications, particularly where good fatigue properties are important.

Constructional alloy steels, nitriding steels, and tool steels containing nitride-forming alloying elements are used to fabricate workpieces. Nitride-forming elements are aluminum, chromium, molybdenum, vanadium, tungsten, titanium, and niobium. Hardening and tempering are performed prior to nitriding. In common with other nitriding methods, this allows quenching distortion and stresses to be corrected or removed prior to nitriding. Hardened and tempered, the steel has useful core strength and usually is machinable.

Single-phase epsilon iron-nitride compound zones having an Fe_2N-Fe_3N structure, as shown in Fig. 19(b), are formed when the process gas includes a carbonaceous component such as methane. The epsilon structure is slightly harder and less ductile than gamma prime.

Thickness of the epsilon compound zone is not process limited; a zone 50 μm (2 mil) deep can be formed. Industrially, zones 10 to 20 μm (0.4 to 0.8 mil) deep are applied to carbon steels and cast irons where core hardness is usually low. Applications with light loads or broad area contact predominate. In addition to providing increased mechanical strength, the thicker compound zone is a good barrier against corrosion.

Treatment time is typically 2 to 4 h at 570 °C (1060 °F), similar to other short-cycle nitrocarburizing processes. The compound zone is, however, pore-free with low surface roughness.

Comparison of Ion Nitriding and Ammonia-Gas Nitriding Compound Zone Structures. Ammonia-gas nitriding produces a compound zone that is a mixture of both epsilon and gamma-prime structures. High internal stresses result from differences in volume growth associated with the formation of each phase. The interfaces between the two crystal structures are weak. Thicker compound zones, formed by ammonia-gas nitriding, limit accommodation of the internal stresses resulting from the mixed structure. Thickness, internal stresses, and weak crystal boundaries allow the white layer to be fractured by small applied loads.

Under cyclic loading, cracks in the compound zone can serve as initiation points for the propagation of fatigue cracks. The single-phase gamma-prime compound zone, which is thin and more ductile, exhibits superior fatigue properties, as shown in Fig. 20. Reducing the thickness of the ion-nitrided compound zone further improves fatigue performance. Maximization occurs at the limiting condition, where compound zone depth equals zero (Fig. 21).

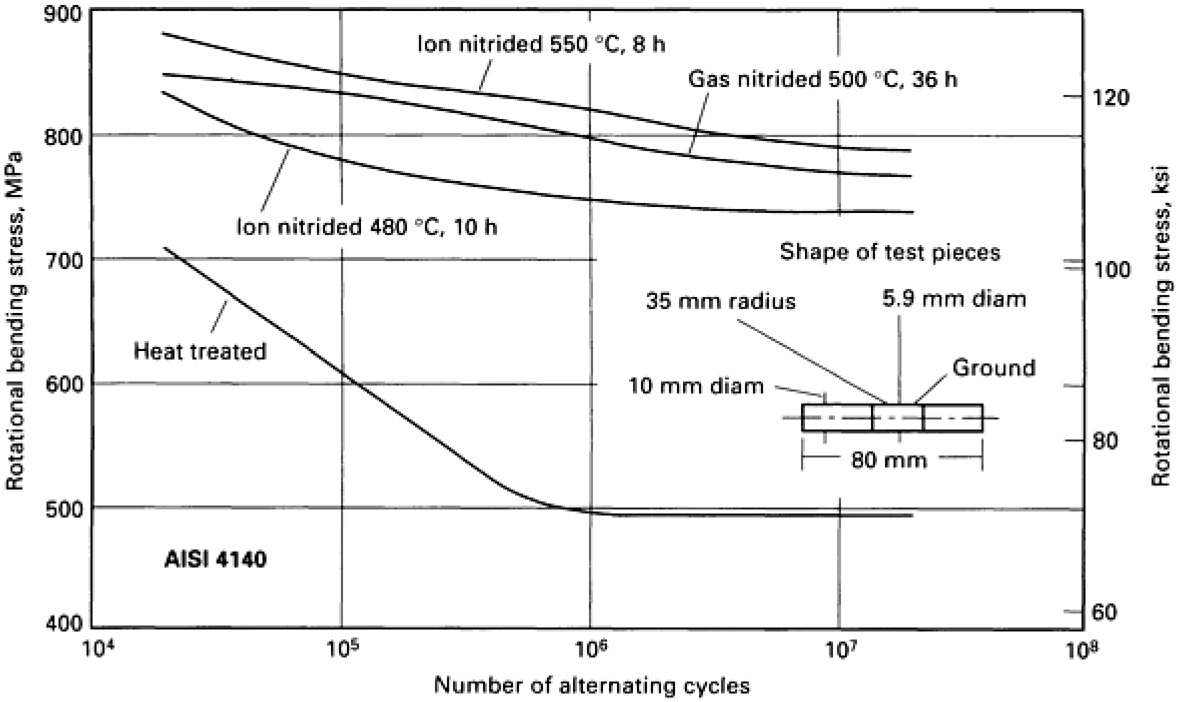
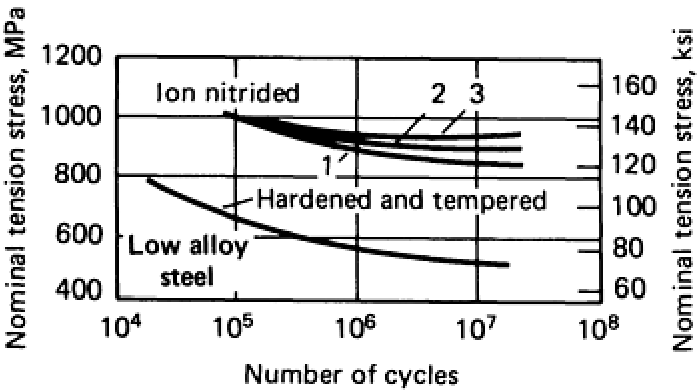


Fig. 20 Influence of nitriding on fatigue strength



Specimen	Compound zone thickness		Thickness of nitride-free zone(a)	
	µm	mil	µm	mil
1	5	0.2	60	2.4
2	1	0.04	80	3.1

(a) Near-surface zone was free of carbonitride precipitates at the grain boundaries.

Fig. 21 Fatigue strengths of ion-nitrided, quenched and tempered steel specimen (unnotched rotating beam 6 mm, or 0.24 in., diam). See table for zone thickness of specimens.

Case Hardness. The bulk of the thickness of the nitride case is the diffusion zone where fine iron/alloy nitride precipitates impart increased hardness and strength. Compressive stresses are also developed, as in other nitriding processes. Hardness profiles resulting from ion nitriding are similar to ammonia-gas nitriding (Fig. 22), but near-surface hardness may be greater with ion nitriding, a result of lower processing temperature.

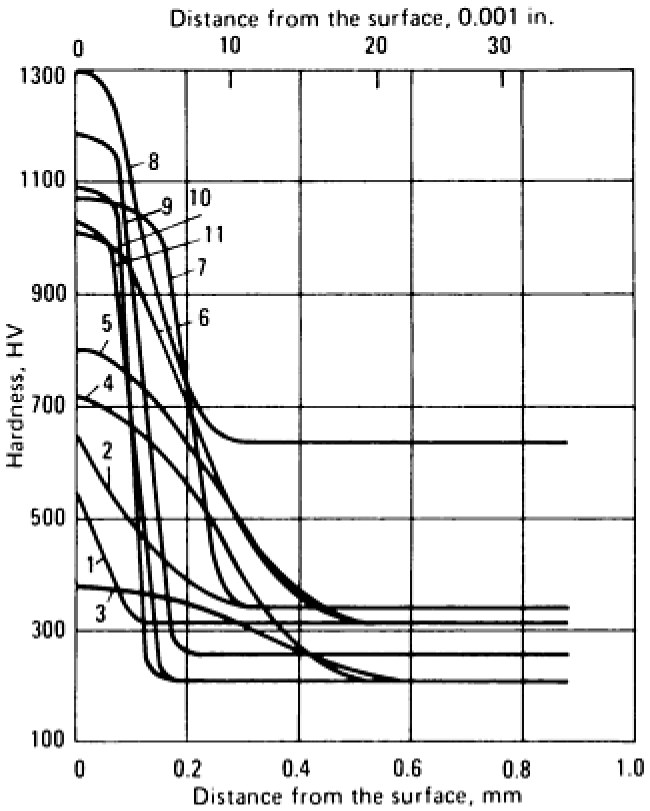


Fig. 22 Hardness profiles for various ion-nitrided materials. 1, gray cast iron; 2, ductile cast iron; 3, AISI 1040; 4, carburizing steel; 5, low-alloy steel; 6, nitriding steel; 7, 5% Cr hot-work steel; 8, cold-work die steel; 9, ferritic stainless steel; 10, AISI 420 stainless steel; 11, 18-8 stainless steel

The concentration and size of alloy nitride precipitates formed, together with parent material hardness, determine the hardness observed in a nitrided case. Figure 23 shows the results of ion nitriding a 0.32C-3Cr-1Mo-0.3V alloy steel at several temperatures, with time held constant. Case depth increases with temperature, and near-surface hardness is maximized near 450 °C (840 °F). Figure 24 shows a similar effect on M2 tool steel quenched and tempered to 62 HRC. Processing at temperatures just above the hardness maximum offers several advantages such as:

- Higher core hardness can be retained by reducing tempering temperatures
- The possibility of distortion is reduced
- Parts with low surface roughness remain virtually unchanged

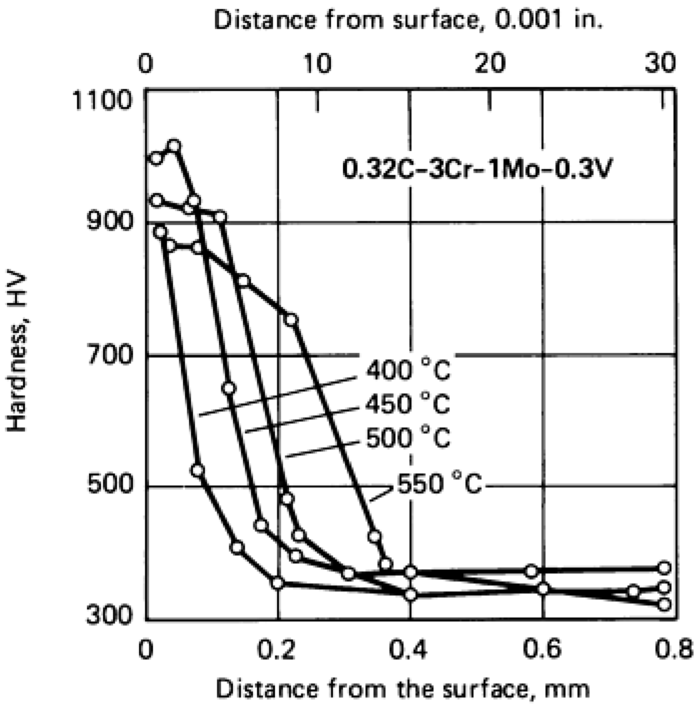


Fig. 23 Influence of treatment temperature on hardness profile

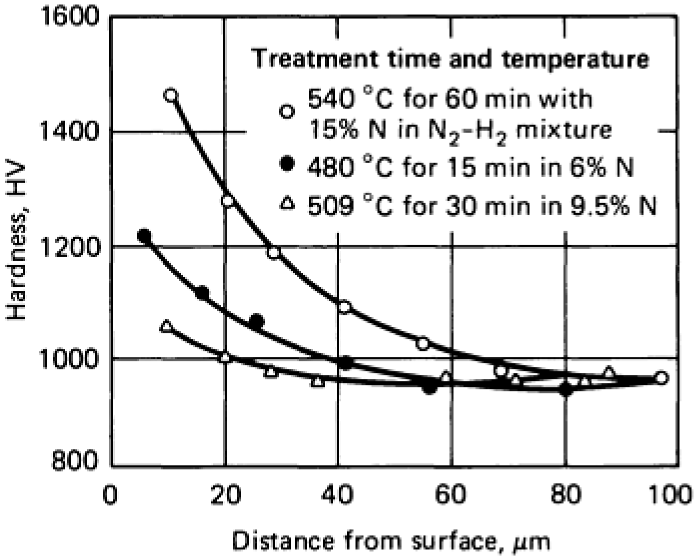


Fig. 24 Microhardness profile of nitrided layer in quenched and tempered M2 tool steel (tempered to 62 HRC) after various plasma nitriding conditions

Advantages and Disadvantages of Ion Nitriding. Ion nitriding achieves repetitive metallurgical results and complete control of the nitrided layers. This control results in superior fatigue performance, wear resistance, and hard layer ductility. Moreover, the process ensures high dimensional stability, eliminates secondary operations, offers low operating-temperature capability, and produces parts that retain surface finish. Among operating benefits are:

- Total absence of pollution
- Efficient use of gas and electrical energy
- Total process automation
- Selective nitriding by simple masking techniques
- Process span that encompasses all subcritical nitriding
- Reduced nitriding time

The limitations of ion nitriding include high capital cost, need for precision fixturing with electrical connections, long processing times compared to other short-cycle nitrocarburizing processes, and lack of feasibility of liquid quenching for carbon steels.

Applications. Among general applications requiring metallurgical properties obtainable by ion nitriding are:

- Structural elements subject to cyclic loading
- Workpieces requiring precision dimensions
- Components subject to sliding wear
- Parts exposed to mild corrosion

Metallurgical properties required by these applications are used frequently in combination for such products as: plastics processing machinery; automotive engine, transmission, chassis, and accessory components; cold-forming tools; and hot-forming tools.

Screws and cylinders for plastic extrusion require close dimensional tolerances. In service, they are subject to high mechanical loads and severe sliding wear. The hot plastic creates abrasive, corrosive, and erosive conditions at various locations along the length. Nitriding steel, pretreated for strength and toughness, receives a hard ductile layer by ion nitriding to meet this demanding service.

Components for Rotary Internal Combustion Engines. Side and middle housings of Wankel engines, made of gray iron, are stress relieved and finish machined prior to ion nitriding. Water passage areas are covered with sheet metal shields, so that only the rotor contact surfaces will be nitrided. Dimensional changes are extremely low, permitting direct use without a refinishing operation.

Similar to the Wankel engine housings are side plates for rotary automotive air-conditioning compressors. Also made of cast iron, they must be extremely flat, with good surface finish, and must be free of contamination. The epsilon layer produced by ion nitriding prevents seizure resulting from adversely hot operation.

Synchronizer components for transmissions are ion nitrided to meet close dimensional tolerances. Conventional techniques such as carbonitriding fail to meet dimensional requirements. A 10 μm (0.0004 in.) thick epsilon layer, with a superficial hardness of 550 HV (5 kg load), is typically produced. Ion nitriding has proved a satisfactory substitute for more expensive chrome plating on automobile shock absorber rods. The required wear and corrosion resistance is provided by an epsilon layer about 10 μm (0.0004 in.) thick.

Reduction gears for marine steam turbines were an early applications of ion nitriding, now firmly established as the preferred nitriding method. Dimensional accuracy and fatigue properties are superior to ammonia-gas nitriding. Nitriding is confined to the tooth area by masking with sheet metal covers. Significant labor economies are achieved.

Deep-drawing punches made of high-carbon, high-chrome steel are subjected to high compressive stresses in service. A core hardness of 62 HRC or higher is required after ion nitriding. Lowering the ion-nitriding temperature to 470 °C (880 °F) allows retention of the core hardness along with the hardness of the surface layer to about 1200 HV. The considerably reduced coefficient of friction results in a great increase in service life.

Hot-forging dies are an important application of ion nitriding. Die life is increased by improved resistance to thermal and mechanical cracking. The surface layer formed reduces the sticking of scale and inclusion of oxides.

Vacuum Nitrocarburizing

There are two main approaches to subatmospheric pressure thermochemical processing. One is known as the glow-discharge method, and the other involves use of conventional cold-wall vacuum furnaces. Because the processes are closely related to ion nitriding, they are discussed in this section. Further data on other types of nitrocarburizing processes are contained in the articles on gaseous ferritic nitrocarburizing.

Ion nitriding, which is being used increasingly as an alternative to conventional gas nitriding in ammonia atmospheres, was the first thermochemical treatment to use the glow-discharge technique. In glow-discharge nitrocarburizing, which is

a simple development of the ion-nitriding process, the components become the cathode of an electrical circuit. They are subsequently subjected to a glow discharge generated by applying a critical voltage between the furnace chamber, which acts as anode, and the components. Consideration of glow-discharge nitriding conditions indicates that a pressure in the range of 20 to 2000 Pa (0.15 to 15 torr) and a critical applied voltage of between 400 and 1000 V should be used.

The metallographic structure of pure iron after treatment in a nitrocarburizing atmosphere at 570 °C (1060 °F) for 15 h is shown in Fig. 25(a). A corresponding concentration analysis is given in Fig. 25(b), where the predominance of the epsilon carbonitride phase is shown.

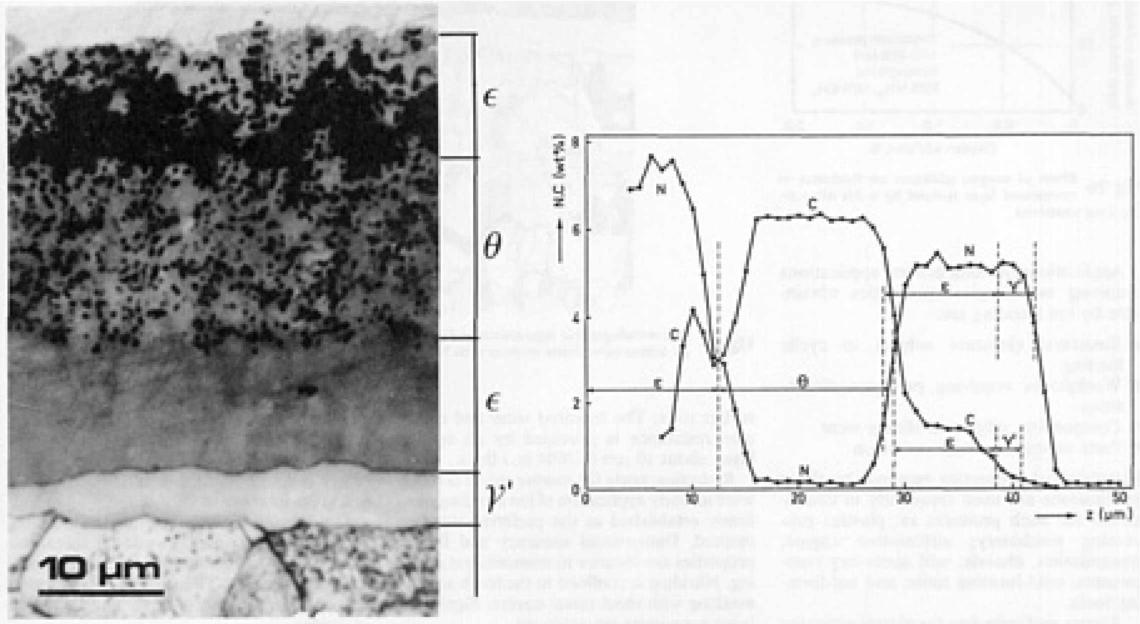


Fig. 25 (a) Compound layers and (b) concentration profiles of iron gas nitrocarburized at 570 °C (1058 °F) for 15 h

Cold-Wall Vacuum Furnaces. Extension of the use of cold-wall vacuum furnaces from purely thermal treatments, such as annealing and sintering, to thermochemical treatments was a natural development following introduction of such furnaces with oil-quench facilities. Although vacuum carburizing has received some attention in the literature, nitrocarburizing in a vacuum furnace is a more recent development. Although there was some evidence that the presence of oxygen gave a marginal improvement in the antiscuffing behavior of the epsilon carbonitride compound layer, the significance of the role of oxygen in the kinetics of compound layer growth was not at all clear.

It had been shown that oxygen was necessary to improve the carbon mass transfer characteristics of hydrocarbon carburizing gases, and that increasing the partial pressure of oxygen in the atmosphere speeded the kinetics of carbon exchange. Similarly, the presence of oxygen had been shown to increase the rate of compound layer formation during conventional gas nitriding. Consequently, with the advent of the capability of absolute atmosphere control using vacuum furnaces, investigations of vacuum nitrocarburizing were also able to evaluate the significance of oxygen in relation to the kinetics of compound layer formation. On the basis of earlier studies on gaseous nitrocarburizing treatments, a basic atmosphere of 50% ammonia/50% methane, containing controlled oxygen additions of up to 2%, was used for experiments in a laboratory vacuum furnace. The experiments were reproduced later using a semicontinuous industrial vacuum furnace. The furnace was evacuated to a pressure of 13 Pa (0.1 torr), and then heated to the process temperature under a low flow rate of ammonia balanced against a rotary vacuum pump to give a pressure of 3900 Pa (30 torr). Once the operating temperature of 570 °C (1060 °F) was reached, the hot zone was reevacuated, and the premixed gases were introduced into the hot zone at a pressure of 52 kPa (400 torr). To avoid either fixed flow patterns or stagnant gas pockets, a pulsed atmosphere technique was employed for the duration of the treatment. This involved pressure cycling between 13 to 52 kPa (100 to 400 torr), with 10-min dwells at 52 kPa (400 torr) throughout the treatment, after which the specimens were oil quenched. As a result of this treatment, a compound layer is formed that has a carbon/nitrogen ratio of about 1:7; it consists predominantly of the oxygen-bearing epsilon carbonitride phase.

Layer thickness formed after a 2-h treatment varies with the oxygen content of the atmosphere. Figure 26 shows the compound zone thickness as a function of the oxygen content of the atmosphere in a nominal 50% methane/50% ammonia atmosphere. The metallographic appearance after a typical subatmospheric treatment with a 1% oxygen addition is shown in Fig. 27. The compound zone shows very little porosity, and its overall metallographic appearance is very

similar to the layer formed by gaseous nitrocarburizing in an atmosphere consisting of 50% ammonia and 50% endothermic gas at a treatment temperature of 570 °C (1060 °F). When oxygen levels of about 2% are used, however, the compound zone is quite porous. Wear properties of AISI 1015 materials treated in this manner have been evaluated by standard Amsler wear tests, the results being compared to results of similar tests with other nitrocarburizing treatments (Fig. 28). Three of the treatments confer similar wear-improvement characteristics on low-carbon steels after a treatment time of 2 h at 570 °C (1060 °F).

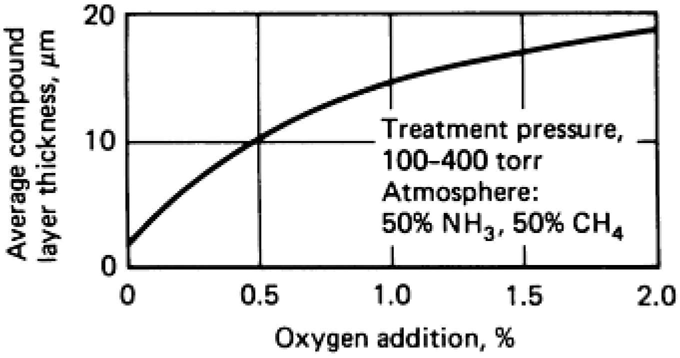


Fig. 26 Effect of oxygen additions on thickness of compound layer formed by a 2-h nitrocarburizing treatment

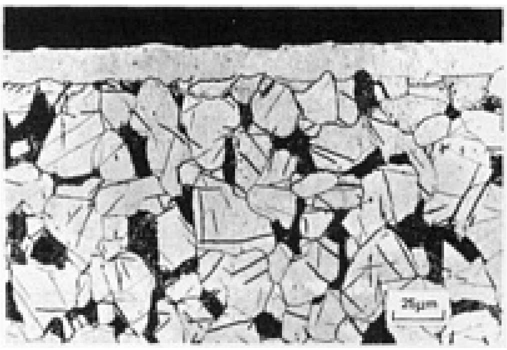


Fig. 27 The metallographic appearance of AISI 1015 material after a 2-h vacuum-nitrocarburizing treatment in an ammonia/methane mixture with 1% oxygen addition

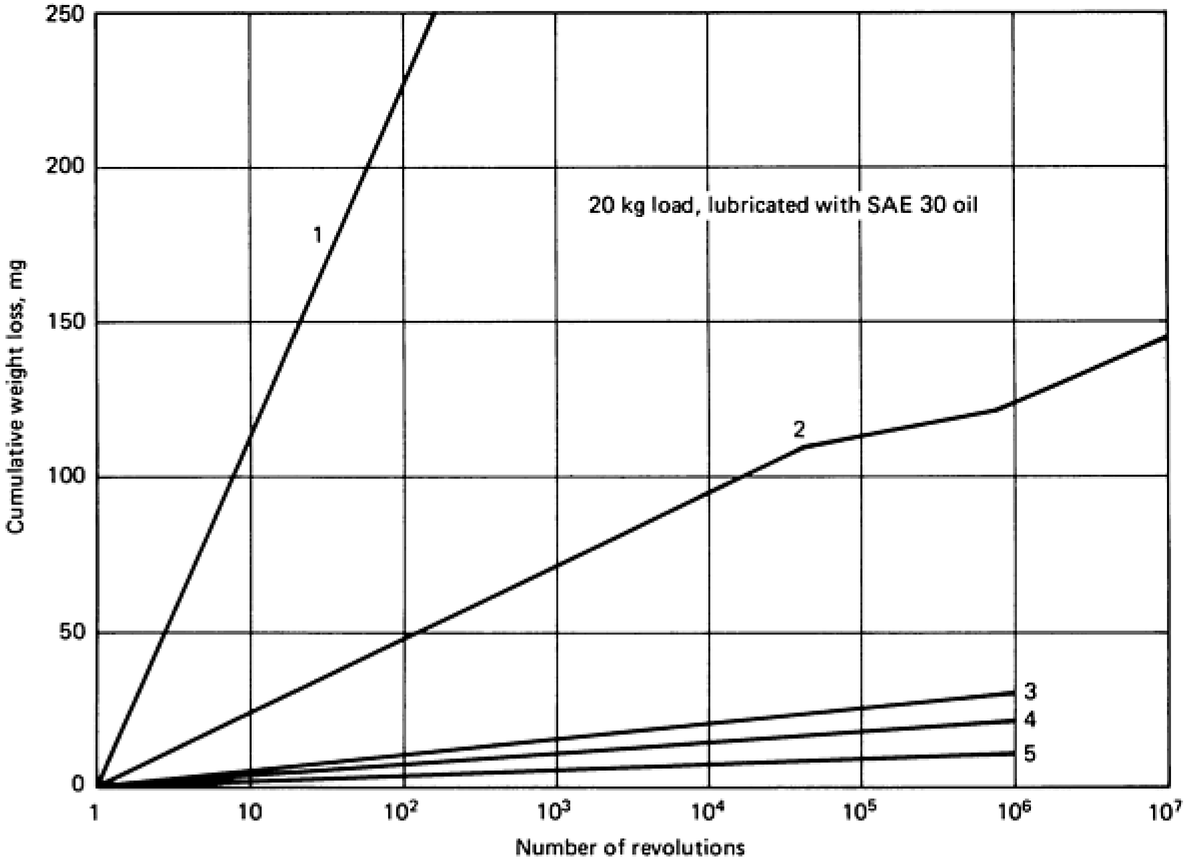


Fig. 28 Comparative Amsler wear tests on AISI 1015 after various ferritic nitrocarburizing treatments. 1, untreated; 2, cyanide-based salt bath nitrocarburizing with sulfur; 3, subatmospheric oxynitrocarburizing; 4, gaseous nitrocarburizing; and 5, cyanide-based salt bath nitrocarburizing (treatment 1)

Hardnesses of compound layers produced by subatmospheric pressure nitrocarburizing are compared (in Table 8) with hardnesses of layers resulting from other treatments. Hardness levels are high considering the ductile nature of the compound zone, and the layer hardness appears to be higher on alloy steel than on plain carbon material.

Table 8 Hardness of nitrocarburized specimens

Material	Treatment	Applied load		Microhardness of compound layer, HV		
		g	oz	Center region	Inner region	Average
Low-carbon steel	Toxic salt	. . .	. . .	. . .	. . .	500-600
AISI 1015	Toxic salt	2500	90	. . .	. . .	536
En41 nitriding steel	Toxic salt	2500	90	. . .	. . .	803
Pure iron	Toxic salt	. . .	. . .	480-680	820-990	. . .
Low-carbon steel	Nontoxic salt	15	0.5	340-450	900-1100	. . .
En40c[(a)]	Gaseous	200	7	. . .	. . .	820
AISI 1015	Gaseous	200	7	. . .	. . .	620
Pure iron	Gaseous	200	7	. . .	. . .	600
AISI 1015	Gaseous	25	1	. . .	. . .	600-900
Pure iron	Gaseous	. . .	. . .	. . .	. . .	1000-1200
Pure iron	Gaseous	. . .	. . .	400-950	780-450	. . .

(a) 3% Cr, 17% Mo nitriding steel

Appendix

Analysis of Exhaust Gas from Gas-Nitriding Operations

Ammonia gas is completely soluble in water. When water is introduced into the dissociation pipette (burette) (Fig. 29), any ammonia present dissolves instantly, reducing the pressure within the burette. Water continues to enter the burette until it occupies a volume equivalent to that previously occupied by the ammonia. The remainder of the exhaust gas,

being insoluble in water, collects at the top of the burette. The height of the water level is read directly from the scale of graduations, and this reading indicates the percentage of non-water-soluble hydrogen-nitrogen gas in the sample. If the sample was generated solely by the breakdown of ammonia, this reading is correctly called percent dissociation. When air is present at the start or end of a cycle, however, no ammonia is being dissociated and the resulting reading is not percent dissociation, but percent air. Accordingly, it is proper to subtract the reading from 100% and refer to the remainder as percent ammonia present in the sample.

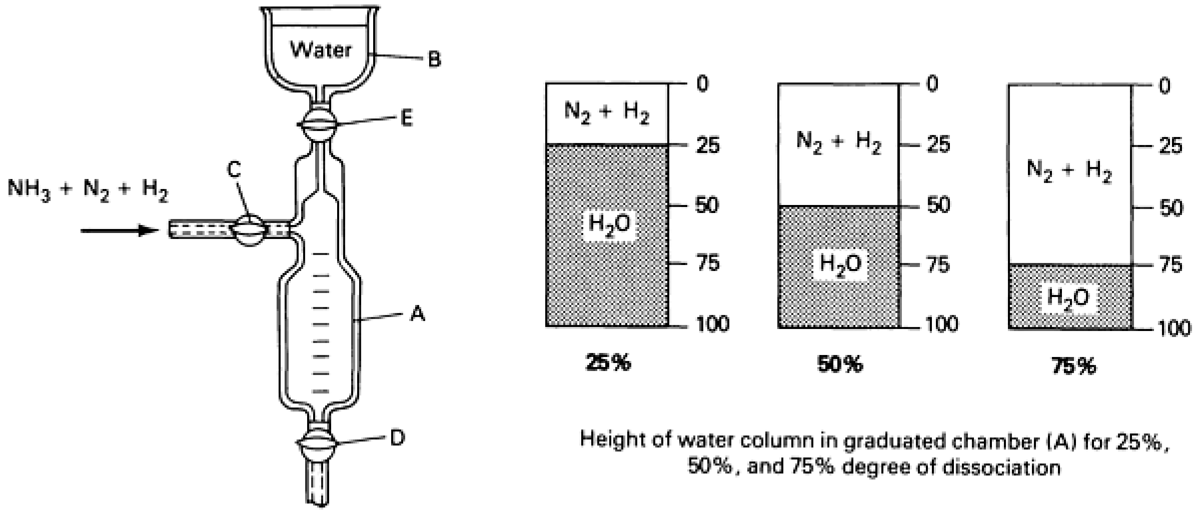


Fig. 29 Dissociation pipette (burette) schematic. To make a measurement, the ammonia gas in the nitriding box is first admitted into A by opening taps C and D. After the air has been expelled, taps C and D are closed. During the measurement, tap E is opened, and the water immediately absorbs the undissociated ammonia. The water takes up precisely the volume previously occupied by the ammonia, but the remaining N_2-H_2 gas (dissociated ammonia) does not dissolve in water.

Inspection and Quality Control

Visual Inspection. It is often evident from a cursory visual inspection that a part, or an isolated surface of a part, is not properly nitrided. Typically, gas-nitrided parts exhibit a uniform dull gray appearance. If surfaces are shiny after nitriding, it is likely that little or no nitrogen was diffused. This assessment should always be checked quantitatively and not assumed.

Indentation tests of the hardness of a nitrided case should be made using relatively light loads, regardless of case depth. These indentation methods include the superficial HR15-N (and to a limited extent, the HR30-N), and the Knoop and Vickers (diamond pyramid hardness, DPH) microhardness tests. The superficial Rockwell test is made on a surface that is ground prior to, and only polished lightly after, nitriding; whereas the Knoop and Vickers microhardness tests are generally performed on cross-sectional specimens that have been metallographically polished. Microhardness tests are generally made with loads of 100 to 500 g (0.2 to 1 lb).

Utilizing lighter loads than the superficial Rockwell test, but greater than are commonly used for microhardness testing, the Vickers test is used extensively in Europe for quality control. Superficial measurements with 2, 5, or 10 kg loads are made directly on nitrided surfaces. Loads in this range accurately reflect surface hardness and require only minimal surface preparation. Good accuracy results from optical measurement necessitated by the small impression.

The superficial Rockwell tests HR15-N or HR30-N should be used to check nitride case hardness. Depending on the depth and hardness of case present, as well as core hardness, it is possible for the diamond indenter to penetrate the case. This results in a misleading composite hardness of both case and core. When this occurs (usually if case is less than 0.13 mm, or 0.005 in.), microhardness testing should be used.

Because of metal flow or spalling, it is difficult to determine accurately by microhardness methods the case hardness at depths of less than 0.025 mm (0.001 in.) from the surface of a cross-section specimen, even when light loads are applied. For this reason, surface hardness is commonly measured by the HR15-N test; the values obtained may be converted to Knoop or Vickers values in accordance with the conversion table given in ASTM E 140.

Comparison of Hardness Measurements. When results of HR15-N and Knoop tests are compared, Knoop hardness is generally found to be higher than the equivalent HR15-N hardness of the higher-hardness portion of the depth of case measured from the nitrided surface, whereas the opposite is experienced for the lower-hardness portion of the case (see Fig. 30).

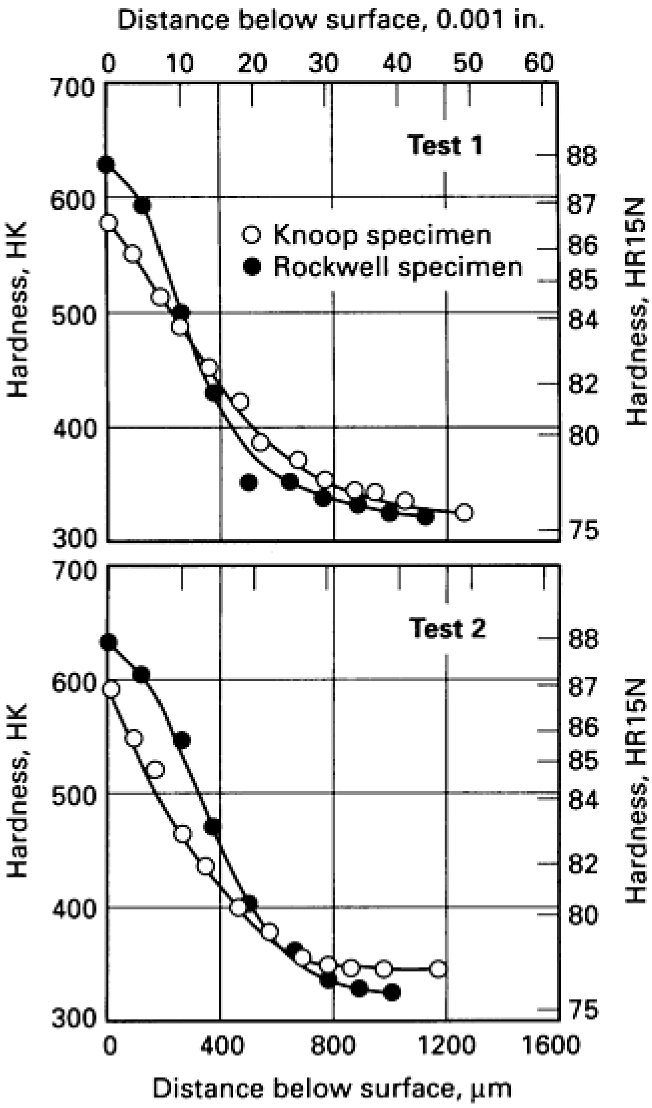


Fig. 30 Comparison between Knoop and HR15-N hardness. 4340 nitrided at 550 °C (1020 °F), 20 h, 20 to 50% dissociation. HR15-N was converted to Knoop hardness.

Evaluation of case depth may be accomplished by preparing a cross section of the case, etching with a suitable agent, and microscopically measuring the depth from the surface to a point of contrast between the case and core. Suitable etchants may be one of the following:

- Distilled water (250 cm^3), ammonium persulfate (109 g), sodium alkyl aryl sulfonate (1 g), and saturated solution of sodium thiocyanate (10 drops)
- 4% nital
- 3% picral plus 1% benzalkonium chloride (zephiran chloride)

Case depth may be determined also by microhardness testing an unetched cross section of the case, using either the Vickers or Knoop tester. Measurement consists of making a hardness survey from near the nitrided surface to the base metal (total case), or to a depth at which a predetermined hardness value (such as 60 HRC) is measured (effective case).

In general, case depth measurements determined by microhardness tests are more accurate and reproducible than those made by visual examination of etched specimens. Frequently, the depth of case determined by examination of an etched

specimen is less than that indicated by a microhardness survey, as shown by the data in Fig. 31. Also, etchants react differently on different steels. For example, the 3% picral and 1% benzalkonium chloride solution darkens the case of aluminum-bearing steels but does not have this effect on 4100 series.

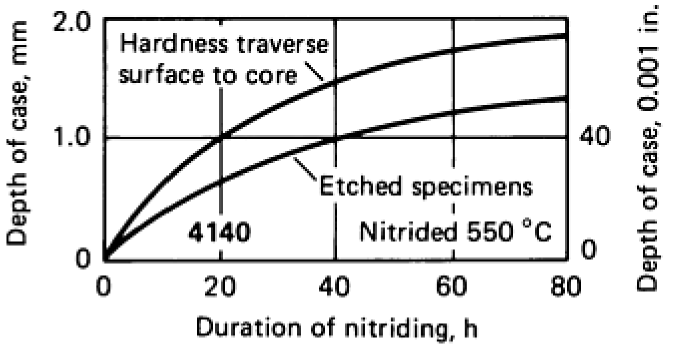


Fig. 31 Comparison of depth of nitrided case determined by hardness traverse and by etching specimens in 2% nital. Before being nitrided, the 4140 steel was oil quenched from 845 °C (1550 °F) and tempered at 595 °C (1100 °F).

When facilities for microhardness or etchant tests are not available, a tapered-wedge control specimen may be used in conjunction with the HR15-N tester to determine case depth of the nitrided parts. Such a specimen is of the same grade of steel as the parts being nitrided and has overall dimensions of 48 by 19 by 10 mm ($1\frac{7}{8}$ by $\frac{3}{4}$ by $\frac{3}{8}$ in.). It is heat treated with the parts to obtain the proper hardness. After removal of 3.2 mm ($\frac{1}{8}$ in.) of material from all surfaces, a 1.8 mm (0.070 in.) taper is ground by placing a 1.8 by 3 by 19 mm (0.070 by $\frac{1}{8}$ by $\frac{3}{4}$ in.) shim under one end of the specimen as indicated in Fig. 32.

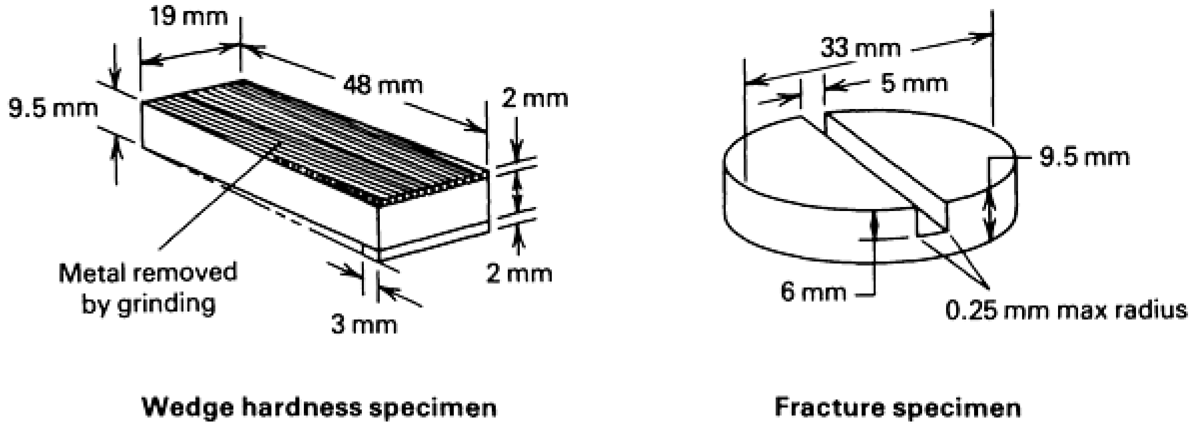


Fig. 32 Wedge specimen for determining case depth when facilities for microhardness or etchant tests are not available and fracture specimen for determining case depth

The tapered specimen is then nitrided with the parts, after which it is reground to remove the taper so that hardness measurements can be taken at right angles to the surface. (Heat generated from grinding must be kept at a minimum to prevent a change in hardness of the case.) This procedure results in a tapered cross section of the case. Thus, when superficial HR15-N hardness measurements are taken at 3.2 mm ($\frac{1}{8}$ in.) increments on this ground surface, each 3.2 mm ($\frac{1}{8}$ in.) increment represents a 0.13 mm (0.005 in.) increment in case depth. Results of this technique are biased, inasmuch as the relatively high load of 15 kg (33 lb) results in a series of case-core composite values.

Test Coupons. Quality control of nitrided parts is normally best accomplished by treating test coupons with each furnace load. One type of test coupon in common use is the fracture specimen illustrated in Fig. 32. Coupons must be of the same material heat treated to the same core hardness as the parts, and should be placed in locations that are

representative of the nitriding conditions of the furnace. Thus, when the material and heat treating are constant, any changes in the nitriding process that may develop may be easily detected.

After nitriding, the test coupons are fractured or sectioned for determination of case depth by means of a Brinell microscope or a hardness survey. They also are used in determining the depth of the white layer, the core hardness of parts that have been nitrided all over, and the case hardness of areas that are not accessible to a hardness test. However, when possible, actual parts should be used for hardness tests of the case and core.

The data obtained from test coupons should be recorded and filed with the furnace records. Furnace temperature charts should include the dissociation readings taken during the nitriding treatment of each load.

Measurement and Removal of White Layer. Normally, the surface of nitrided parts will contain a layer of iron nitride (white layer). This white layer ranges in thickness from 0.005 to 0.05 mm (0.0002 to 0.0020 in.), depending on the length of the cycle and whether single-stage or double-stage nitriding was employed. The thickness of the white layer is measured principally by metallographic methods. A prepared cross section of the nitrided surface is etched with an etchant that darkens the case but not the iron nitride layer; thus, this layer appears white and can be measured microscopically.

The white layer produced by single-stage nitriding is hard and brittle and should be carefully removed. Double-stage nitriding produces a shallower, softer, and more ductile white layer. For some applications, this type of white layer is beneficial; in certain gear systems, for example, it provides a good wear-in surface. The amount of stock removal required for elimination of the white layer should be determined by testing actual parts; however, Table 9 may be used as a guide.

Table 9 General guide to amount of stock removal required for elimination of white layer from nitrided parts

Nitriding cycle, h	Maximun amount of stock removal			
	Single-stage nitriding		Double-stage nitriding	
	mm	10^{-4} in.	mm	10^{-4} in.
12	0.01	5	0.01	5
24	0.03	10	0.03	10
36	0.04	15	0.03	10
48	0.05	20	0.03	10
60	0.06	25	0.04	15

The amount of expensive finish grinding or lapping required for removing white layer is significantly less for parts that are double-stage nitrided than for parts that are single-stage nitrided. The white layer formed during double-stage nitriding usually can be held to a maximum thickness of 0.019 mm (0.00075 in.), although this may still be excessive for certain applications.

One method (U.S. Patent 3,069,296) for totally removing the white layer uses a simple alkaline solution that decomposes the iron nitride, making it friable and easily removable by light blast cleaning. A 200-mesh aluminum oxide grit is recommended for blasting. Depending on surface finish requirements, either liquid-abrasive blasting or peening with glass beads may be substituted for grit blasting. The procedure does not harm the surface finish and has the added advantage of removing copper plate (during immersion in the alkaline solution) from parts plated for selective nitriding. Tests have shown no decrease in hardness, fatigue strength, or impact strength; etching or pitting of the nitrided surface does not occur. The process does not require close control.

Another method (U.S. Patent 2,960,421) removes the iron nitride white layer by a diffusion process. Parts are copper plated all over and then heated to and held at about 525 °C (975 °F) for periods up to 40 h, depending on the thickness of white layer to be removed.

Parts that have been processed for the removal of white layer may be inspected by observing the reaction of nitrided surfaces after swabbing them with a 5% solution of nital or a 10% solution of ammonium persulfate. Areas from which the white layer has been removed will etch dark, whereas areas where the white layer is still present in substantial quantity will not etch. This procedure is not absolutely accurate because areas that etch dark may still contain some white layer; however, the amount of white layer remaining is usually insufficient to affect the service performance of the part.

Liquid Nitriding of Steels

Revised by the ASM Committee on Liquid Nitriding*

Introduction

LIQUID NITRIDING (nitriding in a molten salt bath) employs the same temperature range as gas nitriding, that is, 510 to 580 °C (950 to 1075 °F). The case-hardening medium is a molten, nitrogen-bearing, fused-salt bath containing either cyanides or cyanates. Unlike liquid carburizing and cyaniding, which employ baths of similar compositions, liquid nitriding is a subcritical (that is, below the critical transformation temperature) case-hardening process; thus, processing of finished parts is possible because dimensional stability can be maintained. Also, liquid nitriding adds more nitrogen and less carbon to ferrous materials than that obtained through higher-temperature diffusion treatments.

The liquid nitriding process has several proprietary modifications and is applied to a wide variety of carbon, low-alloy steels, tool steels, stainless steels, and cast irons.

Note

* Q.D. Mehrkam, Ajax Electric Company; J.R. Easterday, Kolene Corporation; B.R. Payne, Payne Chemical Corporation; R.W. Foreman, Consultant; D. Vukovich, Eaton Corporation; and A.D. Godding, Heatbath Corporation

Liquid Nitriding Applications

Liquid nitriding processes are used primarily to improve wear resistance of surfaces and to increase the endurance limit in fatigue. For many steels, resistance to corrosion is improved. These processes are not suitable for many applications requiring deep cases and hardened cores, but they have successfully replaced other types of heat treatment on a performance or economic basis. In general, the uses of liquid nitriding and gas nitriding are similar, and at times identical. Gas nitriding may be preferred in applications where heavier case depths and dependable stopoffs are required (see the article "Gas Nitriding" in this Volume). Both processes, however, provide the same advantages: improved wear resistance and antigalling properties, increased fatigue resistance, and less distortion than other case-hardening processes employing through heating at higher temperatures. Four examples of parts for which liquid nitriding was selected over other case-hardening methods appear in Table 1.

Table 1 Automotive parts for which liquid nitriding proved superior to other case-hardening processes for meeting service requirements

Component	Requirement	Material and process originally used	Resultant problem	Solution
Thrust washer	Withstand thrust load without galling and deformation	Bronze, carbonitrided 1010 steel	Bronze galled, deformed; steel warped	1010 steel nitrided 90 min in cyanide-cyanate bath at 570 °C (1060 °F) and water quenched[(a)]
Shaft	Resist wear on splines and bearing area	Induction harden through areas	Required costly inspection	Nitride for 90 min in cyanide-cyanate salt bath at 570 °C (1060 °F)
Seat bracket	Resist wear on surface	1020 steel, cyanide treated	Distortion; high loss in straightening[(b)]	1020 nitrided 90 min in cyanide-cyanate salt bath and water quenched[(c)]
Rocker arm shaft	Resist water on surface; maintain geometry	SAE 1045 steel, rough ground, induction hardened, straightened, finish ground, phosphate coated	Costly operations and material	SAE 1010 steel liquid-nitrided 90 min in low-cyanide fused salt at 570 to 580 °C (1060 to 1075 °F)[(d)]

(a) Resulted in improved product performance and extended life, with no increase in cost.

(b) Also, brittleness.

(c) Resulted in less distortion and brittleness, and elimination of scrap loss.

(d) Eliminated finish grinding, phosphatizing, and straightening

The degree to which steel properties are affected by liquid nitriding may vary with the process used and the chemical control maintained. Thus, critical specifications should be based on prior test data or documented information.

Liquid Nitriding Systems

The term liquid nitriding has become a generic term for a number of different fused-salt processes, all of which are performed at subcritical temperature. Operating at these temperatures, the treatments are based on chemical diffusion and influence metallurgical structures primarily through absorption and reaction of nitrogen rather than through the minor amount of carbon that is assimilated. Although the different processes are represented by a number of commercial trade names, the basic subclassifications of liquid nitriding are those presented in Table 2.

Table 2 Liquid nitriding processes

Process identification	Operating range composition	Chemical nature	Suggested post treatment	Operating temperature		U.S. patent number
				°C	°F	
Aerated cyanide-cyanate	Sodium cyanide (NaCN), potassium cyanide (KCN) and potassium cyanate (KCNO), sodium cyanate (NaCNO)	Strongly reducing	Water or oil quench; nitrogen cool	570	1060	3,208,885
Casing salt	Potassium cyanide (KCN) or sodium cyanide (NaCN), sodium cyanate (NaCNO) or potassium cyanate (KCNO), or mixtures	Strongly reducing	Water or oil quench	510-650	950-1200	
Pressure nitriding	Sodium cyanide (NaCN), sodium cyanate (NaCNO)	Strongly reducing	Air cool	525-565	975-1050	
Regenerated cyanate-carbonate	Type A: Potassium cyanate (KCNO), potassium carbonate (K_2CO_3); Type B: Potassium cyanate (KCNO), potassium carbonate (K_2CO_3), 1-10 ppm, sulfur (S)	Mildly oxidizing	Water, oil, or salt quench	580	1075	4,019,928
		Mildly oxidizing	Water, oil quench, or salt	540-575	1000-1070	4,006,643

A typical commercial bath for liquid nitriding is composed of a mixture of sodium and potassium salts. The sodium salts, which comprise 60 to 70% (by weight) of the total mixture, consist of 96.5% NaCN, 2.5% Na_2CO_3, and 0.5% NaCNO. The potassium salts, 30 to 40% (by weight) of the mixture, consist of 96% KCN, 0.6% K_2CO_3, 0.75% KCNO, and 0.5% KCl. The operating temperature of this salt bath is 565 °C (1050 °F). With aging (a process described in the section "Operating Procedures" in this article), the cyanide content of the bath decreases, and the cyanate, and carbonate contents increase (the cyanate content in all nitriding baths is responsible for the nitriding action, and the ratio of cyanide to cyanate is critical). This bath is widely used for nitriding tool steels, including high-speed steels, and a variety of low-alloy steels, including the aluminum-containing nitriding steels.

Another bath for nitriding tool steels has a composition as follows:

Component	Amount, %
NaCN	30.00 max
Na_2CO_3 or K_2CO_3	25.00 max
Other active ingredients	4.00 max
Moisture	2.00 max
KCl	rem

A proprietary nitriding salt bath has the following composition by weight: 60 to 61% NaCN, 15.0 to 15.5% K_2CO_3, and 23 to 24% KCl.

Several special liquid nitriding processes employ proprietary additions, either gaseous or solid, that are intended to serve several purposes, such as accelerating the chemical activity of the bath, increasing the number of steels that can be processed, and improving the properties obtained as a result of nitriding.

Cyanide-free liquid nitriding salt compositions have also been introduced. However, in the active bath, a small amount of cyanide, generally up to 5.0%, is produced as part of the reaction. This is a relatively low concentration, and these compositions have gained widespread acceptance within the heat-treating industry because they do contribute substantially to the alleviation of a potential source of pollution.

Three processes, liquid pressure nitriding, aerated bath nitriding, and aerated low-cyanide nitriding, are described in the sections that follow.

Liquid Pressure Nitriding

Liquid pressure nitriding is a proprietary process in which anhydrous ammonia is introduced into a cyanide-cyanate bath. The bath is sealed and maintained under a pressure of 7 to 205 kPa (1 to 30 psi). The ammonia is piped to the bottom of the retort and is caused to flow vertically. The percentage of nascent nitrogen in the bath is controlled by maintaining the ammonia flow rate at 0.6 to 1 m^3/h (20 to 40 ft^3/h). This results in ammonia dissociation of 15 to 30%.

The bath contains sodium cyanide and other salts, which permits an operating temperature of 525 to 565 °C (975 to 1050 °F). Because the molten salts are diffused with anhydrous ammonia, a new bath does not require aging and may be put into immediate operation employing the recommended cyanide-cyanate ratio, namely, 30 to 35% cyanide and 15 to 20% cyanate. Except for dragout losses, maintenance of the bath within the preferred ratio range is greatly simplified by the anhydrous ammonia addition, which serves continuously to counteract bath depletion.

The retort cover may be opened without causing complete interruption of the nitriding process. Loss of pressure within the retort results in a reduction in the nitriding rate. However, when the retort is sealed and pressure is reinstated through the resumption of ammonia gas flow, nitriding proceeds at the normal rate.

Depth of case depends on time at temperature. The average nitriding cycle is 24 h, although total cycle time may vary between 4 and 72 h. To stabilize core hardness, it is recommended that all parts be tempered at a temperature at least 28 °C (50 °F) higher than the nitriding temperature before they are immersed in the nitriding bath.

Hardness gradients and case depths resulting from pressure nitriding of 410 stainless steel, AISI type D2, and SAE 4140 are shown in Fig. 1, 2, and 3.

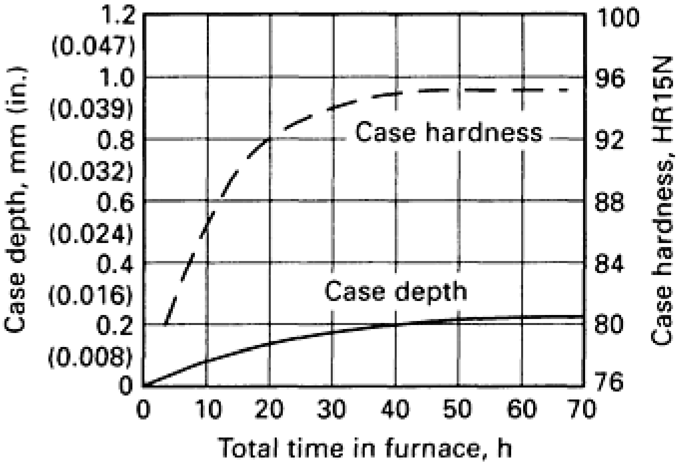


Fig. 1 Results of liquid pressure nitriding on type 410 stainless steel (composition, 0.12C-0.45Mn-0.41Ni-11.90Cr; core hardness, 24 HRC)

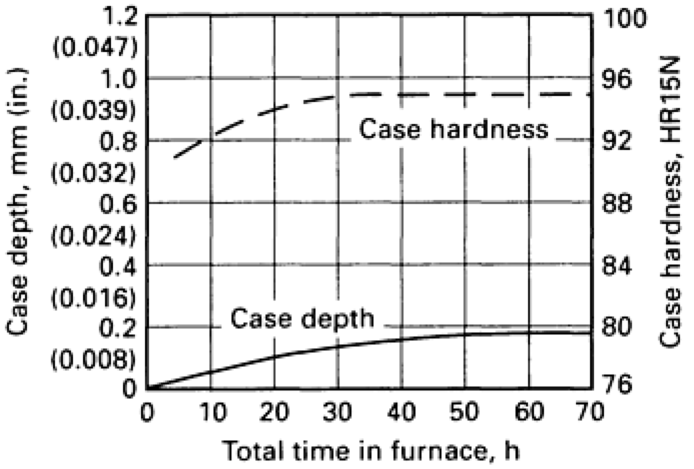


Fig. 2 Results of liquid pressure nitriding on AISI type D2 tool steel (composition, 1.55C-0.35Mn-11.50Cr-0.80Mo-0.90V; core hardness, 52 HRC)

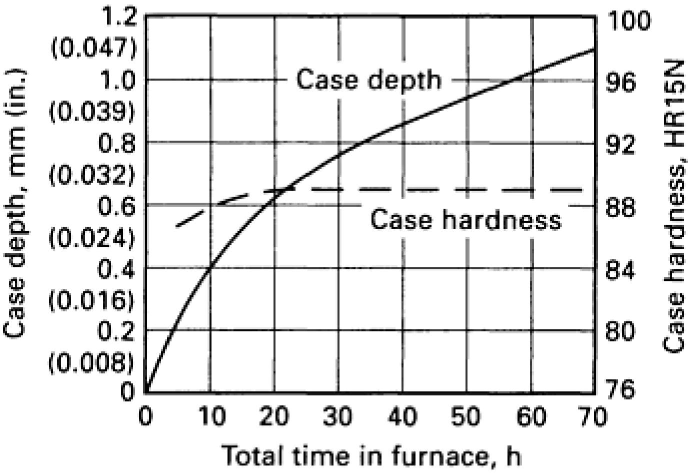


Fig. 3 Results of liquid pressure nitriding on SAE 4140 low-alloy steel (composition, 0.38C-0.89Mn-1.03Cr-0.18Mo; core hardness, 35 HRC)

Aerated Bath Nitriding

Aerated bath nitriding is a proprietary process (U.S. Patent 3,022,204) in which measured amounts of air are pumped through the molten bath. The introduction of air provides agitation and stimulates chemical activity. The cyanide content of this bath, calculated as sodium cyanide, is maintained at preferably about 50 to 60% of the total bath content, and the cyanate is maintained at 32 to 38%. The potassium content of the fused bath, calculated as elemental potassium, is between 10 and 30%, preferably about 18%. The potassium may be present as the cyanate or the cyanide, or both. The remainder of the bath is sodium carbonate.

This process produces a nitrogen-diffused case 0.3 mm (0.012 in.) deep on plain carbon or low-alloy steels in a $1\frac{1}{2}$ h cycle. The surface layer (0.005 to 0.01 mm, or 0.0002 to 0.0005 in. deep) of the case is composed of ε Fe_3N and a nitrogen-bearing Fe_3C; the nitrided case does not contain the brittle Fe_2N constituent.

Beneath the compound zone of Fe_3N, a diffusion zone exists that consists of a solid solution of nitrogen in the base iron. Depth of nitrogen diffusion in 1015 steel as a function of nitriding time at 565 °C (1050 °F) is shown in Fig. 4. The outer compound layer provides wear resistance, while the diffusion zone improves fatigue strength.

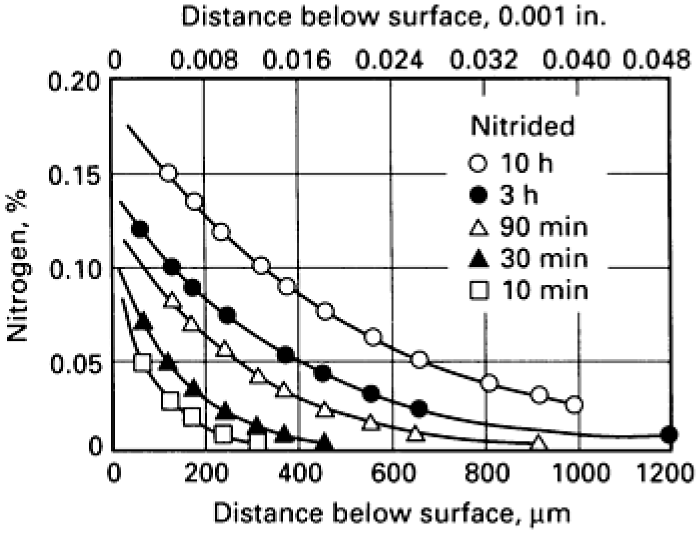


Fig. 4 Nitrogen gradients in 1015 steel as a function of time of nitriding at 565 °C (1050 °F), using the aerated bath process

It should be noted that only chromium-, titanium-, and aluminum-alloyed steel respond well to conventional bath nitriding. Plain carbon (nonalloyed) steels respond well to aerated bath nitriding but not to conventional nitriding. Thus, the aerated process should be specified for nitriding all plain carbon steels because test data show that plain carbon steel will not develop adequate hardness in a nonaerated nitriding bath. However, the full effect of nitriding will not be realized unless an alloy steel is selected. See the section "Hardness of Compound Layer" in Appendix 1 of this article.

Aerated Cyanide-Cyanate Nitriding. Another aerated process for liquid nitriding is a high-cyanide, high-cyanate system that is proprietary (U.S. Patent 3,208,885). The cyanide content of the fused salt is maintained in the range of 45 to 50% calculated as potassium cyanide, and the cyanate content is maintained in the range of 42 to 50% calculated as potassium cyanate. Makeup salt consists of a precise mixture of sodium and potassium cyanides that are oxidized by aeration to the mixed cyanate. The ratio of sodium ions to potassium ions is important in duplicating the integrity of the compound zone and the diffusion zone.

The process is performed in a titanium-lined container, and it produces a compound zone of ε iron nitride to a depth of 0.010 to 0.015 mm (0.0004 to 0.0006 in.) and a diffusion zone of 0.356 to 0.457 mm (0.014 to 0.018 in.) in plain carbon steels with a 90-min treating time, as shown in Fig. 5. The surface hardness of the compound zone may vary between 300 HK and 450 HK if carbon or low-alloy steels are being treated. Surface hardness of stainless steels treated by this process may reach 900 HK as shown in AMS 2755B, a portion of which is reproduced in Appendix 2 of this article.

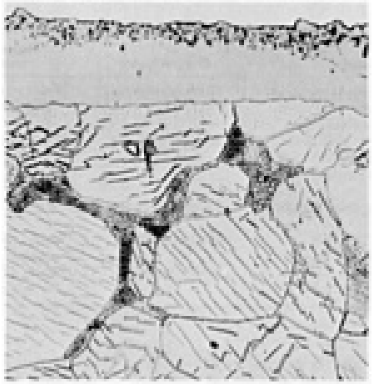


Fig. 5 Nitrided case and diffusion zone produced by cyanide-cyanate liquid nitriding. The characteristic needle structure is seen only after a 300 °C (570 °F) aging treatment.

Aerated Low-Cyanide Nitriding. Environmental concerns have led to the development of cyanide-free processes for liquid nitriding. In these proprietary processes, the base salt is supplied as a cyanide-free mixture of potassium cyanate and a combination of sodium carbonate and potassium carbonate, or sodium chloride and potassium chloride. Minor percentages of cyanide develop during use in these compositions. The problem is overcome in one process (U.S. Patent 4,019,928), by quenching in an oxidizing quench salt that destroys the cyanide and cyanate compounds (which have pollution capabilities) and produces less distortion than that resulting from water quenching. An alternate method utilized

by U.S. Patent 4,006,643 is the incorporation of lithium carbonate plus minute amounts of sulfur (1 to 10 ppm) in the base salt to hold cyanide formation to below 1.0%.

These low-cyanide processes have been shown in tests to produce the same results as those developed in the previously mentioned liquid nitriding processes. The diffusion curves and case depths are quite similar to those shown in Fig. 1, 2, and 3. Because a high cyanate (65 to 75% KCNO) level in the absence of cyanide would be expected to produce iron nitride compound zones slightly lower in carbon and slightly higher in nitrogen, it is good practice to develop new tests and operational data when converting to one process from another. Excerpts from the AMS 2753 specification developed for low-cyanide liquid salt bath nitriding are shown in Appendix 1 .

Case Hardness. According to AMS 2755C, case hardness varies markedly with the alloy being nitrided. Hardness and other requirements of this specification are summarized in Appendix 2 .

Effects of Steel Composition. Although the properties of alloy steels are improved by the compound and diffusion layers, relatively greater improvement is achieved with plain carbon steels of low and medium carbon content. For example, the improvement in fatigue strength of unnotched test bars of 1015 steel nitrided by this process for 90 min at 565 °C (1050 °F) and water quenched (to further enhance fatigue properties) is roughly 100%. Improvement obtained with similarly treated test bars made of 1060 steel is about 45 to 50%.

The diffusion of nitrogen in carbon steels is directly affected by carbon content, as shown in Fig. 6. The nitride-forming alloying elements also inhibit nitrogen diffusion. For example, the inhibiting effect of chromium on diffusion is shown in Fig. 7, which compares nitrogen in a low-carbon steel (1015) and a chromium-containing low-alloy steel (5115).

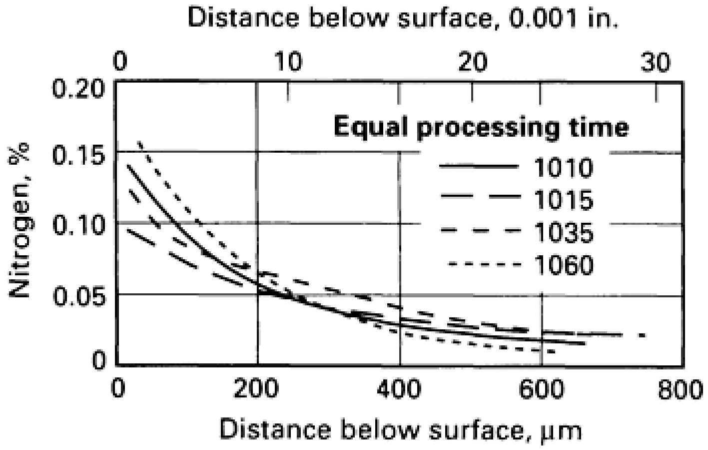


Fig. 6 Effect of carbon content in carbon steels on the nitrogen gradient obtained in aerated bath nitriding

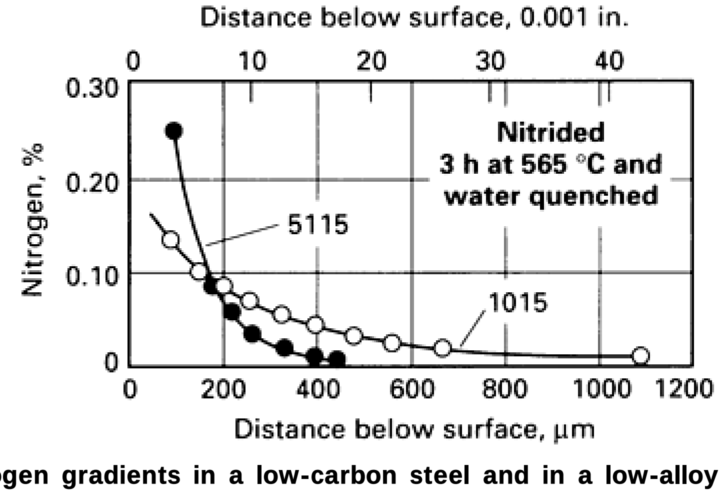


Fig. 7 Comparison of nitrogen gradients in a low-carbon steel and in a low-alloy steel containing chromium, both nitrided by the aerated bath process

Although the visible nitrogen diffusion zone shown by the Fe_4N needles in Fig. 5 can be measured under the microscope to a depth of approximately 0.41 mm (0.016 in.), actual nitrogen penetration can be measured up to 1.02 mm (0.040 in.) as shown in Fig. 8. This nitrogen is in solution, is under stress, and is precipitated as Fe_4N. It is responsible for the fatigue

improvement resulting from liquid nitriding. The improvement is more apparent in plain carbon steels, resulting in the substitution of these steels for high-carbon and low-alloy steels in many applications (Table 3).

Table 3 Improvement in fatigue properties of low-temperature liquid nitrided ferrous materials

Steel type	Property improvement, %
Low-carbon steels	80-100
Medium-carbon steels	60-80
Stainless steels	25-35
Low-carbon, chrome manganese steels	25-35
Chrome alloy, medium-carbon steels	20-30
Cast irons	20-80

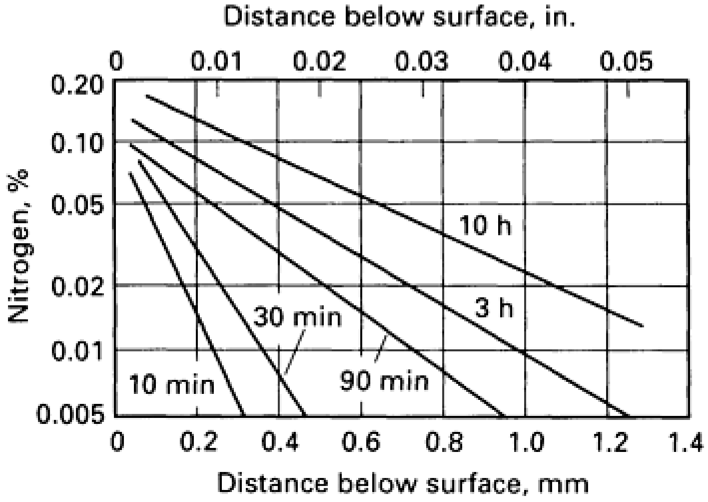


Fig. 8 Nitrogen diffusion in AISI 1015 steel

Case Depth and Case Hardness

Data indicating depth of case obtained in liquid nitriding various steels in a conventional bath at 525 °C (975 °F) for up to 70 h are shown in Fig. 9. The steels include three chromium-containing low-alloy steels (4140, 4340, and 6150), two aluminum-containing nitriding steels (SAE 7140 and AMS 6475), and four tool steels (H11, H12, M50, and D2). All were nitrided in a salt bath with an effective cyanide content of 30 to 35% and a cyanate content of 15 to 20%. Case depths were measured visually on metallographically prepared samples that were etched in 3% nital. Before being nitrided, samples were tempered to the core hardnesses indicated.

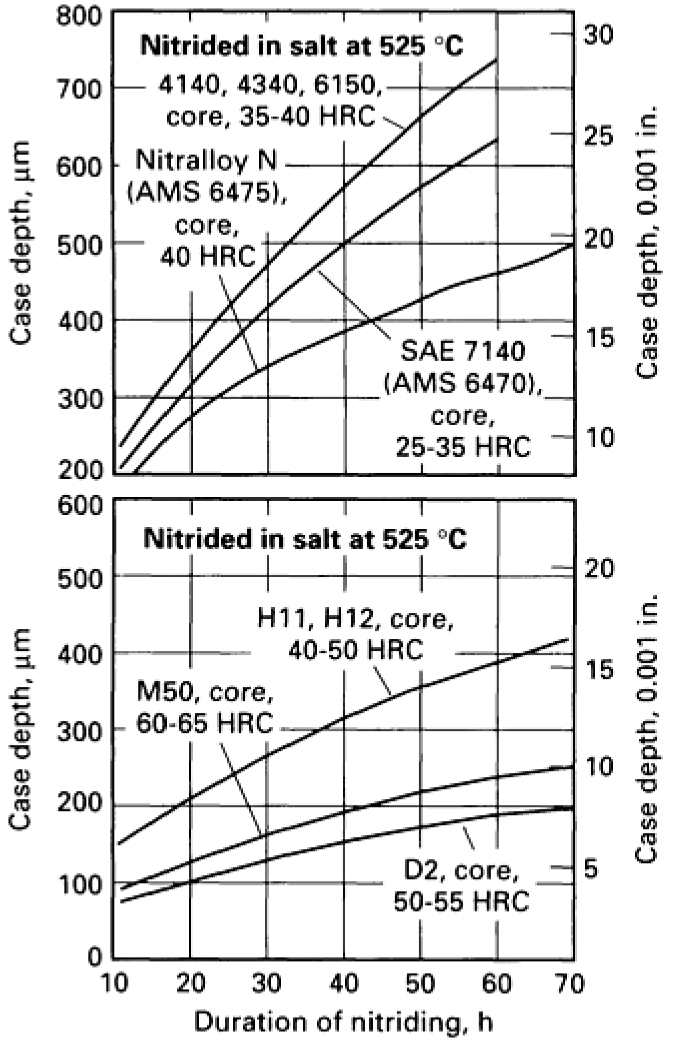


Fig. 9 Depth of case for several chromium-containing low-alloy steels, aluminum-containing steels, and tool steels after liquid nitriding in a conventional salt bath at 525 °C (975 °F) for up to 70 h

Figure 10 presents data on case hardness obtained in liquid pressure nitriding the following alloy steels and tool steels: SAE 7140, AMS 6475, 4140, 4340, medium-carbon H11, low-carbon H11, H15, and M50. The various core hardnesses, nitriding temperatures, and cycle times were as noted in the graphs in Fig. 10. Case depth and hardness results are comparable to those obtained in single-stage gas nitriding.

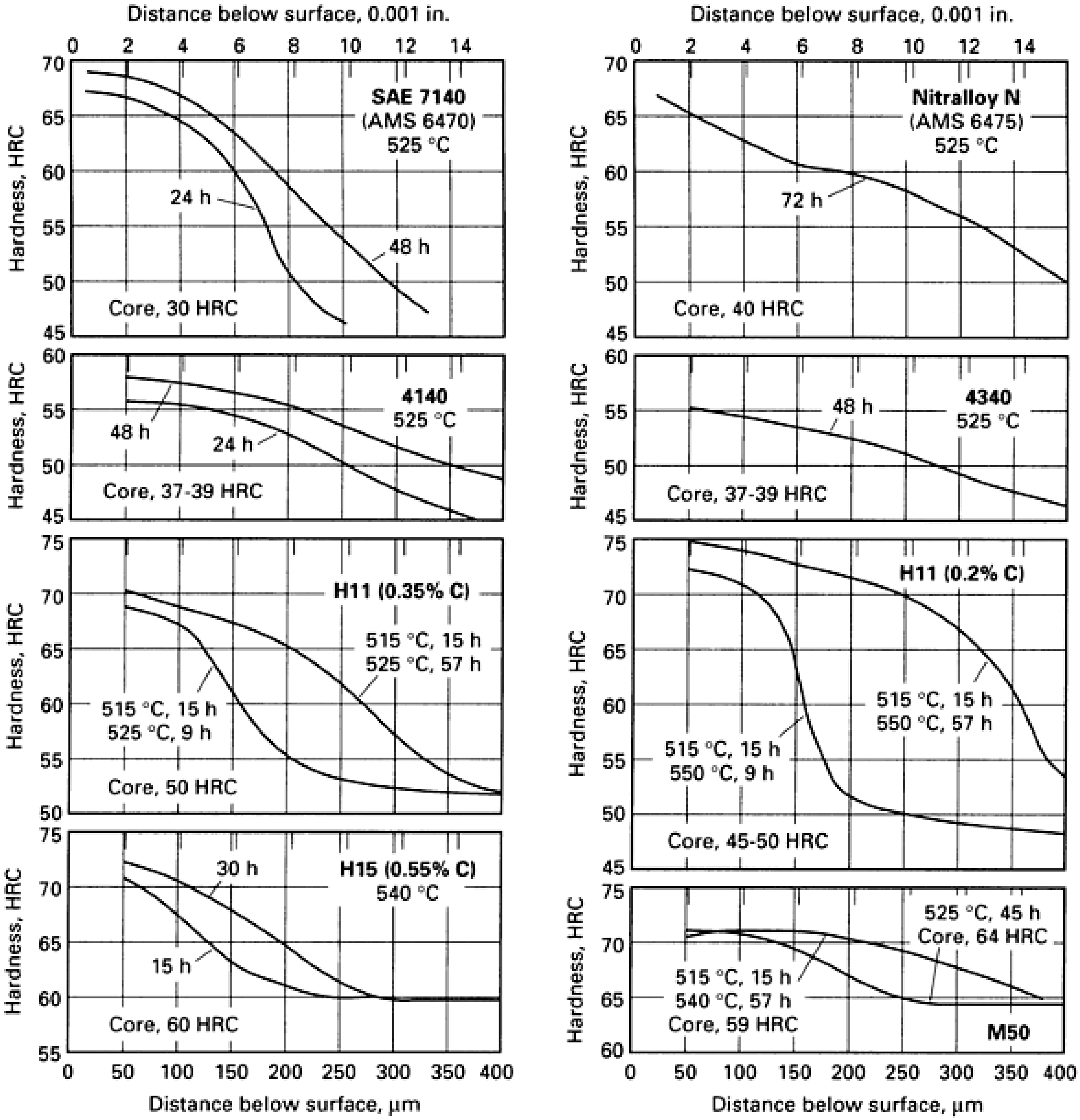


Fig. 10 Hardness gradients for several alloy and tool steels nitrided in salt by the liquid pressure process. Rockwell C hardness values are converted from Knoop hardness measurements made using a 500 g load. Temperatures are nitriding temperatures.

High-Speed Steels. Compared to gas nitriding of high-speed steel cutting tools, liquid nitriding can produce a more ductile case with a lower nitrogen content. Nitrided case hardness data, together with details of liquid nitriding these materials, are given in the Section "Heat Treating of Tool Steels" in this Volume.

Operating Procedures

Among the important operating procedures in liquid nitriding are the initial preparation and heating of the salt bath, aging of the molten salts (when required), and analysis and maintenance of salt bath composition. Virtually all steels must be quenched and tempered for core properties before being nitrided or stress relieved for distortion control. So prior heat treatment may be considered an essential part of the operating procedure.

Prior Heat Treatment. Alloy steels usually are given a prior heat treatment similar to that preferred for gas nitriding (see the article "Gas Nitriding" in this Volume). Maintenance of dimensional and geometric stability during liquid nitriding is enhanced by hardening of parts prior to nitride treatment. Tempering temperatures should be no lower than the nitriding temperature and preferably slightly above.

Depending on steel composition, the effect of core hardness is similar to that encountered in gas nitriding.

Starting the Bath. Case-producing salt compositions may vary with respect to manufacturers, but they are basically sodium and potassium cyanides, or sodium and potassium cyanates. Cyanide, the active ingredient, is oxidized to cyanate by aging as described below. The commercial salt mixture (60 to 70% sodium salts, 30 to 40% potassium salts) is melted at 540 to 595 °C (1000 to 1100 °F). *Caution: During the melting period, a cover should be placed over the retort to guard against spattering or explosion of the salt, unless the equipment is completely hooded and vented. It is mandatory that the salts be dry before they are placed in the retort; the presence of entrapped moisture may result in an eruption when the salt mixture is heated.*

Externally versus Internally Heated Salt Baths. Salt baths may be heated externally or internally. For externally heated salt baths, startup power should be limited to 37% of total capacity until signs of melting are apparent on all sides of the salt bath. For internally heated salt baths, natural gas flame torches having a moderate flame are effective in melting a pool of molten salt for a conductive path between electrodes.

Aging the Bath. Liquid nitriding compositions that do not contain a substantial amount of cyanate in the original melt must be aged before use in production. Aging is defined as the oxidation of the cyanide to cyanate. Aging is not merely a function of temperature alone, but also depends on the surface-to-volume ratio of the molten bath. It is the surface air (oxygen)-to salt contact that oxidizes cyanide to cyanate.

Molten salts in conventional baths should be aged by being held at 565 to 595 °C (1050 to 1100 °F) for at least 12 h, and no work should be placed in the bath during the aging treatment. Aging decreases the cyanide content of the bath and increases the cyanate and carbonate contents. Before nitriding is begun, a careful check of the cyanate content should be made. Nitriding should not be attempted until the cyanate content has reached at least the minimum operating level recommended for the bath.

Bath Maintenance. To protect the bath from contamination and to obtain satisfactory nitriding, all work placed in the bath should be thoroughly cleaned and free of surface oxide. An oxide-free condition is especially important when nitriding in low-cyanide salts. These compounds are not strong reducing agents and therefore are incapable of producing a good surface on any oxidized work. Either acid pickling or abrasive cleaning is recommended prior to nitriding. Finished clean parts should be preheated before being immersed in the bath to rid them of surface moisture.

A high cyanate content (up to about 25%) will provide good results, but carbonate content should not exceed 25%. Carbonate content can be readily lowered by cooling the bath to 455 °C (850 °F) and allowing the precipitated salt to settle to the bottom of the salt pot. It can then be spooned from the bottom by means of a perforated ladle.

To minimize corrosion at the air-salt interface, salts should be completely changed every three or four months (replacement of salt is usually far more economical than replacement of the pot). When the bath is not in use, it should be covered; excessive exposure to air causes a breakdown of cyanide to carbonate and adversely affects pot life.

The ratio of cyanide content to cyanate content varies with the salt bath process and the composition of the bath. The commercial NaCN-KCN bath, after aging for one week, achieves a ratio of 21 to 26% cyanide to 14 to 18% cyanate. The bath used in liquid pressure nitriding operates with a cyanide content of 30 to 35% and a cyanate content of 15 to 20%. The aerated bath is controlled to a ratio of 50 to 60% cyanide to 32 to 38% cyanate. The aerated noncyanide nitriding process is controlled to a ratio of 36 to 38% cyanate to 17 to 19% carbonate.

Oxidation products that promote unfavorable temperature gradients must be periodically removed from all baths. In normal operation, overheating of any bath (above 595 °C, or 1100 °F) should be avoided.

Safety. Some of the compositions employed in liquid nitriding processes contain sodium cyanide or potassium cyanide, or both. These compounds can be handled safely with proper equipment and neutralized by chemical means before discharge. *Caution: The compounds are highly toxic, however, and great care should be exercised to avoid taking them internally or allowing them to be absorbed through skin abrasions. Contact between the compounds and mineral acids also generates another hazard: the formation of hydrogen cyanide (HCN) gas, an extremely toxic product. Exposure to hydrogen cyanide can be fatal.*

Neutralization of Cyanide Waste. The destruction of cyanide by chlorine is believed to proceed in three steps, according to the following equations:

$$NaCN + Cl_2 \rightarrow CNCl + NaCl \quad \textbf{(Eq 1)}$$

$$CNCl + 2NaOH \rightarrow NaCNO + NaCl + H_2O \quad \textbf{(Eq 2)}$$

$$2NaCNO + 4NaOH + 3Cl_2 \rightarrow 6NaCl + 2CO_2 + 2H_2O \quad \textbf{(Eq 3)}$$

The first reaction (Eq 1), oxidation to cyanogen chloride, is almost instantaneous, occurring at all pH levels. The second reaction (Eq 2) is hydrolysis of the cyanogen chloride to cyanate. The rate of hydrolysis is primarily dependent upon the pH, and at a pH of 11 or higher, is virtually completed in minutes. At pH values lower than 10.5 the rate of hydrolysis is slowed considerably, and pHs below this value should be avoided due to the toxicity of the cyanogen chloride.

The third step (Eq 3), oxidation of the cyanate to harmless nitrogen and carbon dioxide, is pH dependent and is accelerated by a decreasing pH. At a pH of 7.5 to 8.0, about 10 to 15 min are required for the reaction to go to completion. At a pH of 9.0 to 9.5, about 30 min are required.

In practice, about 8.0 parts of chlorine and 7.3 parts of sodium hydroxide per part of cyanide are required for the overall reaction. Occasionally, chlorination to cyanate only is sufficient because the cyanate ion is only 1/1000th as toxic as cyanide. About 3.2 parts of chlorine and 3.8 parts of sodium hydroxide per part of CN are required for the oxidation of cyanides to cyanates.

The waste will also contain small amounts of heavy metal cyanides in addition to the sodium or potassium cyanide. These will be broken down and the metal salts precipitated in reactions analogous to those for the sodium cyanide. Some metal complexes react much more slowly with the chlorine as oxidant. Silver cyanide, for instance, may require at least an hour of retention time for complete destruction.

Equipment

Salt bath furnaces used for nitriding may be heated by gas, oil, or electricity, and are essentially similar in design to salt bath furnaces used for other processes. Although batch installations are most common, semi-continuous and continuous operations are feasible. Generally, the same furnace equipment can be used for other heat-treating applications by merely changing the salt. Further details on specific types of furnaces may be found in the article "Liquid Carburizing and Cyaniding" in this Volume.

A variety of materials are used for the pots, electrodes, thermocouple protection tubes, and fixtures employed in salt bath nitriding, depending primarily on the salt mixture and process. For example, low-carbon steel is sometimes used for furnace liners although titanium is recommended for one of the processes (U.S. Patent 3,208,885). Inconel 600 is presently being applied to the noncyanide process described in U.S. Patent 4,019,928. Type 430 stainless steel is recommended for a low-cyanide process described in U.S. Patent 4,006,643. Cast HT alloy is a satisfactory fixture material, and type 446 stainless steel has been used for fixtures and thermocouple protection tubes. One plant reports the successful use of Inconel pots in liquid pressure nitriding; the same plant reports also that electrodeposited nickel performs satisfactorily as a stopoff in the liquid pressure bath. In general, however, nickel-bearing materials are not recommended for nitriding salt baths.

Maintenance Schedules

Certain maintenance procedures should be performed on a daily and weekly basis to ensure optimum operation of the salt bath used for nitriding.

Daily. The following procedures should be done on a daily basis:

- Check temperature-measuring instruments
- Check flowmeters, if these are required for air or anhydrous ammonia
- Check surface condition of work for desired steel-gray color and possible pitting

- Check case depth and case hardness to determine operating condition of the bath

Weekly. The following procedures should be done on a weekly basis:

- Analyze salt bath composition at least once a week; a semiweekly analysis is preferred. Make necessary additions to maintain level
- Check air-salt interface on pot for undercutting. Remove salts and recharge whenever undercutting is observed
- Check bath for nickel content. To remove traces of nickel, a steel plate-out panel should be placed in the bath overnight
- Contamination in the form of $Na_4Fe(CN)_6$ (a complex ferrocyanide that forms in cyanide-type baths) should be removed from the bath by holding the bath at 650 °C (1200 °F) for about 2 h to settle out the compound in the form of sludge

Safety Precautions

The following safety precautions should be observed when operating salt bath furnaces for nitriding steels:

- Operating personnel must be carefully instructed in handling the poisonous cyanide-containing salts
- All chemical containers must be clearly /marked to indicate contents
- Personnel should be provided with facilities for washing their hands thoroughly to prevent contamination by the cyanide salts
- Shields, gloves, aprons, and eye protection should be worn by operating personnel
- Parts and workpiece support fixtures should be preheated to drive off any moisture that may be present before they are immersed in the molten salt bath
- Proper venting of furnace and rinse tanks to the outdoors is recommended in order to provide safety against fumes and spattering and to minimize corrosion in the work area
- *Caution: Nitrate-nitrite salts must not come in contact with nitriding salts in the molten state. Contact will result in an explosion. Storage of these salts should be properly labeled and stored apart*

Liquid Nitrocarburizing

In liquid nitrocarburizing processes, both carbon and nitrogen are absorbed into the surface. High-cyanide nitrocarburizing baths have been in use since the late 1940s. Initially, the sulfur-containing variant was used to produce a wear-resistant surface of iron sulfide (see Process 2). A sulfur-free high-cyanide bath was developed in the mid-1950s, now known as aerated bath nitriding (Process 1). This process and a low-cyanide variant of it (Process 4) are commonly used.

Both Processes 1 and 2 are similar in that components are typically preheated to about 350 to 480 °C (660 to 900 °F), and then transferred to the nitrocarburizing salt bath at 570 °C (1060 °F). The major components of the baths for both processes are normally alkali metal cyanide and cyanate. Salts are predominately potassium, with sodium.

Liquid nitrocarburizing processes are used to improve wear resistance and fatigue properties of low-to-medium carbon steels, cast irons, low-alloy steels, tool steels, and stainless steels. For additional information on nitrocarburizing treatments, see the article "Gaseous and Plasma Nitrocarburizing" in this Volume.

Process 1: High Cyanide without Sulfur. At the treatment temperature of 570 °C (1060 °F), the process is controlled largely by two reactions, an oxidation reaction and a catalytic reaction. The oxidation reaction involves transformation of cyanide to cyanate:

$$4NaCN + 2O_2 \rightarrow 4NaCNO \quad \textbf{(Eq 4)}$$

$$2KCN + O_2 \rightarrow 2KCNO \quad \textbf{(Eq 4a)}$$

Though this reaction can proceed by natural oxidation of the cyanide bath, eventually leading to the desired cyanate content, the mechanism of natural aging does not provide the higher cyanate level made possible with aeration. To provide agitation and stimulate chemical activity, therefore, dry air is introduced into the bath.

The catalytic reaction involves breaking down cyanate in the presence of the steel components being treated, thus supplying carbon and nitrogen to the surface:

$$8NaCNO \rightarrow 2Na_2CO_3 + 4NaCN + CO_2 + (C)_{Fe} + 4(N)_{Fe} \quad \textbf{(Eq 5)}$$

$$8KCNO \rightarrow 2K_2CO_3 + 4KCN + CO_2 + (C)_{Fe} + 4(N)_{Fe} \quad \textbf{(Eq 5a)}$$

As a result of this treatment, a wear-resistant compound zone, rich in nitrogen and carbon, is formed on component surfaces (Fig. 11).

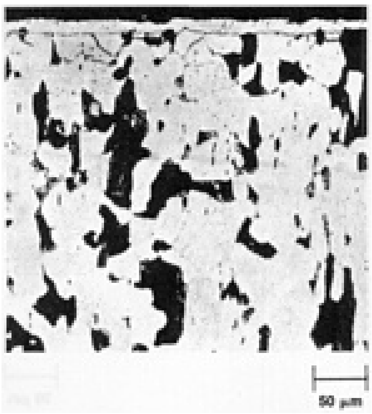


Fig. 11 Metallographic appearance of salt bath nitrocarburized mild steel after 1.5 h at 570 °C (1060 °F) followed by water quenching

Process 2: High Cyanide with Sulfur. The same basic oxidation and catalytic reactions of Process 1 also occur in this process. In addition, further reactions take place because of sulfites in the melt. These sulfites are reduced to sulfides, in conjunction with the oxidation of the cyanide to cyanate, as follows:

$$Na_2SO_3 + 3NaCN \rightarrow Na_2S + 3NaCNO \quad \textbf{(Eq 6)}$$

$$K_2SO_3 + 3KCN \rightarrow K_2S + 3KCNO \quad \textbf{(Eq 6a)}$$

Thus, the sulfur present in the bath acts as an accelerator, with the result that the cyanate is produced more readily than if the sulfur compounds were absent. Consequently, external aeration is not normally used in the process. Potassium and sodium cyanates produced by the reactions in Eq 4 and 6 catalytically decompose at the surface of ferrous materials to liberate carbon monoxide and nascent nitrogen. The carbon monoxide dissociates to liberate active carbon. The carbon, in conjunction with the nascent nitrogen, diffuses into the material being treated to form the compound zone.

The exact mechanism by which sulfur is impregnated into the material is not clear. Various sulfides react with the component being treated to form iron sulfide; this is the black deposit observed on the surface of components after treatment.

The compound layer formed on mild steel after a 90-min treatment, followed by water quenching, is shown in Fig. 12. The compound layer formed by cyanide salt bath nitrocarburizing treatments, and, in particular, by the sulfur-containing

high-cyanide process, contains an outer region of microporosity. These pores, which readily absorb oil, may assist the antiscuffing properties of treated components under lubrication conditions.

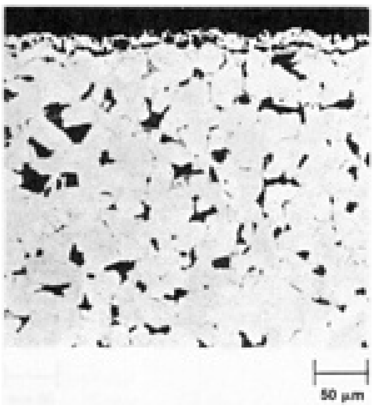


Fig. 12 Metallographic appearance of mild steel after similar treatment to Fig. 11. Iron-sulfide inclusions in the outer region of the compound zone are apparent after this treatment, in which sulfur acts as an accelerator.

Although little systematic investigation has been done to establish the optimum thickness of the compound layer for maximum improvement in wear and antiscuffing properties, it is believed that comparable results are obtained provided the layer is 10 to 20 μm (400 to 800 μin.) thick.

Composition and Structural Analysis of the Compound Layer. X-ray diffraction investigations into the structure of the compound layer formed by the two high-cyanide salt bath nitrocarburizing processes have indicated a variety of carbon and nitrogen-base phases.

One study of cyanide nitrocarburizing treatments indicated that the best antiscuffing properties were obtained when the compound layer consisted mainly of a hexagonal close-packed (hcp) phase of variable carbon and nitrogen concentration. Examination of the appropriate isothermal section of the iron-carbon-nitrogen ternary phase diagram (Fig. 13) indicates that this phase is the ε carbonitride phase. Furthermore, it is believed that provided the ε phase was predominant within the compound layer, small amounts of other phases, particularly Fe_4N and Fe_3C, had no serious adverse effects on antiscuffing behavior. It has been shown that with Process 1, compound layers with less than about 2% C and less than about 6% N contained a mixture of the ε iron carbonitride and Fe_4N. With these processing times in excess of 3 h, the proportion of Fe_4N was found to decrease. Furthermore, when more than 2% C was in the compound layer, a compound with the structure of cementite, $Fe_3(CN)$, could also be detected.

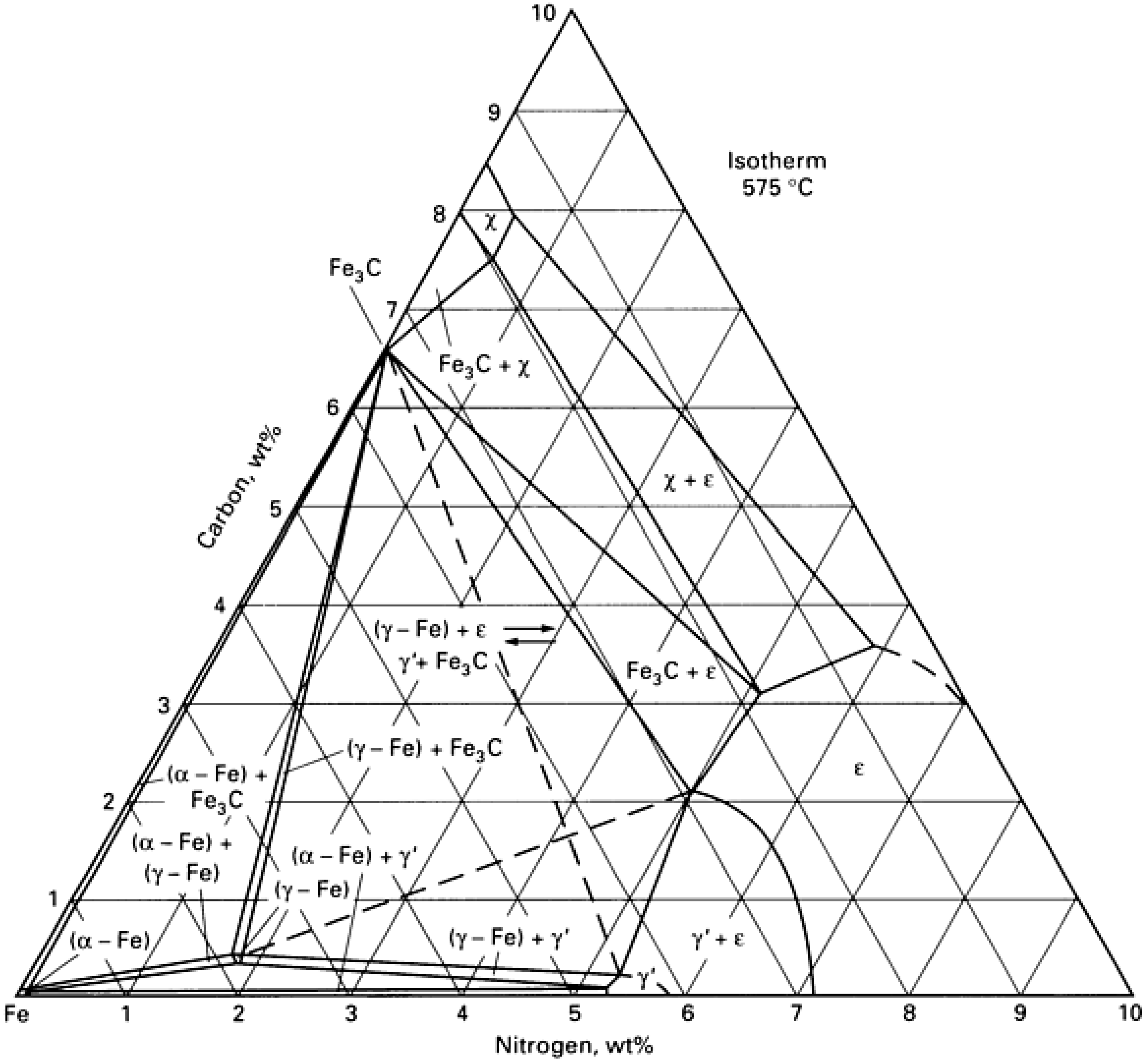


Fig. 13 Phase diagram at 575 °C (1065 °F) of the ternary iron-carbon-nitrogen system

In samples treated by Process 1, a high level of oxygen within the compound layer has been reported. But whether the presence of oxygen, which is known to accelerate the formation of the compound layer by promoting the cyanide-to-cyanate oxidation reaction, is essential for improved frictional properties has not been rigorously established.

Similarly, the question arises as to whether sulfur, present in Process 2, contributes significantly to enhanced antiscuffing properties. The predominant presence of an ε carbonitride phase is required for enhanced antiscuffing properties. Electron probe microanalysis of the compound layers formed by the two processes are presented in Fig. 14.

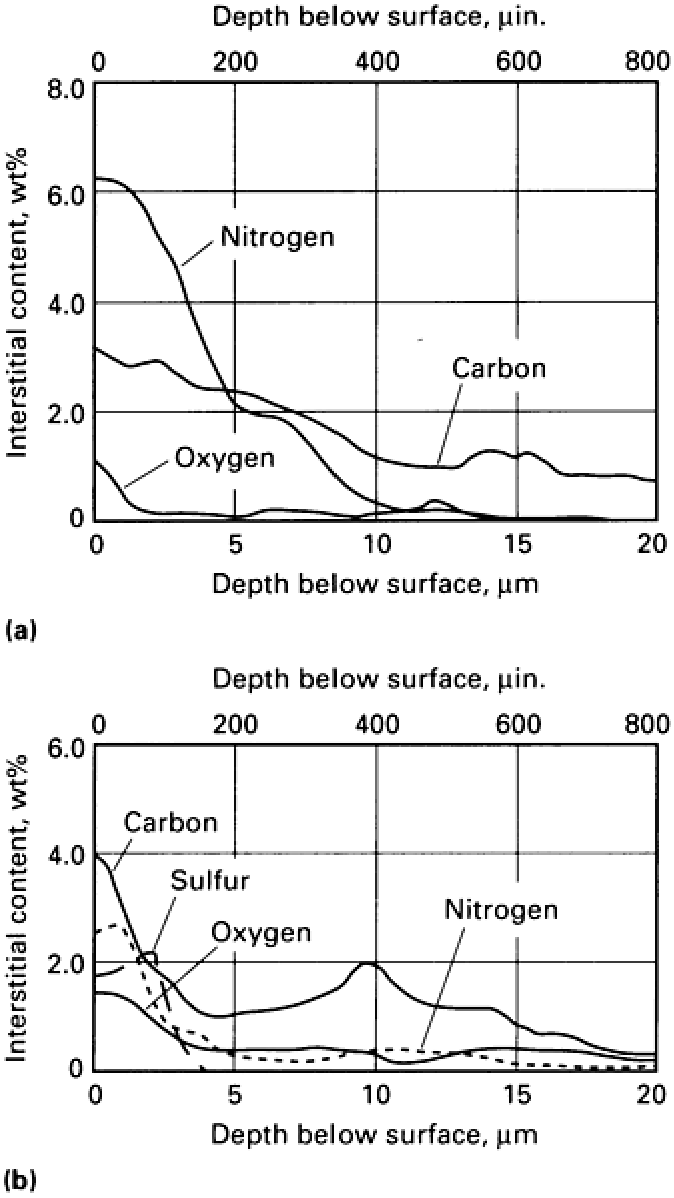


Fig. 14 Electron microprobe traces of compound layers. (a) Nitrogen, carbon, and oxygen in the compound layer formed by Process 1. (b) Nitrogen, carbon, oxygen, and sulfur in the compound layer formed by Process 2. Both treatments, 90 min

Nontoxic Salt Bath Nitrocarburizing Treatments

Environmental considerations and the increased cost of detoxification of cyanide-containing effluents have led to development of low-cyanide salt bath nitrocarburizing treatments.

Cyanates are the active nitriding constituent of both high-cyanide and low-cyanide nitrocarburizing baths. Reduction of the cyanide content permits markedly higher cyanate concentrations in the low-cyanide baths; this results in greatly increased nitriding activity. Unlike the reducing high-cyanide baths, the nominal cyanate and carbonate composition of the low-cyanide baths is oxidizing. The baths are composed of primarily potassium salts with some sodium salts. During nitriding, cyanates yield nitrogen to the steel and form carbonates. Cyanate concentration is maintained by the use of organic regenerators, which supply nitrogen to reform cyanates from carbonates.

Process 3: Low Cyanide with Sulfur. This patented process confers sulfur, nitrogen, and presumably, carbon and oxygen to surfaces of ferrous materials. The process is unique in that lithium salts are incorporated in the bath composition. Cyanide is held to very low levels: 0.1 to 0.5%. Sulfur species, present in the bath at concentrations of 2 to 10 ppm, cause sulfidation to occur simultaneously with nitriding. Sulfur levels near 10 ppm result in an apparently porous compound zone (Fig. 15); the dark areas are actually iron sulfide nodules, not voids. This compound zone is similar to the high-cyanide, sulfur-containing nitrocarburizing process that has, however, columnar iron-sulfide inclusions.

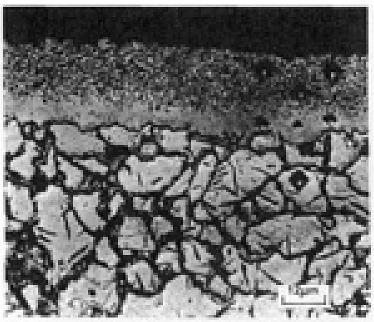


Fig. 15 Sample of plain carbon steel after low-cyanide salt bath nitrocarburizing treatment (Process 3). The high level of apparent porosity is a characteristic of high sulfur content in the compound zone; dark areas are actually iron-sulfide nodules, not voids.

Bath composition can be adjusted to lower sulfur levels (2 ppm) to form a less porous layer with a lower iron sulfide content.

A compound layer 20 to 25 μm (800 to 1000 μin.) thick forms in 90 min at 570 °C (1060 °F) on AISI 1010 steel, compared with the 8 to 10 μm (320 to 800 μin.) layer formed by the high-cyanide sulfur-bearing nitrocarburizing process in the same time. Figure 16 shows the thickness of the compound layer as a function of the treatment time for the nontoxic and cyanide-based treatments.

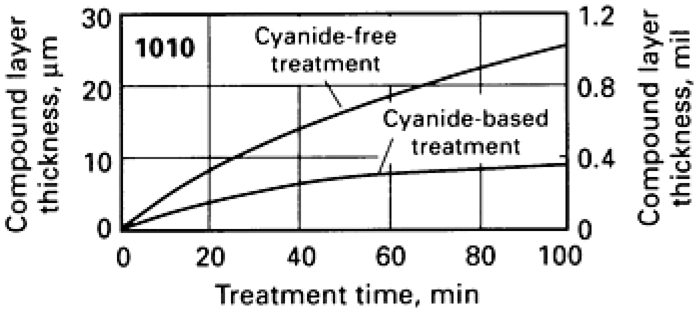


Fig. 16 Comparison of compound zone thickness produced by low-cyanide and cyanide-based treatments containing sulfur

Process 4: Low Cyanide without Sulfur. A low-cyanide alternative to the cyanide-based Process 1 has been developed. This process, like Process 3, is a cyanate bath with no lithium or sulfur compounds and very low cyanide levels (2 to 3%). Melon, an organic polymer, is used for bath regeneration.

When water quenching is employed, the low level of cyanide permits easier detoxification. Alternatively, quenching into a caustic-nitrate salt bath at 260 to 425 °C (500 to 795 °F) may be used for cyanide/cyanate destruction.

Processing temperature for Process 4 is 570 to 580 °C (1060 to 1080 °F); the rate of compound zone formation is comparable to that of Process 3. Metallurgical results are virtually identical with the cyanide-based Process 1.

Wear and Antiscuffing Characteristics of the Compound Zone Produced in Salt Baths

The resistance to scuffing after salt bath nitrocarburizing treatments has been frequently tested with a Falex lubricant testing machine (Fig. 17, 18, 19). A 32 by 6.4 mm (1.25 by 0.25 in.) test piece is attached to the main drive shaft by means of a shear pin, and two anvils or jaws having a 90° V-notch fit into holes in the lever arms. During testing, the jaws are clamped around the test piece, which rotates at 290 rpm, and the load exerted by the jaws is gradually increased. Both test pieces and jaws can be immersed totally in a small tank containing lubricant or other fluid, or tests can be carried out dry.

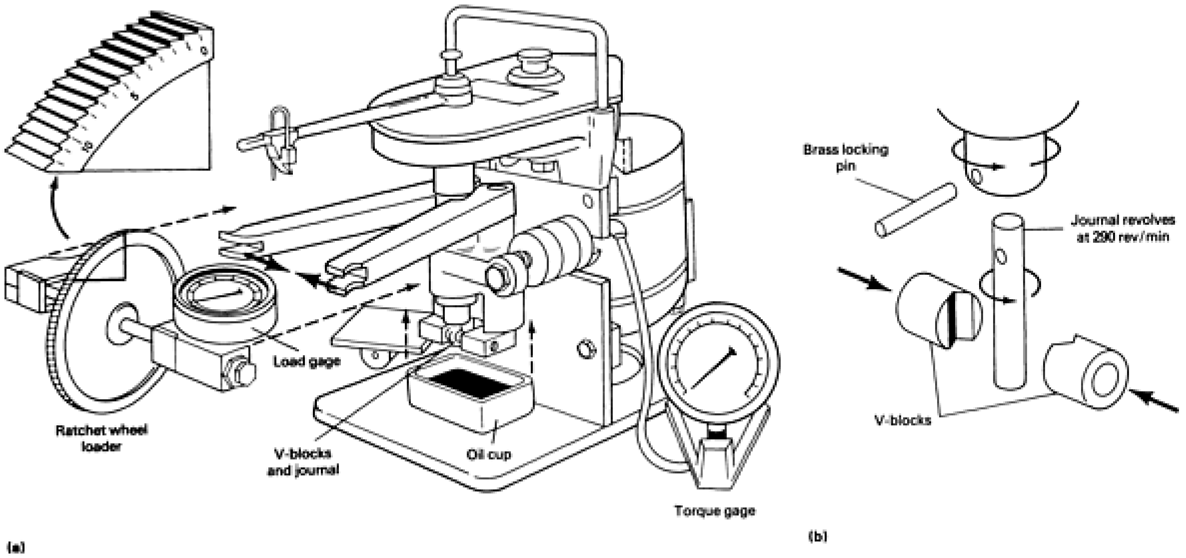


Fig. 17 Lubricant tester used to measure endurance (wear) life and load-carrying capacity of either dry solid-film lubricants or wet lubricants in sliding steel-on-steel applications. (a) Key components of instrument. (b) Exploded view showing arrangement of V-blocks and rotating journal

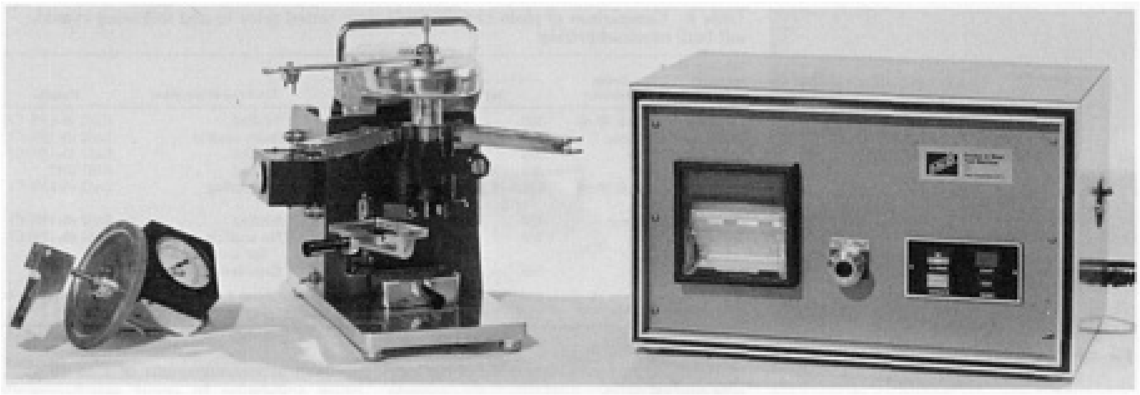


Fig. 18 State-of-the-art lubricant-testing machine incorporating a recorder to monitor the torque data used to determine wear life of the sample journal. The instrument provides both an instantaneous readout of the torque via a digital display and a continuous permanent record of torque values during the test on a strip chart. Workpiece failure is indicated by a torque rise of 1.1 N · m (10 lbf · in.) above the steady-state value or breakage of the shear pin, whichever failure criteria is reached first (per ASTM D 2625-83). Courtesy of Falex Corporation

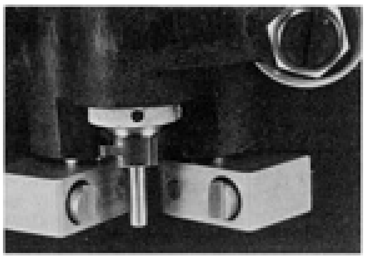


Fig. 19 Close-up view of a journal and V-block setup ready for testing in a lubricant-testing machine. Wear is indicated by a reduction or distortion in the diameter of the journal as well as deformation of the notch in the V-block. Courtesy of Falex Corporation

Table 4 lists results of a few representative Falex tests for plain low-carbon steels both before and after cyanide salt bath nitrocarburizing treatments. The untreated low-carbon steel specimens do not show any significant scuffing resistance even when tested under oil-lubricated conditions. After treatment, however, even when tested dry, there is a considerable improvement in antiscuffing properties. Specimens tested in the dry condition after salt bath nitrocarburizing generate so much heat that they eventually become red hot and are extruded under the applied load. Untreated test pieces seize at relatively low loads before becoming red hot, whereas treated samples, even after extrusion, show no signs of scuffing.

During testing in oil, the specimens become highly polished. Similar Falex test results are reported for low-cyanide salt bath nitrocarburizing treatments.

Table 4 Comparison of plain carbon steels wear tested prior to and following cyanide salt bath nitrocarburizing

Condition of test pieces and jaws	Testing medium[(a)]	Applied load		Condition of test pieces	Material
		kgf	lbf		
Untreated	SAE 30 oil	320	700	Scuffed	En32 (0-15% C)
Untreated	Water	270	600	Badly scuffed	En32 (0-15% C)
Untreated	Air	320	700	Scuffed	En32 (0-15% C)
Untreated	Air	205	450	Scuffed	AISI 1045
Treated[(b)]	SAE 30 oil	Limit of gage, 1150	Limit of gage, 2500	No scuffing	En32 (0-15% C)
Treated[(b)]	Water	450	1000	Scuffed	En32 (0-15% C)
Treated[(b)]	Air	760	1675	No scuffing, became hot and extruded	En32 (0-15% C)
Treated[(c)]	Air	660	1450	Extruded	AISI 1045

(a) Falex scuffing tests at 290 rpm in EN8 (0.4% C) jaws, 90 min running time.

(b) Treatment 2, cyanide nitrocarburizing salt bath, with sulfur present as an accelerator.

(c) Treatment 1, cyanide nitrocarburizing salt bath

Appendix 1**: Liquid Salt Bath Nitriding Noncyanide Baths

Hardening. Parts requiring core hardness shall be heat treated to the required core hardness before processing. Tempering to produce the specified core hardness shall be at a temperature not lower than 590 °C (1090 °F), except when tempering is conducted in conjunction with nitriding.

Stress Relief. Parts in which residual stresses may cause cracking or excessive distortion due to thermal shock or dimensional change because of metallurgical transformations during nitriding shall be stress relieved prior to final machining. Stress relieving shall be performed at a temperature not lower than 590 °C (1090 °F).

Cleaning. Parts, at the time of nitriding, shall be clean and free of scale or oxide, entrapped sand, core material, metal particles, oil, and grease, and shall be completely dry.

Preheating. Parts shall be preheated in air at 260 to 345 °C (500 to 650 °F) to maintain bath temperature and to avoid thermal shock upon immersion in the nitriding salt.

Nitriding. Parts shall be immersed in an aerated cyanate bath as indicated in Table 5.

Table 5 Recommended procedures for liquid salt bath nitriding in noncyanide baths

Material	Recommended time, h		Temperature	
	min	max	°C	°F
Carbon and low-alloy steels	1	2	580 ± 5	1075 ± 10
Tool and die steels (structural)	$\frac{1}{2}$	3	540-580	1000-1075
Tool steels (cutting)	$\frac{1}{12}$	1	540-580	1000-1075
Corrosion- and heat-resistant steels	1	2	580 ± 5	1075 ± 10
Ductile, malleable, and gray cast iron	1	4	580 ± 5	1075 ± 10

Quenching. Following treatment, parts shall be quenched in fused salts, water, oil, soluble oil solution, or air. Parts, except those made of air-hardening tool steels, may be cooled to 290 to 400 °C (550 to 750 °F) prior to actual quenching, when permitted by the purchaser.

Depth of compound layer shall be determined in accordance with SAE J423, microscopic method, at magnification of 500×, as indicated in Table 6.

Table 6 Depth of compound layer after liquid salt bath nitriding in a noncyanide bath

Material	Case depth[a]	
	mm	in.
Carbon and low-alloy steels	0.0038-0.02	0.00015-0.001
Tool and die steels (structural)	0.003-0.012	0.0001-0.0005
Tool and die steels (cutting)	. . . 0.003	. . . 0.0001
Corrosion- and heat-resistant steels	0.0038-0.02	0.00015-0.001
Ductile, malleable, and gray cast iron	0.0038-0.02	0.00015-0.001

(a) Ranges show minimum and maximum case depth.

Quality of Compound Layer. Any continuous surface porosity present shall not extend deeper than one-half the observed depth of the compound layer, determined by examining specimens metallographically at 500× magnification.

Hardness of compound layer shall be determined by microhardness measurements in accordance with ASTM E 384 on the nitrided surface or on metallographically prepared cross sections of the nitrided case using Knoop or another appropriate hardness tester, as agreed upon by purchaser and vendor (see Table 7).

Table 7 Hardness of the compound layer obtained after liquid salt bath nitriding in a noncyanide bath

Material	Hardness, min (HK at 100 gf load)
Carbon steels	300
Low-alloy steels	450
Tool and die steels	700
Corrosion- and heat-resistant steels	900
Ductile, malleable, and gray cast iron	600
Powder metal products (ferrous)	600

Note cited in this section

** Adapted from AMS 2753A (Jan 1985)

Appendix 2† : Liquid Salt Bath Nitriding

Nitriding salts shall consist of a mixture of sodium and potassium cyanide and other salts.

Salt Bath. The cyanate, cyanide, and iron contents of the bath shall be controlled within percentages by weight:

Content	Concentration, %	
	min	max
Cyanate determined as KNCO	42	50
Cyanide determined as KCN	45	50

Nitriding. Parts shall be immersed in an aerated cyanide-cyanate bath as indicated in Table 8.

Table 8 Recommended procedures for liquid salt bath nitriding in cyanide-cyanate baths

Material	Recommended time, h		Temperature	
	min	max	°C	°F
Carbon and low-alloy steels	1	2	570 ± 5	1060 ± 10

Tool and die steels (structural)	$\frac{1}{2}$	3	540-570	1000-1060
Tool steels (cutting)	$\frac{1}{12}$	1	540-570	1000-1060
Corrosion- and heat-resistant steels	1	2	570 ± 5	1060 ± 10
Ductile, malleable, and gray cast iron	2	4	570 ± 5	1060 ± 10
Powder metal products (ferrous)	$\frac{1}{2}$	2	570 ± 5	1060 ± 10

Quenching. Following treatment, the parts shall be quenched in water, oil, soluble oil solution, or air. Parts, except those made of air-hardening tool steels, may be cooled to 290 to 400 °C (550 to 750 °F) prior to actual quenching, when permitted by the purchaser.

Depth of case shall be determined in accordance with SAE J423 (microscopic method) at 500× magnification as indicated in Table 9.

Table 9 Depth of case measurements obtained following liquid salt bath nitriding in cyanide-cyanate baths

Material	Case depth	
	mm	in.
Plain carbon and low-alloy steels	0.004-0.03	0.00015-0.001
Tool and die steels (structural)	0.003-0.0	0.0001-0.0005
Tool and die steels (cutting)	. . . 0.003	. . . 0.0001
Corrosion- and heat-resistant steels	0.004-0.03	0.00015-0.001
Ductile, malleable, and gray cast iron	0.004-0.03	0.00015-0.001
Powder metal products (ferrous)	0.004-0.03	0.00015-0.001

Case Quality. Any surface porosity present shall not extend deeper than one-half the observed depth of the compound layer, determined by examining specimens metallographically at 500× magnification.

Case hardness shall be determined by microhardness measurements in accordance with ASTM E 384 on the nitrided surface or on metallographically prepared cross sections of the nitrided case using Vickers, Knoop, or another appropriate hardness tester, as agreed upon by purchaser and vendor (see Table 10).

Table 10 Hardness of the compound layer obtained after liquid salt bath nitriding in a cyanide-cyanate bath

Material	Hardness, min (HK at 200 gf load)
Plain carbon steels	300
Low-alloy steels	450
Tool and die steels	700
Corrosion- and heat-resistant steels	900
Ductile, malleable, and gray cast iron	600
Powder metal products (ferrous)	600

Note cited in this section

† Adapted from AMS 2755C (April 1985). Process also referred to as the "Tufftride" process

Plasma (Ion) Nitriding of Steels

James M. O'Brien, O'Brien & Associates; Dan Goodman, Surface Combustion, Inc.

Introduction

PLASMA, OR ION, NITRIDING, is a method of surface hardening using glow discharge technology to introduce nascent (elemental) nitrogen to the surface of a metal part for subsequent diffusion into the material. In a vacuum, high-voltage electrical energy is used to form a plasma, through which nitrogen ions are accelerated to impinge on the workpiece. This ion bombardment heats the workpiece, cleans the surface, and provides active nitrogen. Ion nitriding provides better control of case chemistry and uniformity and has other advantages, such as lower part distortion than conventional (gas) nitriding. A key difference between gas and ion nitriding is the mechanism used to generate nascent nitrogen at the surface of the work.

Case Structures and Formation

The case structure of a nitrided steel, which may include a diffusion zone with or without a compound zone (Fig. 1), depends on the type and concentration of alloying elements and the time-temperature exposure of a particular nitriding treatment. Moreover, because the formation of a compound zone and/or a diffusion zone depends on the concentration of nitrogen, the mechanism used to generate nascent nitrogen at the surface of the workpiece also affects the case structure. These factors are discussed below, with emphasis on the differences between gas and plasma nitriding.

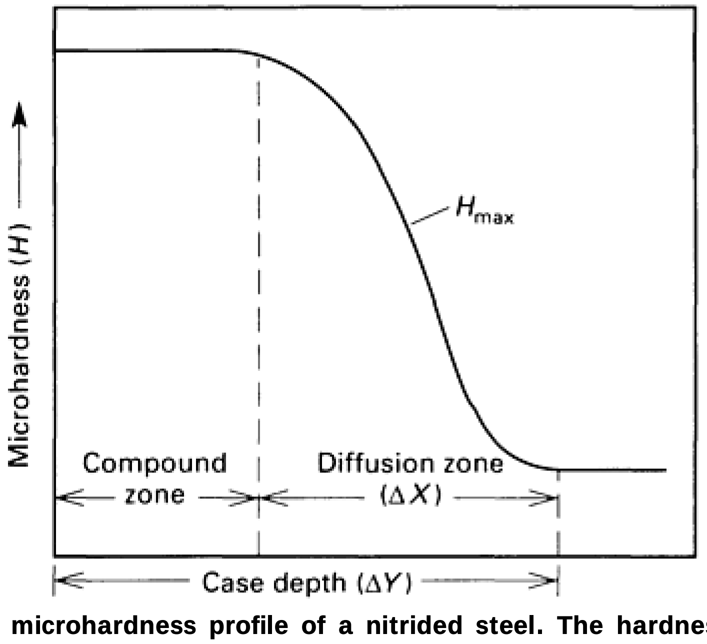


Fig. 1 Factors affecting the microhardness profile of a nitrided steel. The hardness of the compound zone is unaffected by alloy content, while the hardness of the diffusion zone is determined by nitride-forming elements (Al, Cr, Mo, Ti, V, Mn). ΔX is influenced by the type and concentration of alloying elements; ΔY increases with temperature and decreases with alloy concentration.

Diffusion Zone of a Nitrided Case. The diffusion zone of a nitrided case can best be described as the original core microstructure with some solid solution and precipitation strengthening. In iron-base materials, the nitrogen exists as single atoms in solid solution at lattice sites or interstitial positions until the limit of nitrogen solubility (; 0.4 wt% N) in iron is exceeded. This area of solid-solution strengthening is only slightly harder than the core. The depth of the diffusion zone depends on the nitrogen concentration gradient, time at a given temperature, and the chemistry of the workpiece.

As the nitrogen concentration increases toward the surface, very fine, coherent precipitates are formed when the solubility limit of nitrogen is exceeded. The precipitates can exist both in the grain boundaries and within the lattice structure of the

grains themselves. These precipitates, nitrides of iron or other metals, distort the lattice and pin crystal dislocations and thereby substantially increase the hardness of the material.

In most ferrous alloys, the diffusion zone formed by nitriding cannot be seen in a metallograph because the coherent precipitates are generally not large enough to resolve. In Fig. 2, for example, martensite in the diffusion zone cannot be visually distinguished from that in the core. In some materials, however, the nitride precipitate is so extensive that it can be seen in an etched cross section. Such is the case with stainless steel (Fig. 3), in which the chromium level is high enough for extensive nitride formation.

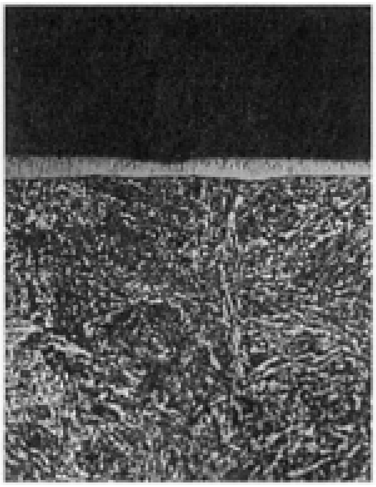


Fig. 2 Compound layer of γ' (Fe_4N) on the ion-nitrided surface of quenched and tempered 4140 steel. The γ' compound layer is supported by a diffused case, which is not observable in this micrograph. Nital etched. 500×

Fig. 3 Observable diffusion zone on the unetched (white) portion of an ion-nitrided 416 stainless steel. Nital etched. 500×

Compound Layers in Nitrided Steels. The compound zone is the region where the γ' (Fe_4N) and ε($Fe_{2-3}N$) intermetallics are formed. Because carbon in the material aids ε formation, methane is added to the process gas when an ε layer is desired. Hydrogen also tends to catalyze Fe_2N formation. These compound layers are called white layers because they appear white on a polished, etched cross section.

Structure of Gas-Nitrided Steel Case. Gas nitriding with ammonia produces a compound zone that is a mixture of the γ' and ε compounds; the mixture is due to the variability of ammonia dissociation, and therefore of nitriding potential, as the compound layer is formed. In conventional gas nitriding, the nascent nitrogen is produced by introducing ammonia (NH_3) to a work surface that is heated to at least 480 °C (900 °F). Under these conditions, the ammonia, catalyzed by the metal surface, dissociates to release nascent nitrogen into the work and hydrogen gas into the atmosphere of the furnace. The nitriding potential, which determines the rate of introduction of nitrogen to the surface, is determined by the NH_3 concentration at the work surface and its rate of dissociation. This nitriding potential, which can vary significantly in the gas process, is responsible for the limited control of microstructure in the nitrided case.

X-ray diffraction has shown that from the outer surface to the beginning of the diffusion zone the dominant compound changes from ε to γ'. However, both phases exist throughout the entire white layer, which is referred to as a dual-phase layer.

The dual-phase layer has two characteristics that make it susceptible to fracture:

- Weak bonding at the interface between phases
- Different thermal-expansion coefficients in the two phases

Layers that are particularly thick or that are subjected to temperature fluctuation in service are particularly prone to failure.

Another mechanical weakness in the gas-nitrided white layer is porosity in the outer region of the layer. As the compound zone builds, ammonia dissociation becomes more sluggish without the catalytic action of the steel surface, and gas bubbles begin to form in the layer.

Structure of Ion-Nitrided Steel Case. In the ion-nitriding process, nitrogen gas (N_2) can be used instead of ammonia because the gas is dissociated to form nascent nitrogen under the influence of the glow discharge. Therefore the nitriding potential can be precisely controlled by the regulation of the N_2 content in the process gas. This control allows precise determination of the composition of the entire nitrided case, selection of a monophase layer of either ε or γ', or total prevention of white-layer formation (Fig. 4)

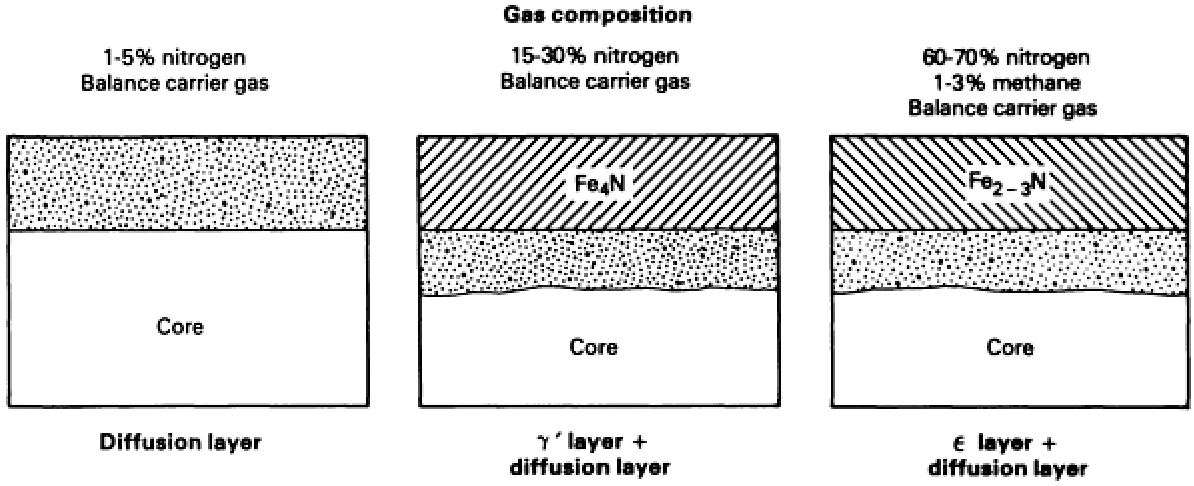


Fig. 4 Typical gas compositions and the resulting metallurgical configurations of ion-nitrided steel

General Process Description

An ion-nitriding system is shown in Fig. 5. The parts to be nitrided are cleaned, usually by vapor degreasing, loaded into the vacuum vessel, and secured. The subsequent process of plasma nitriding can be broken down into four steps: vessel evacuation, heating to nitriding temperature, glow-discharge processing at nitriding temperatures, and cooling.

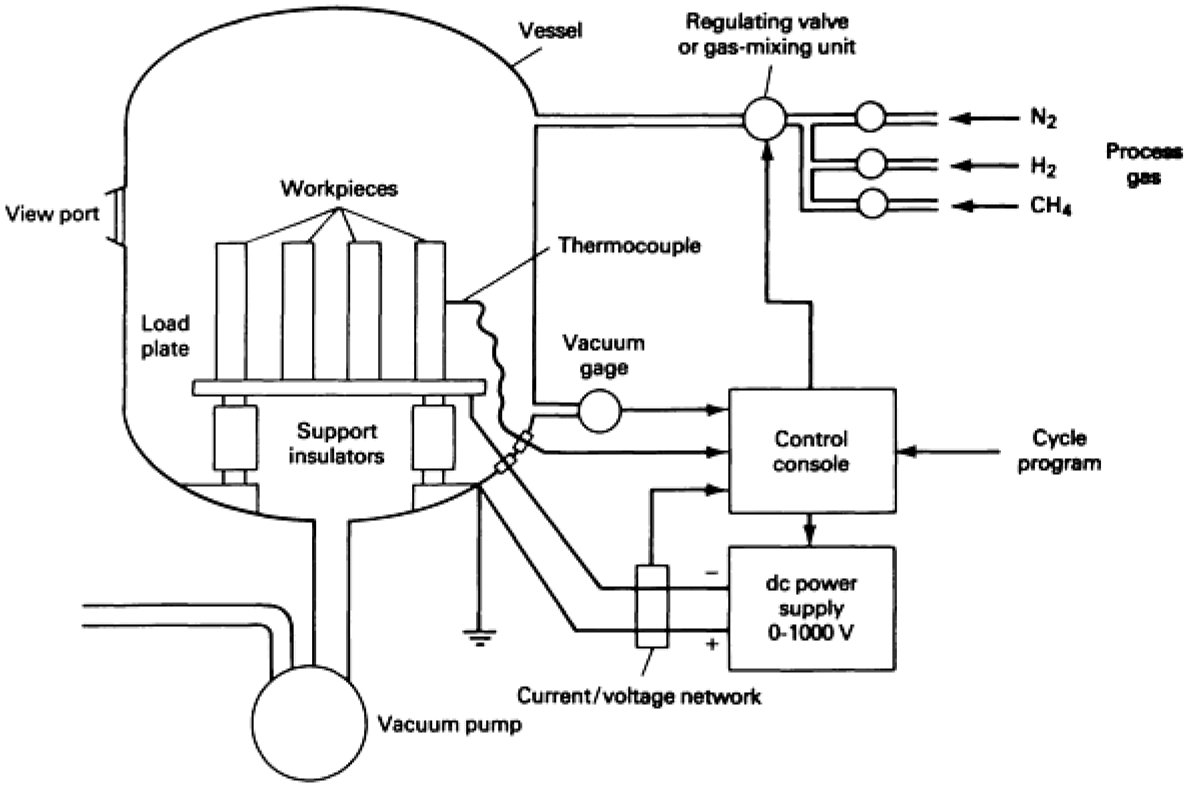


Fig. 5 Typical ion-nitriding vessel

Vessel evacuation is performed by a roughing pump or roughing pump-blower combination so that pressure is reduced to a level of 0.05 to 0.1 torr (mm of mercury). This is necessary to remove most of the initial air and any contaminants. Harder vacuum levels can be achieved but are not necessary for most materials.

The method of heating the load to nitriding temperature has evolved over the years. In the past, loads were heated only by the glow discharge itself. This method presented some difficulty because moisture and other impurities on the work surface tended to cause arcing to the parts in the early stages of the heating cycle. The methods applied to extinguish or prevent arcs also tended to lengthen the heating cycle significantly.

Today, resistance heaters or cathode shields are normally used to bring the load to nitriding temperatures (375 to 650 °C, or 700 to 1200 °F) before glow discharge. Heating of the load can be with glow discharge only, using a cathode preheating shield arrangement up to an intermediate temperature, and then switching to glow discharge on the parts using resistance heating elements or convection. The most common approach is with resistance heating. While heating, the pressure is increased so that the glow seam does not get too thick and cause localized overheating.

Glow-Discharge Process. After the work load is heated to desired temperature, process gas is admitted at a flow rate determined by the load surface area. Pressure is regulated in the 1 to 10 torr range by a control valve just upstream from the vacuum pump. The process gas is normally a mixture of nitrogen, hydrogen, and, at times, small amounts of methane.

In the presence of this process gas, the load is maintained at a high negative dc potential (500 to 1000 V) with respect to the vessel, which is grounded. Under the influence of this voltage, the nitrogen gas is dissociated, ionized, and accelerated toward the workpiece (the cathode). Within a short distance of the workpiece, the positively charged nitrogen ion then acquires an electron from the cathode (workpiece) and thus emits a photon. This photon emission during the return of nitrogen ions to their atomic state results in the visible glow discharge that is characteristic of plasma techniques. Upon impact with the workpiece, the kinetic energy of the nitrogen atoms is also converted into heat, which can totally (or in combination with an auxiliary heating source) bring the load to nitriding temperature.

The glow discharge surrounding negatively charged workpieces forms at voltages of 200 to 1000 V (Fig. 6) with gas pressures of 1 to 10 torr. The thickness of the glow envelope (or glow seam) can be altered by pressure, temperature, gas mix composition, dc voltage, and current. Typically a large or thick glow envelope is created with higher temperature, lower pressure, high hydrogen concentration in the gas mix, and higher dc voltage and current. A desirable glow-discharge thickness is about 6 mm (0.25 in.), unless parts with holes or slots require a thinner glow envelope.

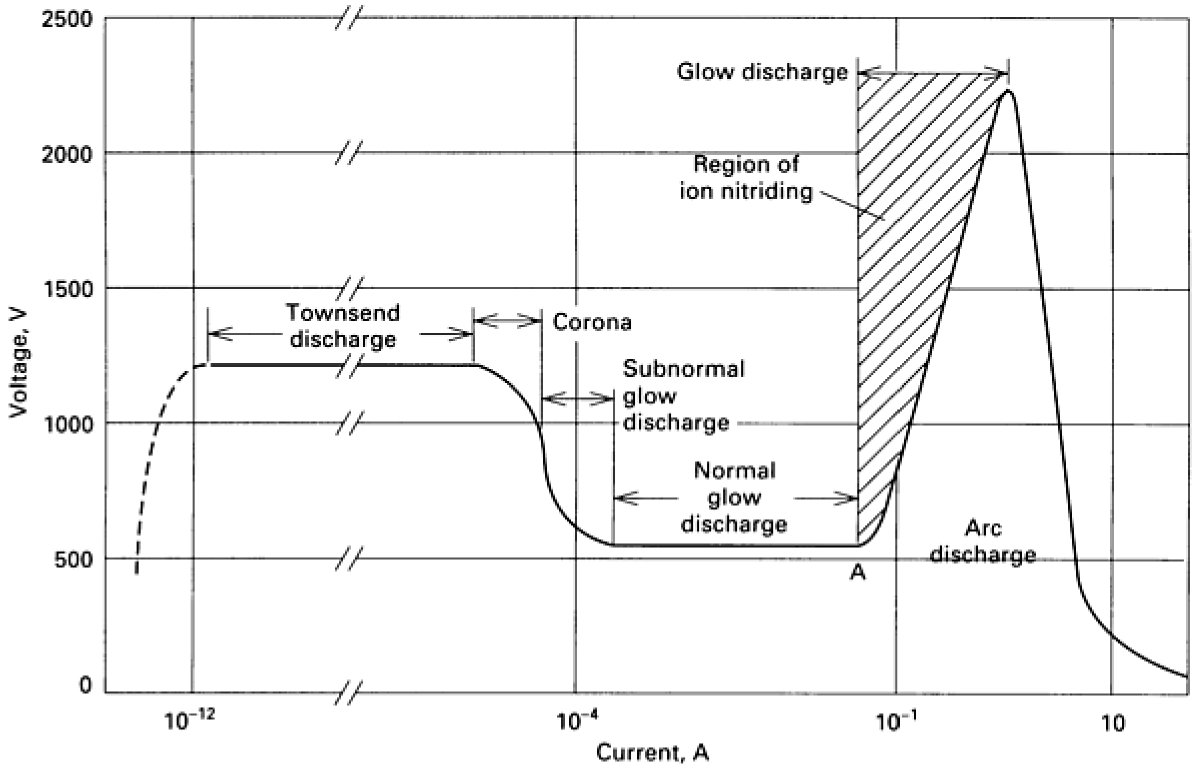


Fig. 6 Voltage versus current characteristics of different types of discharge in argon

During the glow-discharge process, different alloy or iron atoms combine with the nitrogen as it diffuses into the material, forming a hardened surface and case. Figure 7 shows these mechanisms for iron. The nitriding current (proportional to the nitrogen ion flux), temperature, and process time determine the depth of the nitride case achieved. A uniform glow-discharge envelope is also necessary for proper case uniformity, especially when part geometry is complex (as with a gear or fuel injector).

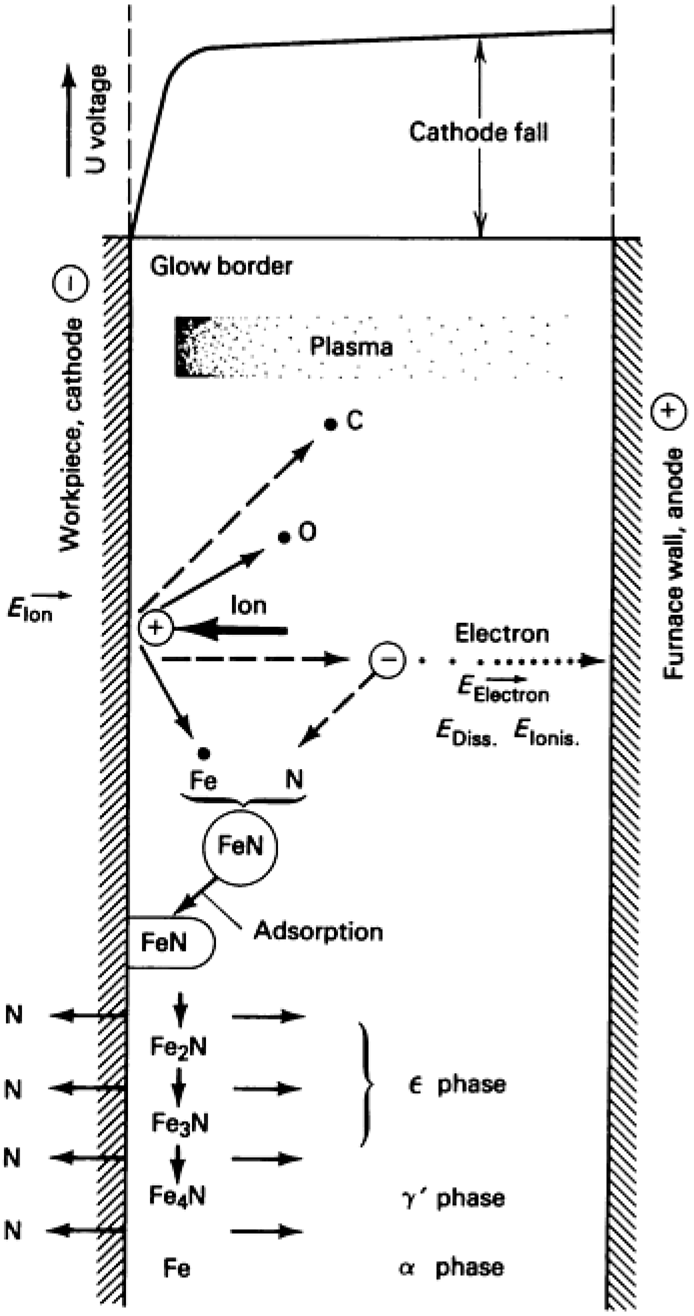


Fig. 7 Glow-discharge ion-nitriding mechanisms (Koelbel's model)

Cooling. After the glow-discharge process, the voltage and process gas flow are terminated, and the load is cooled by inert-gas circulation. Cooling is accomplished by backfill ing with nitrogen or other inert gases and recirculating the gas from the load to a cold surface such as the cold wall. From that point, the heat can be transferred and removed via the water in the cooling jacket.

Equipment

A basic ion-nitriding system (Fig. 5) consists of a vacuum chamber, a power supply, and a process gas system with a gas-mixing panel or other mass flow controls. An isolated hearth or work support fixturing is also required to ensure electrical isolation between the workpiece and vacuum vessel. An auxiliary heating system and a rapid cooling system can also be included to improve cycle time.

Ion-nitriding control systems may vary in complexity. Microprocessor systems are generally used to control or monitor several parameters. These include the work temperature, vessel wall temperature, vacuum (absolute pressure) level, glow-discharge voltage and current, auxiliary heating source voltage and current, and gas mix composition. The microprocessor will also control the various inputs and outputs necessary for activating/stopping or sequencing valves and motors.

Vessel Construction. The vessel is a vacuum chamber, which can be a hot-walled design, but is more often a dual-walled and water-cooled design. The vessel can be horizontally or vertically loaded in a drop-bottom, pit, or bell arrangement. Typically, no internal insulation is required because of the lower temperature (less than 650 °C, or 1200 °F) and the desire to create sufficient heat loss to support a steady dc power supply output to the work load.

The isolated-hearth arrangement is divided into three basic areas:

- High-voltage feed-through arrangement, which carries the voltage through the vessel wall while maintaining a good vacuum seal
- Load support insulators, which carry the actual load weight while providing good dielectric qualities
- Charge plate or fixture, which has the workpieces placed on it or provides mechanical masking if desired

Sight ports placed around the vessel provide a view of the ion-nitriding process and are necessary for checking the load and ensuring that the selected parameters are accurate and that no detrimental hollow cathode disturbances (overlapping glow-discharge envelopes) have developed.

Power Supply and Control. The dc power supply is the most important component of an ion-nitriding system. The power supply must provide an output voltage from 0 to 1000 V and an output current matched to the size of the vessel and work load. Typical current ratings range from 25 to 450 A (dc). The amount of power applied to the load determines the temperature. Most power supplies provide proportional output control through silicon-controlled rectifiers (SCRs).

Another important design consideration in the power supply is arc detectioni suppression controls. Arcing can occur because the glow-discharge process causes the removal of surface impurities, which are always present. The impurities are removed in the form of an arc, in which there is a sudden decrease in voltage and increase in current. Because of this, both minimum and maximum current levels and voltage rate of change (dV/dt) and voltage/current relationships (slope) must be constantly monitored. When an arc is detected, the power output is momentarily shut off and the existing power diverted from the work load to avoid any possible damage. This is accomplished by placing an inductive load (choke) in line with the output of the power supply and using a crowbar SCR to short the output and momentarily dissipate the power.

Atmosphere and Pressure Control. The gas-mixing panel is used for blending gases, usually nitrogen, hydrogen, and methane. A typical composition for a γ' compound layer would be 75% H and 25% N. For an ε compound layer, a typical gas mixture would be 70% N, 27% H, and 3% methane. The mixing can be accomplished by injecting the gases through orifices at an equal pressure and varying the time of flow to establish the correct percentage concentration, or mixing can be done with mass flow control systems.

Ion nitriding is generally performed at absolute pressure levels of 130 to 1300 Pa (1 to 10 torr), necessitating a means of controlling pressure levels. Control is accomplished in two stages. First, a motorized needle valve on the inlet line to the vessel, in series with the gas-mixing panel, proportionally controls the gas flow up to a maximum level. At this point, a reverse-acting valve on the evacuation line between the vessel and the vacuum pump controls the amount of gas being evacuated until the desired pressure set point is met.

Fixturing to hold or mask the workpieces mechanically can be designed to optimize load placement or performance. Fixturing must minimize gaps between areas of glow discharge to avoid overlapping (hollow cathode disturbances) of the glow envelope. Also, the cross section of masking should resemble that of the workpieces to allow better temperature uniformity.

Auxiliary Heating. If the workpiece is large, auxiliary heating is necessary when the glow-discharge process is insufficient for direct heating. Auxiliary heating can be accomplished in several ways, the most common of which are cathode preheating and resistance heating.

Cathode preheating, which occurs during the beginning stages of the ion-nitriding process, requires an internal shield that is electrically isolated from the vessel wall. This shield is electrically charged and heats up and radiates the heat to the work load, allowing a faster heat-up time.

Resistance heating generally uses a low-voltage ac power supply such as a variable reactance transformer connected to graphite or alloy heating elements. As with cathode preheating, the elements heat up and radiate to the workpieces to speed the heat-up time.

Workpiece Factors

As mentioned in the section "Case Structures and Formation," the nitrogen concentration achieved during nitriding affects the depth and hardness of the case. In addition, the microstructure and resulting mechanical properties of a nitrided case also depend on the original composition and microstructure of the workpiece.

Suitability of Materials. In general, the response of a material to nitriding depends on the presence of strong nitride-forming elements. Plain carbon steels can be nitrided, but the diffused case is not significantly harder than the core. The strongest nitride formers are aluminum, chromium, molybdenum, vanadium, and tungsten. Because the white-layer constituents are only compounds of iron and nitrogen, the hardness of these layers is essentially independent of alloy content.

The premier nitriding steels are the Nitralloy series, which combine approximately 1 wt% Al with 1.0 to 1.5 wt% Cr. Other alloys that form excellent diffused cases are the chromium-bearing alloys, such as the 4100, 4300, 5100, 6100, 8600, 8700, 9300, and 9800 series. Other good nitriding materials include most of the tool and die steels, stainless steels, and precipitation-hardening alloys.

Parts made by powder metallurgy (P/M) can also be ion nitrided, but precleaning is more critical than with wrought alloys because of the porosity characteristic. A baking operation should precede the ion nitriding P/M parts to break down or release agents and/or to evaporate any cleaning solvents.

Significant hardening in the diffusion zone cannot be developed in carbon steels or cast iron. However, a compound zone can be formed and is often excellent for wear resistance in lightly loaded parts. Because the compound zone is supported by a relatively soft diffusion zone, applications involving high localized stresses should be avoided with these materials.

Effect of Prior Microstructure. As with other diffusion methods, the initial microstructure can also influence the response of a material to nitriding. In the case of alloy steels, a quenched and tempered structure is considered to produce the optimum nitriding results. The tempering temperature should be 15 to 25 °C (30 to 50 °F) above the anticipated nitriding temperature to minimize further tempering of the core during the nitriding process.

If the nitriding of a nonmartensitic matrix is desired, it is important that prior heat treatment be accompanied by as fast a cooling as possible to provide a relatively low-temperature austenite transformation and retain a high percentage of the nitride-forming element in solution for subsequent precipitation.

Hardness profiles for typical ion-nitrided alloys are shown in Fig. 8. The hardness increase of an ion-nitrided layer is virtually the same as for any nitriding process that provides the same nitrogen concentration profile. As previously mentioned, the hardness of the diffused case depends on precipitation hardening, while that of the white layer depends on the type and thickness of the compound formed. Because the white layers are compounds of only iron and nitrogen, the hardness of these layers is essentially independent of alloy content.

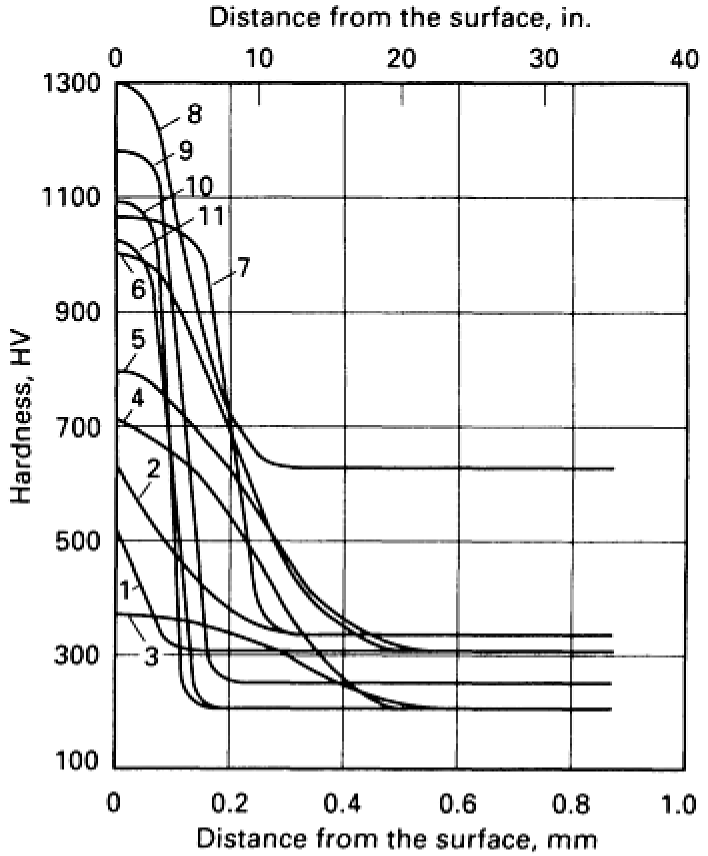


Fig. 8 Hardness profile for various ion-nitrided materials. 1, gray cast iron; 2, ductile cast iron; 3, AISI 1040; 4, carburizing steel; 5, low-alloy steel; 6, nitriding steel; 7, 5% Cr hot-work steel; 8, cold-worked die steel; 9, ferritic stainless steel; 10, AISI 420 stainless steel; 11, 18-8 stainless steel

White-Layer Properties. In general, case depth and white-layer composition should be selected for the anticipated operating conditions of the nitrided component. The ε layer is best for wear and fatigue applications that are relatively free of shock loading or high localized stresses. The γ' layer is somewhat softer and less wear resistant, but is tougher and more forgiving in severe loading situations. The white layer also provides increased lubricity. In addition to mechanical properties, the white layer, which is relatively inert, provides increased corrosion resistance in a variety of environments.

Fatigue strength, in addition to hardness and wear resistance, is significantly improved by nitriding (Fig. 9). The formation of precipitates in the diffused case results in lattice expansion. The core material, in an attempt to maintain its original dimension, holds the nitrided case in compression. This compressive stress essentially lowers the magnitude of an applied tensile stress on the material and thus effectively increases the endurance limit of the part.

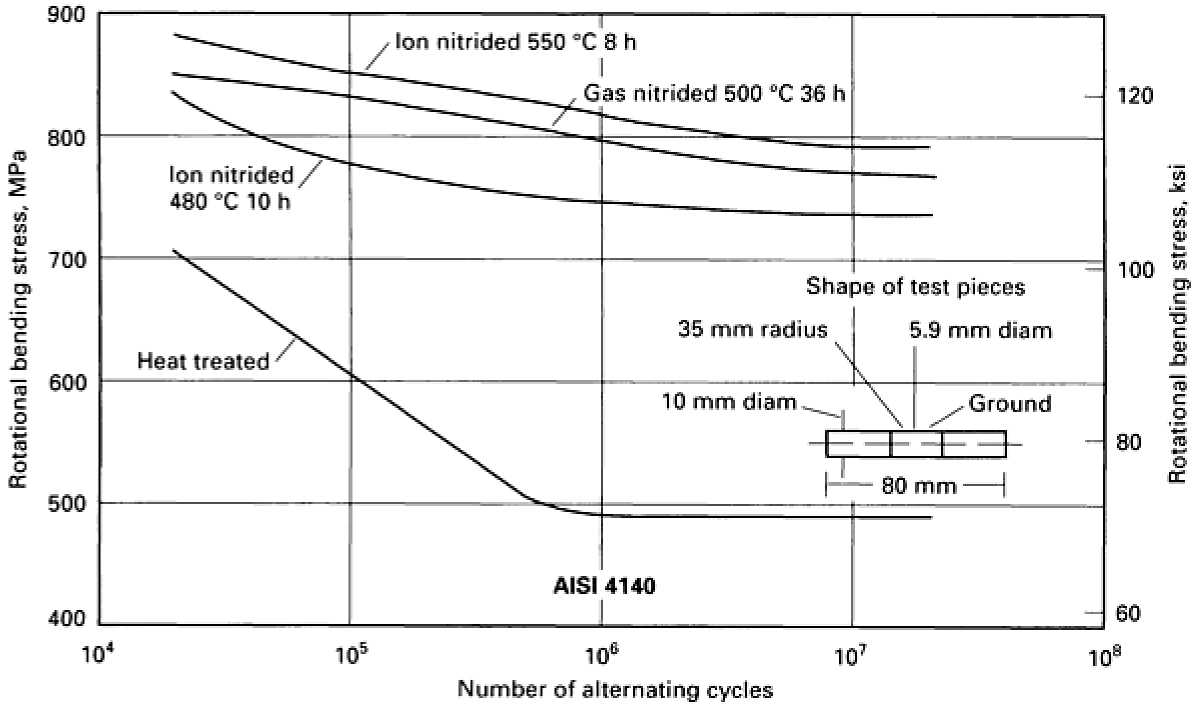


Fig. 9 Effect of nitriding on fatigue strength

Ion-Nitriding Applications

Various alloy steel and cast iron wear components, including gears, crankshafts, cylinder liners, and pistons, are excellent candidates for the ion process. In one case, P/M transmission gears are being ion nitrided to improve mechanical properties. In general, case depth and white-layer composition should be selected for the anticipated operating conditions of the nitrided component.

One rapidly growing area of ion nitriding is the fuel systems industry. Components used in fuel injection systems experience erosive wear from the fuel and fatigue from rapid cycling of fuel pressure. Ion nitriding greatly enhances the resistance to both of these effects.

The increased lubricity of white layers combined with hardness and fatigue strength has generated significant growth of the ion process in the tool and die industry. Hot work dies, which usually fail by thermal fatigue and sticking, have particularly benefited from ion nitriding following quenching and tempering.

Advantages and Disadvantages. Ion nitriding, when compared to conventional (gas) nitriding, offers more precise control of the nitrogen supply at the workpiece surface and the ability to select either an ε or a γ' monophase layer or to prevent white-layer formation entirely (Fig. 4). Other advantages of ion nitriding are:

- Improved control of case thickness
- Lower temperatures (as low as 375 °C, or 700 °F, due to plasma activation, which does not exist in gas nitriding)
- Lower distortion
- No environmental hazard (freedom from handling ammonia)
- Reduced energy consumption
- Ability to automate
- Ability to shield areas where nitriding is not desired by simple mechanical masking

A disadvantage of the ion process is the need to fixture parts to avoid localized overheating.

Sputtering and Ion Nitriding of Stainless Steels. Ion nitriding has a strong advantage over competing processes in the case of stainless steels, particularly austenitic or 300 series materials. The chromium-oxide passive layer on the surface of these materials represents a barrier to nitriding and must be removed prior to processing. With the gas nitriding

of stainless steels, several processes, such as wet blasting, pickling, and chemical reduction, have been developed to remove the oxide. With ion nitriding, however, this passive layer can be removed by sputtering in hydrogen in the vessel itself just prior to introducing the process gas. With most materials, even the sputtering that occurs naturally during the actual nitriding process is enough to yield good nitriding results.

When nitriding stainless alloys by any method, the hardening mechanism involves the formation of chromium-nitrides, decreasing the chromium content in the alloy. This chromium depletion in turn lowers the corrosion resistance of the case.

Alternative to Carbonitriding for Dimensional Control. Ion nitriding is becoming a replacement for carbonitriding in some areas. The driving force for this decision is the growing industry focus on dimensional control and the desire to reduce or eliminate machining after heat treatment.

The distortion of carbonitrided parts occurs in three ways:

- Heating to the austenitic range relieves residual stress
- Oil quenching introduces high thermal stresses and some localized plastic deformation
- The expansion of the case during martensite formation can cause some part distortion

Ion nitriding can be performed at temperatures as low as 375 °C (700 °F), which minimizes the amount of residual stress relieved. Because loads are gas cooled, they do not experience distortion from temperature gradients or martensite formation.

Gaseous and Plasma Nitrocarburizing of Steels

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Introduction

FERRITIC NITROCARBURIZING processes are those thermochemical treatments which involve the diffusional addition of both nitrogen and carbon to the surface of ferrous materials at temperatures completely within the ferrite phase field (Ref 1, 2). The primary object of such treatments is usually to improve the anti-scuffing characteristics of ferrous engineering components by producing a "compound layer" on the surface which has good tribological properties (Fig. 1). In addition, the fatigue characteristics of the material can be considerably improved, particularly when nitrogen is retained in solid solution in the "diffusion zone" beneath the compound layer. This is normally achieved by quenching into oil or water from the treatment temperature, usually 570 °C (1060 °F).

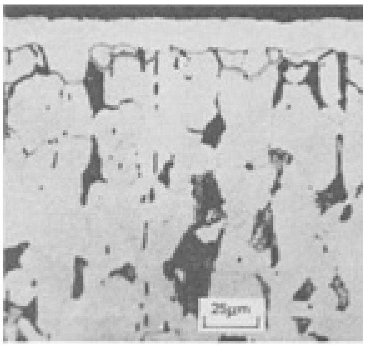

Fig. 1 Mild steel after 3 h gaseous nitrocarburizing in an ammonia/endothermic gas mixture at 570 °C (1060 °F) followed by oil quenching. Source: Ref 2

Nitrocarburizing treatments were first introduced in the early 1950s; since that time an extremely wide range of engineering components, such as rocker-arm spacers, textile machinery gears, pump cylinder blocks and jet nozzles, have been treated for wear resistance, while components such as crankshafts and drive shafts have been treated for improved fatigue properties.

Ferritic nitrocarburizing treatments have been successfully applied to most ferrous materials, including wrought and sintered plain carbon and alloy steels, stainless steels, and cast irons. However, the most marked Improvement in both anti-scuffing and fatigue properties, relative to untreated material, is found with plain low-carbon steels.

Until the late 1960s, the only nitrocarburizing processes available used a medium of molten cyanide-based salts to confer the property improvements required. However, since then concern about the overall environmental aspects of heat-treatment processing with cyanide-based salts has been increasing. Consequently, there has been intense interest in the development of cyanide-free nitrocarburizing treatments as technically and economically viable alternatives to the cyanide-based processes.

Considerable progress has been made over the last 25 years in the development of essentially toxic-free salt bath nitrocarburizing treatments (see the discussion of liquid nitrocarburizing in the article "Liquid Nitriding" in this Volume). However, it is the purpose of this article to review only those scientific and technological studies which have led to both the widespread introduction and greater appreciation of gaseous nitrocarburizing treatments and more recently available plasma methods.

References

1. T. Bell, "Survey of the Heat Treatment of Engineering Components," Code 164, Iron and Steel Institute, 1973
2. T. Bell and S.Y. Lee, Gaseous Atmospheric Nitrocarburising, *Heat Treatment '73,* Book No. 163, The Metals Society, London, 1975, p 99-107

Gaseous Ferritic Nitrocarburizing

As described in the introduction, gaseous ferritic nitrocarburizing involves the introduction of carbon and nitrogen into a steel in order to produce a thin layer of iron carbonitride and nitrides, the "white layer" or compound layer, with an underlying diffusion zone containing dissolved nitrogen and iron (or alloy) nitrides. The white layer enhances surface resistance to galling and wear. The diffusion zone increases the fatigue endurance limit significantly, especially in carbon and low-alloy steel.

The compound layer may contain varying amounts of γ', ε phase, cementite, and various alloy carbides and nitrides. The exact composition is a function of the nitride-forming elements in the material and the composition of the atmosphere as discussed below.

Gaseous nitrocarburizing is performed near 570 °C (1060 °F), a temperature just below the austenite range for the Fe-N system. Treatment times generally range from 1 to 3 h.

Preliminary Treatments.

The surface to be nitrocarburized must be free of contaminants such as oxides, scales, oil, and decarburization, if optimum results are to be obtained. Vapor degreasing is adequate for most applications. It may be necessary, especially on high-chromium materials and cast irons that have been burnished or otherwise highly finished, to grit blast with fine abrasive, to apply a light phosphate coating, or both, before nitrocarburizing. Highly finished surfaces are often associated with superficial metal flow at the surface, with the result that the initiation of nitriding is difficult. Surfaces having very low surface roughness can respond well to nitriding, provided that surface burnishing has been avoided. Finishing techniques with good cutting action are required.

Preliminary heat treatments range from simple stress relieving in order to control distortion to hardening and tempering in order to increase the core strength of the material. Stress relief and tempering temperatures should be at least 25 °C (45 °F) above the nitrocarburizing temperature to prevent alteration of core properties during the nitrocarburizing process.

Furnace Condition and Safety Precautions.

Batch furnaces with integral oil quenches are ideally suited for performing gas nitrocarburizing; however, the overall condition of the furnace is somewhat more critical than when the same furnace is used for other heat-treating operations such as hardening, carburizing, and carbonitriding. The hot chamber temperature should be controllable within ±5 °C (±

10 °F) at 570 °C (1060 °F) throughout the entire volume. Thermocouple and instrument systems designed to operate at the higher temperatures of other heat-treating processes are not always adequate for lower temperatures. Gas leaks in the furnace and around doors must be minimized. *Caution: Safety precautions must be carefully considered and rigorously enforced, because the process involves a combustible atmosphere that is explosive when operated below the self-ignition temperature*. Only minor gas leaks can be allowed, and double pilots should be provided at all doors. An interlock between door operation and pilot function provides added safety. Precautions must be taken to ensure that gas burn-off ports are properly sized, free of clogging, well vented from the building, and equipped with dependable pilots. All outside doors must be equipped with flame screens of sufficient capacity to cover the entire door opening.

The usual precautions also must be practiced with the quench oil:

- Adequate extinguisher equipment
- Assurance that the oil is free from water
- Maintenance of adequate temperature controllers and over-temperature devices to ensure that the oil does not become overheated

Steps also must be taken to ensure that atmosphere flow is sufficient to maintain positive pressure in the furnace during quenching to prevent the egress of air through burn-off or small leaks. At start-up, atmosphere gas may be introduced by heating the furnace above self-ignition temperature--760 °C (1400 °F)--and introducing atmosphere in the usual manner or by purging all the air from the furnace with nitrogen before introducing the reactive atmosphere. On shutdown, the furnace should be heated above self-ignition temperature of 760 °C (1400 °F) before burning the furnace out, or it should be purged with nitrogen.

Physical Metallurgy of Gaseous Ferritic Nitrocarburizing

A particularly important and detailed study into the scientific understanding of gaseous nitrocarburizing treatment was published by Prenosil in 1965 (Ref 3). He investigated the structure and composition of the compound layer formed on relatively pure iron after a gaseous nitrocarburizing treatment at 580 °C (1075 °F) in atmospheres containing approximately 50% ammonia (NH_3) and 50% propane (C_3H_8). In this investigation, it was reported that the presence of a high-carbon content, in what otherwise would be a simple ε nitride compound layer, considerably improved its hardness and wear resistance. These observations have recently been confirmed in more detailed structural studies (Ref 4). Earlier work by Prenosil had shown that conventional nitriding atmospheres with a high dew point led to the presence of oxygen in the ε phase. This oxygen content was found to increase with increasing partial pressure of oxygen, and it was further indicated that a similar saturation of the ε carbonitride phase was to be expected. Although the catalytic effect of oxygen on the rate of absorption of nitrogen into the surface of iron had been reported as early as 1935 by Bramley (Ref 5), the significance of oxygen in gaseous nitriding treatments was not really appreciated until it was investigated in detail by Eckstein and Lerche in 1968 (Ref 6), who showed that it increased the rate of ε nitride formation. On the basis of this evidence, it was concluded by Bell that oxygen should also increase the rate of ε carbonitride formation (Ref 7).

The nitrogen, carbon, and oxygen activities of the nitrocarburizing atmosphere necessary to achieve the desired oxygen-bearing ε carbonitride layer have recently been evaluated scientifically for a range of commercial steels by Slycke and Sproge (Ref 8). The basic consideration behind all gaseous nitrocarburizing processes is the type of atmosphere which can be used to cause carbon and nitrogen to be added simultaneously to the surface of ferrous materials and so produce the desired ε phase. The compositions and activity relations of various types of typical industrial nitrocarburizing atmospheres in quasiequilibrium are shown in Table 1 and are based on data derived from an unpublished mathematical model by Slycke (Ref 9).

Table 1 Calculated quasiequilibrium composition of various nitrocarburizing atmospheres at 580 °C (1075 °F)

Added gas mixture	Quasiequilibrium composition, vol%							Activities[(a)]		
	N_2	H_2	CO	H_2O	CO_2	NH_3	HCN	a_N	c_C	a_O
50% endogas 50% NH_3	24.1	25.9	9.0	0.76	0.68	38.4	1.16	1620	22.4	0.072
40% endogas 10% air 50% NH_3	29.2	24.3	6.7	2.46	1.77	35.4	0.244	1650	4.81	0.25
5% CO_2	58.8	15.5	2.9	2.98	1.45	18.4	0.045	1680	1.09	0.48

60% N_2 35% NH_3										
5% CO_2 5% CO 55% NH_3	54.4	15.9	6.4	2.22	2.31	18.6	0.135	1640	3.32	0.34
5% CO_2 20% H_2 45% N_2 30% NH_3	45.4	26.6	3.4	3.50	1.16	19.9	0.049	806	1.88	0.33

Source: Ref 9

(a) The reference states for the activity values are nitrogen gas at 1 atm, graphite, and wustite for nitrogen, carbon, and oxygen, respectively.

Ammonia is the most readily available source of active nitrogen and at 570 °C (1060 °F) dissociates on ferrous surfaces according to the following reaction:

$$NH_3 \rightarrow N + \frac{3}{2} H_2 \qquad \textbf{(Eq 1)}$$

with the nitriding activity given by:

$$a_N^{'} = K_1 \frac{r\,NH_3}{r\,H_2^{2/3}}$$

where K is the equilibrium constant for the nitriding activity, and pNH_3 and pH_2 are the partial pressures of ammonia and hydrogen, respectively.

In addition, there are small levels of hydrogen cyanide in the furnace atmosphere present as a result of ammonia interaction with carbon monoxide. This has been shown recently by Slycke and Sproge (Ref 8) to supply nitrogen in parallel to the above reaction (Eq 1) as follows:

$$HCN \rightarrow C + N \frac{1}{2} H_2 \qquad \textbf{(Eq 2)}$$

with the nitriding activity given by:

$$a_N^{''} = K_2 \frac{r\,HCN}{a_{cp} H_2^{1/2}}$$

where a_c is the carbon activity and pHCN is the partial pressure of hydrogen cyanide.

The reaction described in Eq 2 is now regarded as the principal source for the mass transfer of nitrogen in the rapid build-up of the compound layer. In practice, the nitrogen activity of endogas-based atmospheres tends to be lower than shown in Table 1. This table also shows that the nitrogen activity of mixed atmospheres can be easily varied by, for example, additions of hydrogen.

The contents of carbon- and oxygen-bearing constituents of the nitrocarburizing atmosphere depend on the reverse water-gas reaction:

$H_2 + CO_2$ € $H_2O + CO$ **(Eq 3)**

The production of carbon monoxide by means of this reaction (Eq 3) is of particular importance in obtaining an atmosphere of sufficiently high carbon activity when carbon dioxide is used as a carbon-bearing feedstock. If the

atmosphere is composed of ammonia and endogas mixture with an inherent high content of carbon monoxide, then the carbon activity will be high and the dominant carburizing reaction at 570 °C (1060 °F) is (Ref 10, 11):

$$CO + H_2 \ \text{€} \ C + H_2O \qquad \textbf{(Eq 4)}$$

with the carburizing activity given by:

$$a_c = K_3 \frac{r\,CO.r\,H_2}{r\,H_2O}$$

The presence of carbon during nitrocarburizing stabilizes the ε phase so that it will form at much lower nitrogen activities than in the absence of carbon. It can be seen from Table 1 that the carbon activity for an endogas-ammonia mixture is markedly higher compared to that of nitrogen-based atmospheres. However, the carbon activity of endogas-based atmospheres can be reduced, if required, by means of, for example, the addition of air. For nitrogen-based atmospheres, the carbon activity can be increased by the addition of, for example, carbon monoxide.

The carbon activity and oxygen activity are related to each other when equilibrium conditions prevail. The effect of oxygen or combined oxygen additions to a nitrocarburizing atmosphere is to lower the carbon activity in the gas phase. Hence the presence of oxygen is now recognized as an important constituent in the atmosphere if good quality nitrocarburizing is to result, that is, with a monophase ε structure. The importance of this has been emphasized by Slycke and Sproge through their studies of the hydrogen cyanide/carbon mass transfer reaction (Eq 2). In this reaction, it can be seen that for each nitrogen atom transferred, one carbon atom is also transferred. This leads to a buildup of carbon in the compound layer and eventually to the formation of cementite (which is undesirable), unless carbon is removed by the decarburizing reaction (Eq 4) with a sufficiently low carbon activity, which can be brought about by the presence of oxygen in the atmosphere.

Compound Layer Formation

Traditionally, it has been accepted that the range of solubilities of carbon and nitrogen for a stable ε carbonitride phase can be derived from the isothermal section of the Fe-C-N phase diagram published by Nauman and Langerscheid in 1965 (Ref 12). However, in 1983 Wells and Bell (Ref 13) demonstrated that stable ε phases can be produced with lower interstitial contents than those predicted by the ternary phase diagram and their data are included in Fig. 2. It is not known whether the presence of oxygen within the ε phase influences the phase limits, but Xu and Li have expressed the opinion that a reduction in the partial pressure of oxygen would considerably change the structure of the phase field (Ref 14). However, it is clear that the structure of the compound layer resulting from a nitrocarburizing treatment cannot necessarily be predicted or explained by reference to the Naumann and Langenscheid version of the Fe-C-N system. Accordingly, there has been considerable interest in recent years in a reappraisal of the Fe-C-N system. In 1987 Xu and Li showed by thermodynamic calculation that the Fe_4N region of the Naumann and Langenscheid Fe-C-N ternary phase diagram was correct, but that the ε region required revision (Ref 14). Furthermore, their calculations showed that most of the experimental data given by Wells and Bell were reasonable. Further experimental data, which have been reviewed in Ref 15 and which are at variance with the Nauman and Langerscheid diagram, include the existence of α+ ε+ cementite around 570 °C (1060 °F) as observed in a number of studies (Ref 13, 16, 17, 18). In addition, during nitriding it has been observed that the pearlitic cementite in low-alloy steels transforms to ε(Ref 16, 17, 18). Thus, at the transformation front, α, ε, and cementite can be in contact with each other, indicating the existence of an α+ ε+ Fe_3C three-phase field. On the basis of such new experimental data, Slycke *et al.* (Ref 15) have proposed a new ternary phase diagram for the iron Fe-N-C system at temperatures around 570 °C (1060 °F). This new diagram, which is shown in Fig. 3, allows for the direct contact between the ferrite and ε phase which, as described above, is frequently observed during nitrocarburizing. Use of this diagram has been shown to eliminate all ambiguity regarding the interpretation of how the compound layer structure evolves under a wide variety of steel processing conditions (Ref 8).

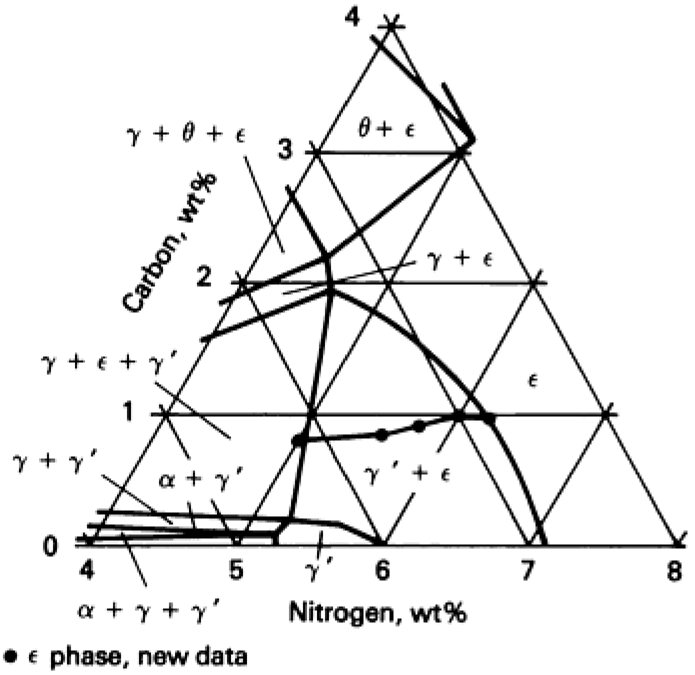

Fig. 2 Auger electron spectroscopy carbon and nitrogen concentration data for ε monophase compound layer produced using methanol/ammonia mixtures superimposed on the Fe-C-N phase diagram according to Ref 12. The five data points of the ε phase derived in Ref 13 are clearly in disagreement with ε phase limits depicted by the ternary diagram.

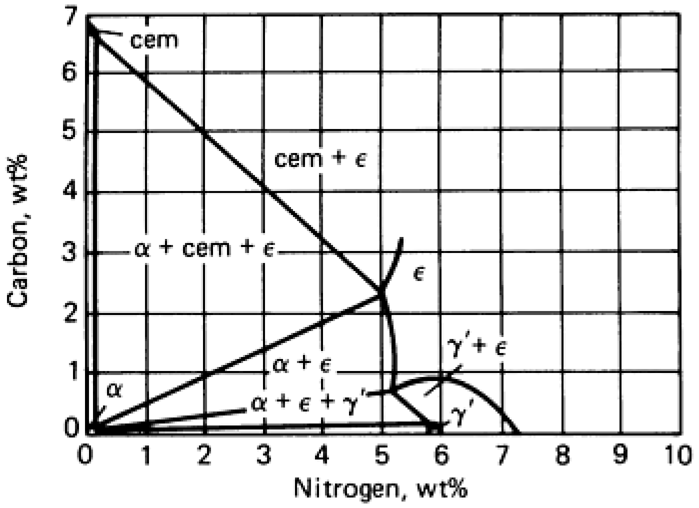

Fig. 3 Tentative Fe-N-C phase diagram at 570 to 580 °C (1060 to 1075 °F). Sizes of α , γ', and cementite (cem) fields are not in scale. Source: Ref 15

By way of example of the use of the new Fe-C-N phase diagram, consider the series of micrographs in Fig. 4, which show the compound layers formed on pure iron (99.9%) after nitrocarburizing in various methanol ammonia mixtures. The structure typical of compound layers formed at low methanol/ammonia ratios is illustrated in Fig. 4(a). X-ray structural analysis demonstrated that the layer is composed predominantly of the ε iron-carbonitride phase. The darker band structure seen in the compound layer was found to consist of the γ' iron nitride phase, which has very restricted carbon solubility. As the methanol/ammonia ratio in the treatment atmosphere was increased, the position of the γ' phase band structure in the compound layer was increasingly displaced away from the layer/matrix interface, as can be seen in Fig. 4(b) to 4(d). At an atmosphere composition of 45-60% methanol/55-40% ammonia, a layer was formed which is free of the γ' phase, or any other detectable secondary phase, and may be described as an ε carbonitride monophase layer (Fig. 4e). The compound layers which were formed in atmospheres with a methanol content in excess of 60% are typified by the structure shown in Fig. 4(f). The layer is thin, duplex in character, and contains a phase identified by x-ray structural analysis as cementite. Schematic representations of the surface compositions from each sample in the series and the resulting gradients from their trails are superimposed in the new Fe-C-N phase diagram in Fig. 5, where it can be seen that there is good agreement with the corresponding phase analysis description outlined above.

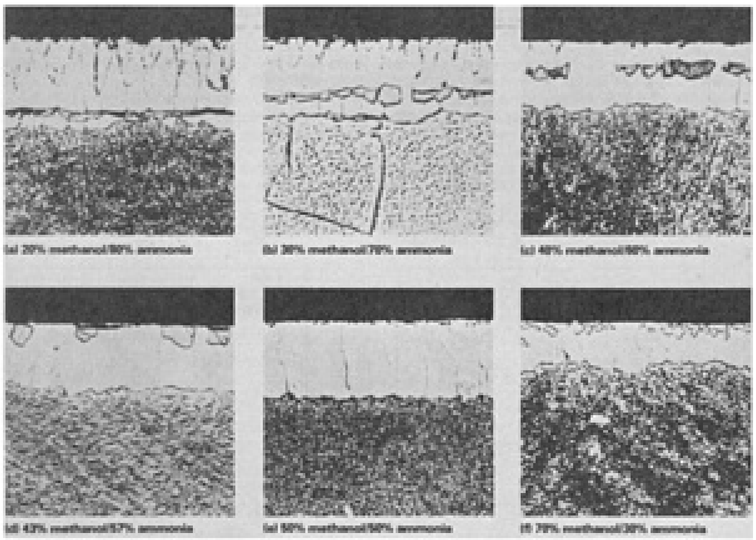

Fig. 4 Compound layers formed on iron by gaseous nitrocarburizing in various methanol/ammonia ratios. Quenched samples, all shown at 80× (a, c, d, e, and f etched in alcoholic ferric chloride and hydrochloric acid with iodine; b, etched in nital with ferric chloride). Source: Ref 13

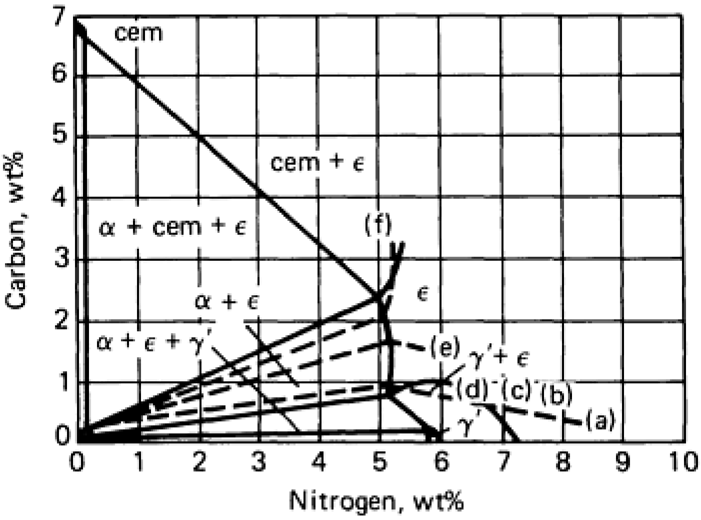

Fig. 5 Schematic representation of the surface composition of the micrographs shown in Fig. 4 superimposed on the revised ternary Fe-N-C phase diagram

Similarly, it has been demonstrated that if a high-carbon steel is treated in atmospheres over a wide range of carbon activities, the following sequence of events may occur (Ref 8):

- Ferrite and cementite dissolve nitrogen
- Cementite transforms into ε phase via ferrite + cementite → ferrite + ε
- Epsilon phase grows at the expense of ferrite until a covering compound layer is formed
- Continued growth of the monophase compound layer is controlled by nitrogen diffusion

A schematic representation of compound layer formation on a high-carbon steel is illustrated in Fig. 6; a corresponding micrograph is shown in Fig. 7.

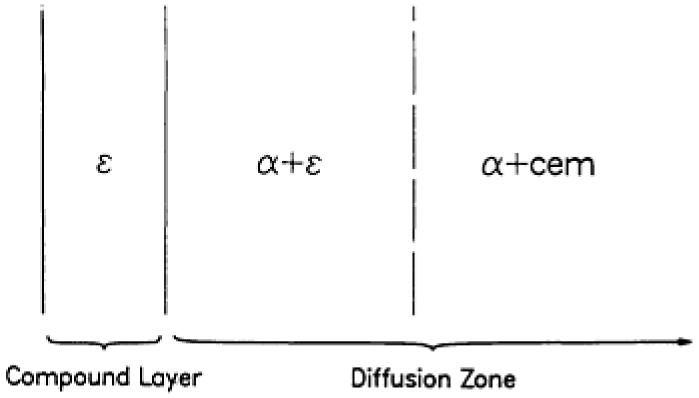

Fig. 6 Schematic sequence of phase development during nitrocarburizing of high-carbon steel. Source: Ref 8

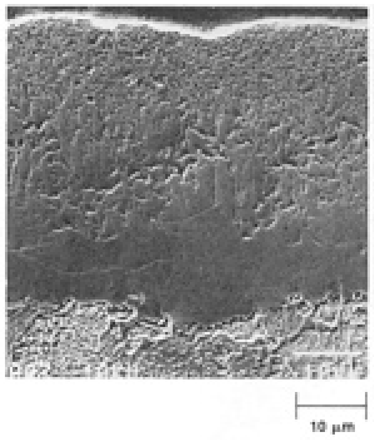

Fig. 7 Compound layer structure of high-carbon steel nitrocarburized in N_2 + 35% NH_3 + 5% CO_2 atmosphere at 580 °C (1075 °F) for 2 h. SEM backscatter mode. Corresponds to the schematic shown in Fig. 6

Diffusion Zone Characteristics and Fatigue Properties

The diffusion zone characteristics are essentially independent of the type of nitrocarburizing media used (Ref 7). During the treatment of plain carbon steels with a large proportion of ferrite, only nitrogen diffuses in from the carbonitride layer, since the ferrite is normally already at its equilibrium concentration with respect to carbon. However, some outward carbon diffusion from high-carbon concentration regions of the matrix into the compound layer can be experienced with most grades of steel and cast iron (Ref 2). While contributing to the quality of the compound layer, this loss of carbon is thought to have no effect on the fatigue properties resulting from the diffusion zone. Using optical (light) metallography, the diffusion zone beneath the compound layer for oil-quenched samples is indistinguishable from the original matrix material (Fig. 1). However, fine scale precipitation of nitrides can be observed by transmission electron microscopy (TEM) following oil quenching (Ref 19). By rapid cooling it is possible to retain most of the nitrogen in supersaturated solid solution and, in this condition, it increases both the yield strength of the base material and its fatigue strength. Indeed, both the bending fatigue strength (Ref 19) and rotating bend strength (Ref 7) of low-carbon steels can be increased by more than 120% (Fig. 8). However, aging, such as atmosphere cooling from the treatment temperature, substantially decreases the fatigue strength (Ref 19). The improvement in fatigue properties is directly related to the depth of nitrogen diffusion, as can be seen in Fig. 9. By using a sufficiently long nitrocarburizing time, it is possible to achieve this fatigue improvement throughout the component section. This is in contrast to conventional surface-hardening processes such as carburizing and carbonitriding of plain carbon steels and the nitriding of alloy steels, where a fatigue strength improvement is obtained as a result of a combination of surface strengthening and by the introduction of a surface compressive macrostress. It has been suggested that for nitrocarburized plain carbon steel, the residual microstresses can have a decisive influence on the endurance limit, even for notched components, since clearly for through hardened nitrocarburized materials there must be zero macroresidual stress effects (Ref 21).

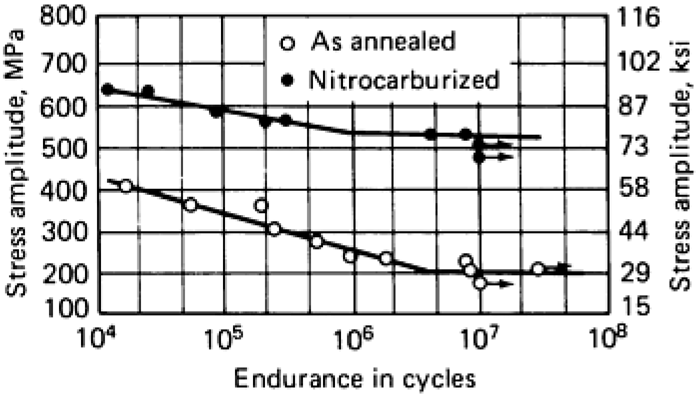

Fig. 8 Wohler fatigue curves for unnotched specimens of untreated and gaseous nitrocarburized mild steel. Source: Ref 2

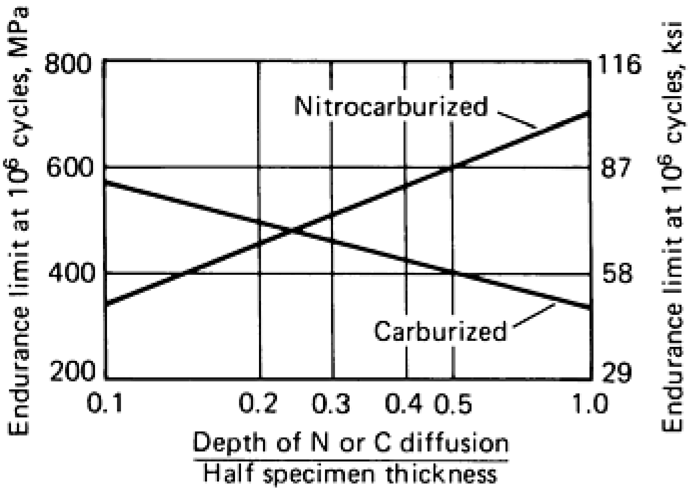

Fig. 9 Fatigue strength of low-carbon steel nitrocarburized at 570 °C (1060 °F) or carburized at 900 °C (1650 °F). Source: Ref 20

Industrial Gaseous Ferritic Nitrocarburizing

In 1961, before the availability of detailed structural and chemical analyses of the compound layer on salt bath nitrocarburized materials, a patent had been applied for by Joseph Lucas (Industries) Ltd. for a type of gaseous nitrocarburizing (Ref 22). This treatment produced, on mild steel, a porous layer which was claimed to have good anti-frictional properties. The complete patent, when published, revealed that the gaseous atmosphere consisted of ammonia and hydrocarbon or other carbon-containing gases of unspecified proportions and that the treatment was undertaken in the temperature range 450 to 590 °C (840 to 1095 °F). At that time, however, no detailed technical information on the property improvements achieved, or of the structures which were responsible, was published. During the 1960s, further research led to consideration of a large range of gaseous nitrocarburizing processes throughout the world. A wide variety of atmospheres were proposed and, indeed, employed in these processes. These included triethanolamine (Ref 23), ammonia/kerosene (Ref 24), and isopropanol/water/urea/ammonia (Ref 25). However, it was only in the early 1970s that gaseous nitrocarburizing received serious industrial attention with the introduction of a variety of gaseous techniques.

The Nitemper process is usually carried out in sealed quench furnaces and uses an inert atmosphere consisting of 50% ammonia and 50% endogas (Ref 26). The treatment temperature is 570 °C (1060 °F) and treatment times usually between 1 and 3 h are used, after which the components are either quenched into oil or cooled under recirculated protective gas (Ref 26). By 1975, the Nitemper process had been in use for several years and furnaces performing the treatment were in operation in Germany, Sweden, the United States, Japan, and the United Kingdom for improving the scuffing and fatigue resistance of ferrous engineering components. The treatment is now used extensively throughout the world, and the possibility of a two-stage Nitemper process is being developed (Ref 27). This involves the use of an atmosphere with a high carbon dioxide level in the initial stage to promote rapid compound layer formation. The influence of controlled additions of carbon dioxide to ammonia-based nitrocarburizing atmospheres under industrial conditions has recently been investigated by Vogel for a wide range of alloy steels (Ref 28). He demonstrated that the proportion of the ε phase in the compound layer increased with increasing carbon dioxide content, that is, lower carbon activities, and that the ε phase more readily formed on alloy steels than on pure iron or plain carbon steels (Fig. 10). In the

second stage of the modified Nitemper process, an atmosphere with a high carbon monoxide content is employed to increase the carbon content of the compound layer for enhanced wear resistance. In essence, therefore, the process involves a combination of the Nitroc process (Ref 29), which utilizes unpurified exothermic gas as the carburizing medium (see description below), and the Nitemper technology. A similar duplex treatment called Deganit has also been proposed (Ref 30)

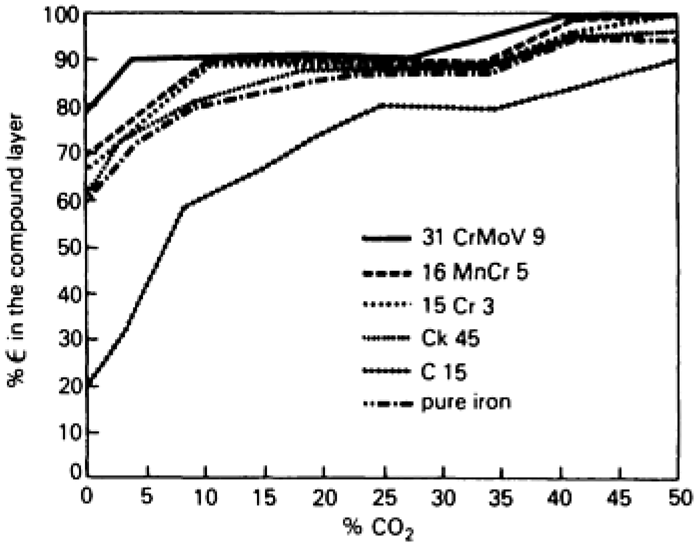

Fig. 10 The influence of CO_2 addition to ammonia on the structure of the compound layer, formed by nitrocarburizing at 580 °C (1075 °F) on pure iron, plain carbon steels, and low-alloy steels. Source: Ref 28

The Alnat-N process is a patented approach to nitrocarburizing whereby nitrous oxide is incorporated in the atmosphere to enhance, through the indirect presence of oxygen, the rate of formation of the compound layer (Ref 31, 32, 33). A further feature of the Alnat-N process is that the addition of a carburizing gas to the basic ammonia/ nitrous oxide/nitrogen mixture is claimed to be unnecessary. Thus, the incorporation of carbon into the compound layer must be via diffusion from the matrix materials.

Control of Gaseous Nitrocarburizing Atmospheres. A possible limitation on the gaseous nitrocarburizing processes developed in the mid-1970s was that optimum processing conditions for all classes of material, including cast irons, tool steels, and stainless steels, could not be assured. A further and perhaps more serious limitation was that reproducibility could be impaired with variable loads and from furnace to furnace. These difficulties were in part overcome through the use of infrared monitoring and control systems (Ref 7). However, gas analysis of atmospheres containing both ammonia and carbon dioxide can be problematic, especially when high ammonia contents and high dew points are concerned. If water is condensed in the sample gas piping, high amounts of ammonia will dissolve and the resulting strong solution can dissolve large amounts of carbon dioxide. If this solution becomes supersaturated a mixture of ammonium carbonate and bicarbonate will precipitate out in the form of a white powder (Ref 8). Experience has shown that when such precipitation has occurred, further measurement of ammonia and carbon dioxide is in error and there is a distinct likelihood that the pipeline of the measurement system will be blocked. Slycke and Sproge have shown that this problem can be largely overcome by suitable heating of the measurement instrumentation and the gas sampling pipeline (Ref 8).

Because of the limitations of the infrared gas analysis approach to the control of gaseous nitrocarburizing atmospheres, attention has been focused recently on the development of solid electrolyte gas sensors for the measurement and control of the nitrogen and oxygen potentials of nitriding and nitrocarburizing atmospheres (Ref 34). Such instruments are, in principle, similar to those widely used for carbon potential control of carburizing gas atmospheres.

Black Nitrocarburizing. Post nitrocarburizing oxidation treatments have been used on a commercial basis since 1976 to enhance the aesthetic properties of gaseous nitrocarburized components for the hydraulics industry (Ref 35). However, in 1982 Dawes and Tranter showed how such black nitrocarburizing treatments, including the Nitrotech process, could be used for the combined enhanced fatigue, wear, and corrosion resistance of mild steels (Ref 20). They showed that this could be achieved by specifically designing a range of cost effective, aesthetically pleasing black oxidized electrical components for use in automobile manufacture.

Particular success has been achieved with vacuum degassed ultra-low carbon deep-drawing steels that have been stabilized with niobium and/or titanium additions. Such steels facilitate many complex thin-sectioned components to be manufactured by single-stage press operations. These steels have very low yield strengths of about 155 MPa (23 ksi) with elongation values of approximately 45%. To achieve optimum engineering properties in the final component, nitrocarburizing can be used. The influence of quenching temperature on the yield strength of these nitrocarburized special steels is shown in Fig. 11. It is clear that low-temperature quenching has resulted in nitride precipitation and loss of strength, and that if a high strength is to be achieved a quenching temperature not less than 550 °C (1020 °F) is necessary. As discussed earlier in the section of this article on diffusion zone characteristics and fatigue properties, this is also the condition for optimum enhancement of the fatigue strength. Another essential feature of this treatment is that distortion of thin sectioned material can be kept to a minimum by controlled quenching into an oil/water emulsion at a temperature of 70 to 80 °C (160 to 175 °F) and that the quench time involved is sufficient to produce an aesthetically pleasing black oxide film of Fe_3O_4 which needs to be less than 1.0 μm in thickness if exfoliation is to be avoided (Fig. 12).

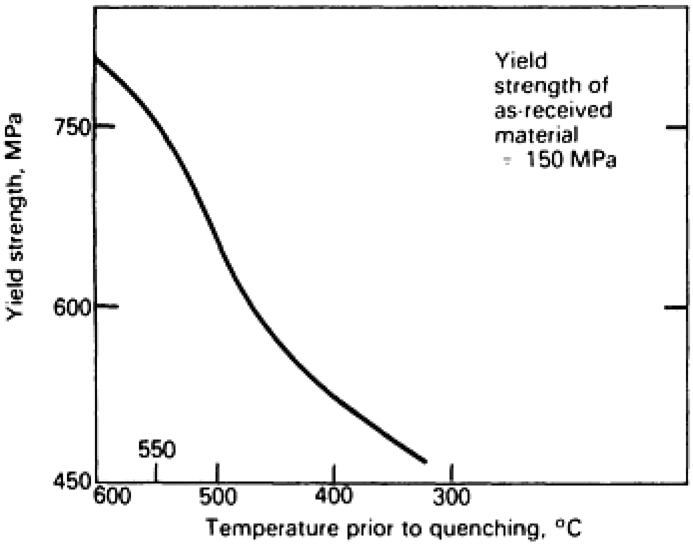

Fig. 11 The influence of quenching temperature on the yield strength of nitrocarburized deep-drawing steels. Source: Ref 20

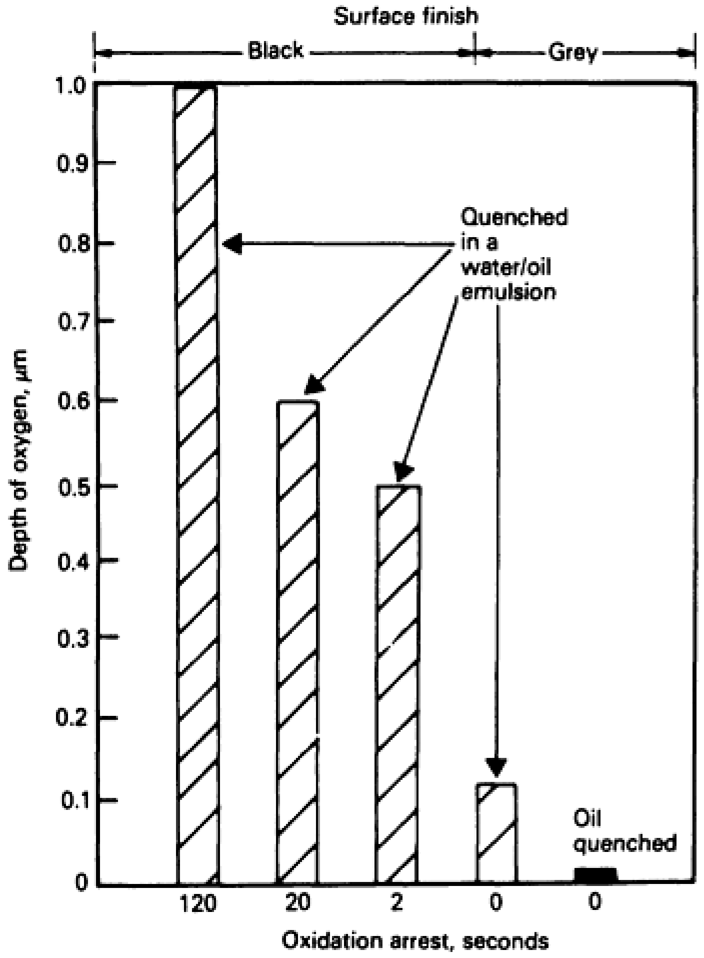

Fig. 12 Influence of depth of oxygen on surface coloration and corresponding oxidation arrest time for various quench media. Source: Ref 20

The flash oxidation parameters of the basic Nitrotec process are designed to produce an oxide structure capable of both conferring a degree of corrosion resistance and acting as a carrier for an organic sealant. Investigations into the composition of organic sealants has resulted in the development of specific formulations which are based on either hydrocarbon-solvent-borne mixtures of metal soaps produced from rosin acids and oxidized petrolatums, or water-based mixtures of emulsified microcrystalline and synthetic hydrocarbon waxes with corrosion inhibitors (Ref 36).

The relative contributions of post-nitro-carburizing oxidation and organic sealing to the overall corrosion resistance resulting from the Nitrotec process is shown in Fig. 13. It can be seen that the degreased nitro-carburized surface itself imparts little inherent corrosion resistance. An example of an automotive fan motor treated by the Nitrotec process and tested relative to zinc plating is illustrated in Fig. 14. Other components now in service using the Nitrotec black nitrocarburizing process include windshield wiper linkage assemblies which have been fitted since 1985 to Austin Rover's Metro, Maestro, and Montego models (Ref 37). The Austin Rover 800 series also uses Nitrotec-treated bumper armatures, while the Renault 25 series has the seat sliders treated. Another application of the process is in the cost-effective manufacture of the viscous slip differential used on Ford Sierra and BMW cars (Ref 38).

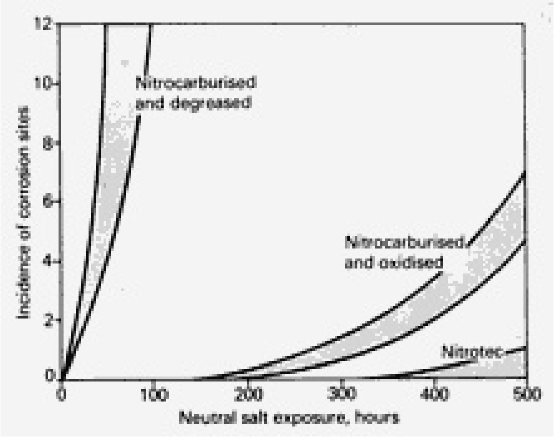

Fig. 13 Relationship between treatment sequence and salt corrosion resistance (ASTM B 117). Source: Ref 36

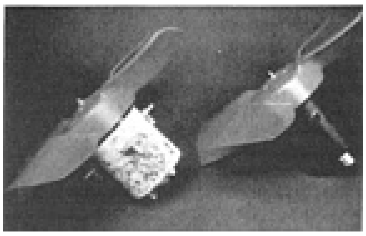

Fig. 14 Electric fan motor treated by Nitrotec process (right side) and neutral salt spray tested for 250 h compared to a zinc-plated component (left side). Source: Ref 20

An alternative black nitrocarburizing finish is the Ashland Nitro Black, which is a patented process utilizing fluidized bed technology (Ref 39). The atmosphere used for the nitrocarburizing stage comprises a mixture of ammonia, natural gas, and nitrogen. After nitrocarburizing, the fluidized bed is purged with nitrogen for 2 min prior to the oxidation step during which steam and air are injected via an integral coil system to impart a thin Fe_2O_3 layer on treated components. Fluidized bed quenching is then followed by coating with a proprietary polymeric emulsion sealant.

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Austenitic Nitrocarburizing (Ref 40)

Nitrocarburizing has been defined by the Terminology Committee of the International Federation for Heat Treatment and Surface Engineering as a "thermochemical treatment which is applied to a ferrous object in order to produce surface enrichment in nitrogen and carbon which forms a compound layer. Beneath the compound layer there is a diffusion zone enriched in nitrogen" (Ref 41). When the treatment temperature is such that partial transformation of the matrix to austenite occurs through enrichment with nitrogen, then the treatment is referred to as austenitic nitrocarburizing.

Austenitic nitrocarburizing was first developed as a cyanide salt bath process, under the trade name Noskuff (Ref 42); an equivalent gaseous treatment was patented in 1977 (Ref 43). The primary objective of the austenitic treatment is to overcome the principal disadvantage of ferritic nitrocarburizing, namely, that with plain carbon steel components there is no significant hardened case below the compound layer and, accordingly, the ability of components to withstand high Hertzian stresses is restricted. With austenitic nitrocarburizing, the subsurface (but not the complete cross section) is transformed to iron-carbon-nitrogen austenite, which is subsequently transformed to tempered martensite and bainite, with a hardness in the range of 750 to 900 HV. This high hardness level provides a means of extending the range of applications of nitrocarburizing treatments.

Physical Metallurgy of Gaseous Austenitic Nitrocarburizing

On the basis of extensive physical metallurgy studies at the Wolfson Institute for Surface Engineering, together with work by the Swedish Institute for Metal Research, it has been shown that gaseous austenitic nitrocarburizing treatments can be carried out successfully in sealed quench furnaces using mixtures of endothermic and ammonia gases (Ref 44, 45). Additional detailed laboratory studies have been conducted into the growth kinetics and characterization of compound layers formed by the action of methyl-alcohol saturated ammonia (Ref 46).

As with the ferritic nitrocarburizing treatment, the compound layer should consist mainly of the ε carbonitride phase, which is predominantly responsible for significant improvements in tribological properties. Experimentally, this can be achieved quite readily in the temperature range 675 to 775 °C (1250 to 1425 °F). The 700 °C (1290 °F) isothermal section of the Fe-C-N phase diagram shown in Fig. 15 describes the phase structures produced at this temperature.

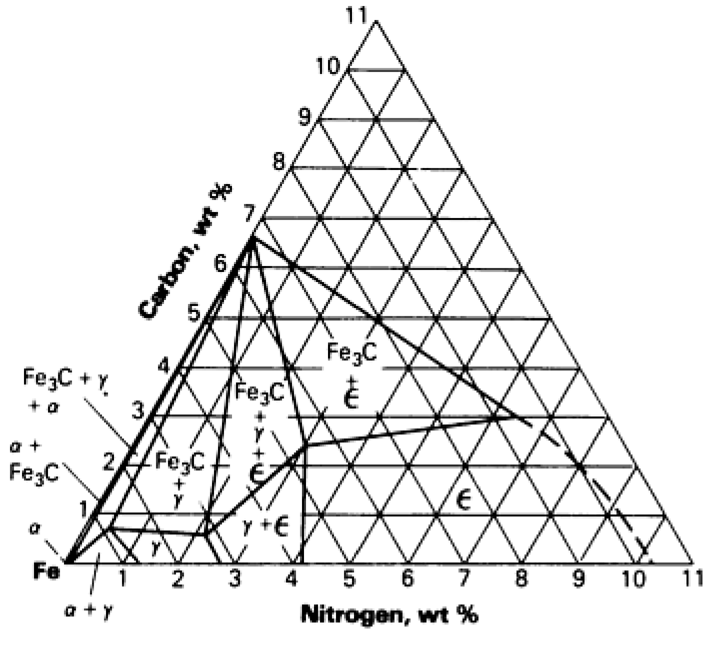

Fig. 15 Isothermal section of the Fe-C-N phase diagram at 700 °C (1290 °F). Source: Ref 12

By way of illustration of the structure and properties resulting from austenitic nitrocarburizing, consider EN32 (BS 080 M 15) steel (0.12 to 0.18% C, 0.10 to 0.40% Si, 0.60 to 1.00% Mn) subjected to an austenitic nitrocarburizing treatment at 700 °C (1290 °F) with a 15% residual ammonia level in the exhaust gas atmosphere of a sealed quench furnace. The appropriate microstructure after 1 h treatment is shown in Fig. 16(a). X-ray diffraction analysis has revealed that the 50 μm thick compound layer consists predominantly of the ε phase. The corresponding interstitial profile analysis as performed with a calibrated electron probe microanalyzer (Ref 47) are shown in Fig. 16(b). It can be seen by reference to Fig. 16(b) that at least the outermost portion of the compound layer falls within the desired monophase ε carbonitride

region. The kinetics of growth of the compound layer obey a parabolic law, as shown in Fig. 17, thus illustrating the diffusion-controlled nature of compound layer formation. The hardness profile of the as-quenched nitrocarburized layer is plotted in Fig. 18. It can be seen clearly that there is a dip in the hardness value at the compound layer/austenite interface associated with the high contents of nitrogen and carbon in solution which depresses the M_S temperature to below ambient. As a result of aging, this hardness dip is removed due to the fine-scale formation of iron-nitrogen bainite.

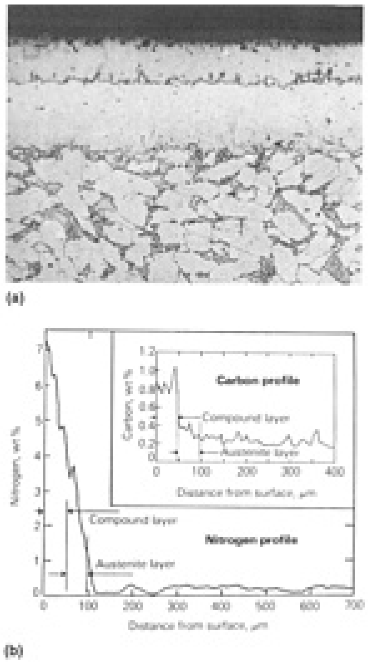

Fig. 16 Structural characteristics of an austenitic nitrocarburized material. (a) Micrograph of EN32 steel nitrocarburized for 1 h at 700 °C (1290 °F) in ammonia/endothermic gas with 15% residual ammonia and oil quenched. (b) Carbon and nitrogen profiles for EN32 nitrocarburized for 1 h at 700 °C (1290 °F) in ammonia/endothermic gas with 15% residual NH_3. Source: Ref 40

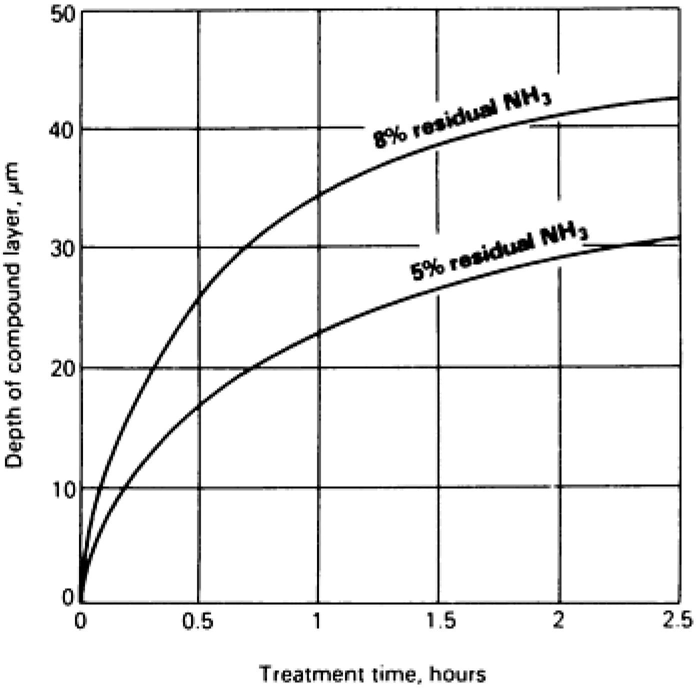

Fig. 17 Growth kinetics of the compound layer at 700 °C (1290 °F) in ammonia/endothermic gas with different residual ammonia levels. Source: Ref 40

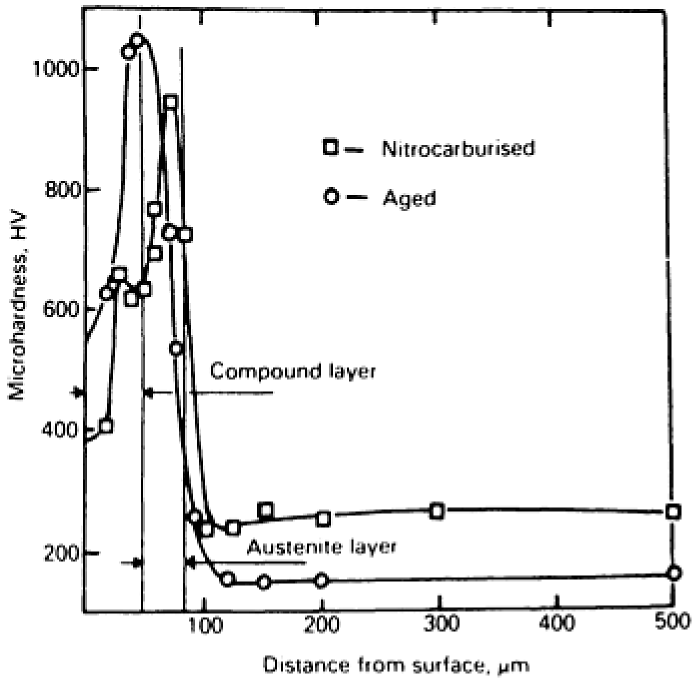

Fig. 18 Microhardness profiles for austenitic nitrocarburized mild steel before and after aging at 250 °C (480 °F) for 2 h. Nitrocarburized for 1 h at 700 °C (1290 °F) in ammonia/endothermic gas with 15% residual NH_3 and oil quenched. Source: Ref 40

As with ferritic nitrocarburizing, the presence of the compound layer significantly enhances the wear resistance (Fig. 19). Similarly, there is a major enhancement in the fatigue strength (approximately 100%) both directly after quenching and after quenching and aging (Ref 40).

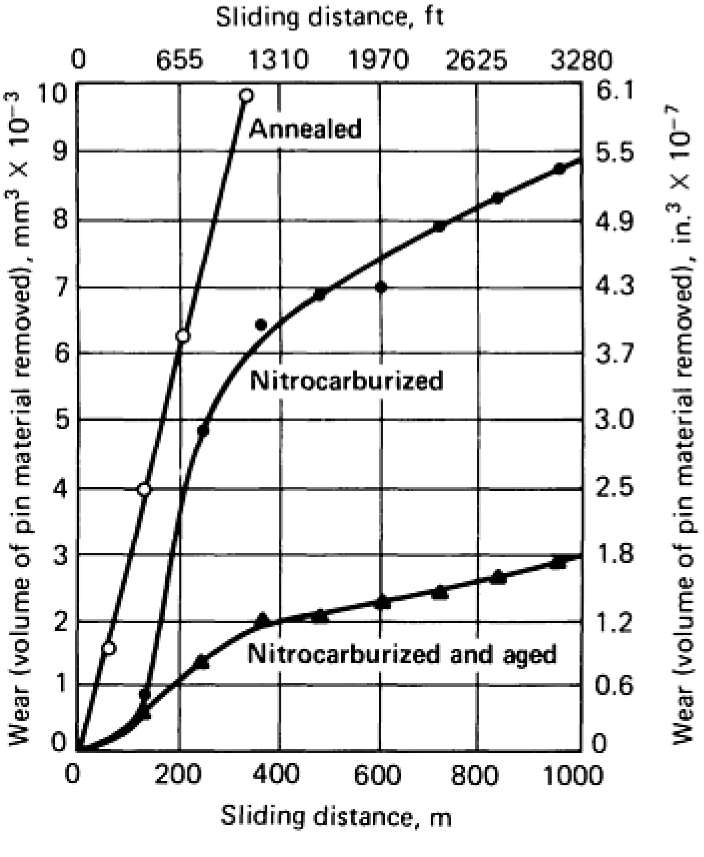

Fig. 19 Wear rates of mild steel in the annealed austenitic nitrocarburized and aged conditions. Nitrocarburized at 700 °C (1290 °F) for 1 h in ammonia/endothermic gas with 15% residual ammonia, oil quenched. Aged at 250 °C (480 °F) for 2 h. Pin-on-disk test with a treated mild steel pin and carbonitrided EN8 disk

Industrial Gaseous Austenitic Nitrocarburizing

It has been illustrated above that in order to obtain maximum subsurface strength, it is necessary to transform the austenitic zone beneath the compound layer into iron-nitrogen-carbon bainite. Typical transformed austenite case thicknesses are in the range 50 to 200 μm, with a hardness of between 750 and 900 HV. However, much deeper cases can be achieved by employing a precarburizing treatment prior to nitrocarburizing (Ref 43). These variants of the austenitic nitrocarburizing process have been exploited commercially with the Alpha Plus and Beta industrial processes (Ref 19). Typical hardness profiles resulting from these treatments using a carrier gas of nitrogen/methanol enriched with ammonia and natural gas are illustrated in Fig. 20; typical industrial applications are summarized in Table 2. Benefits from such treatments include:

- Resistance to wear, scuffing, and seizure
- Predictable growth and low shape distortion
- Increased core strength
- Corrosion resistance
- Indentation resistance

Table 2 Production applications of austenitic nitrocarburizing

Austenitic nitrocarburizing treatment type	Applications
Alpha Plus (0.125 mm, or 0.005 in., underlying case)	**Clutch plates, levers, gears, bushes, thin pressings**
Alpha Plus (0.25 mm, or 0.010 in., underlying case)	**Gears, levers, pulleys, liners**
Beta (0.60 mm, or 0.025 in., underlying case)	**Machine slideways, guide bars, gears, sprockets, pins, bushes, water-pump parts, liners, jigs/fixtures, bearings**

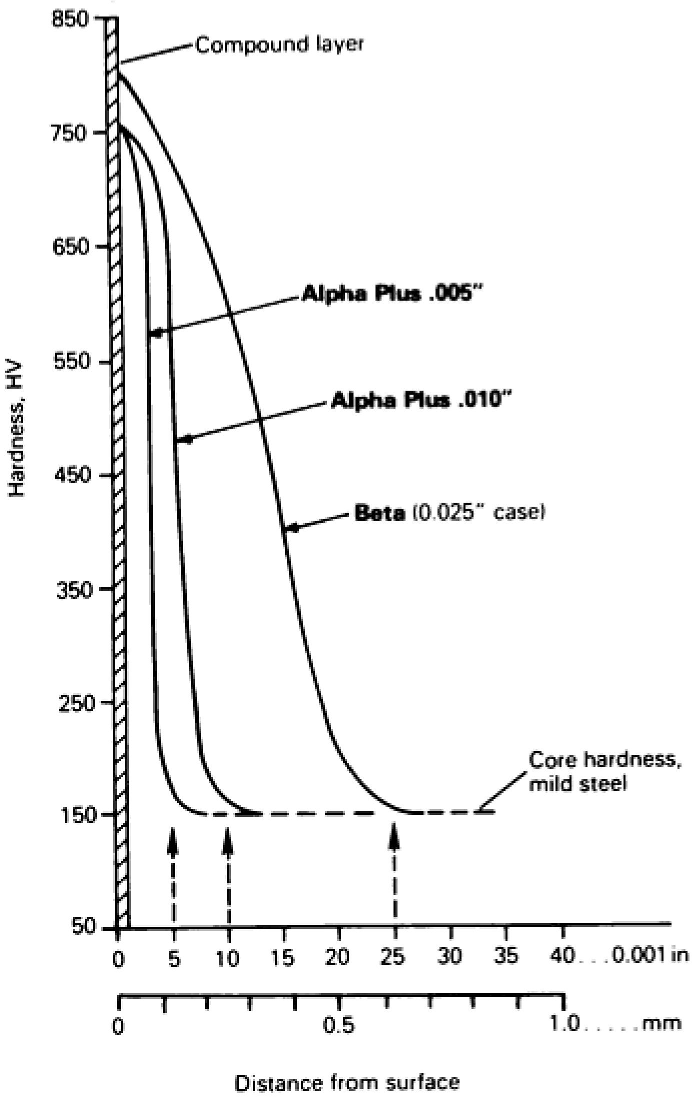

Fig. 20 Hardness profiles resulting from three austenitic nitrocarburizing treatments applied to mild steel. Source: Ref 48

Recently, a deep case variant of the Nitrotec process has been introduced, known as Nitrotec C (Ref 49). This is a black austenitic nitrocarburizing process in which a precarburized substrate is subsequently processed to produce the surface ε compound layer at a temperature that allows for hardening of the carburized zone during quenching.

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Plasma Nitrocarburizing

Plasma nitrocarburizing is in essence a variant of the now well-established glow-discharge plasma nitriding method (see the article "Plasma (Ion) Nitriding" in this Volume), the physical metallurgy of which has been reviewed recently by Sun and Bell (Ref 50). The origins of the plasma thermochemical process lie in the patents filed by Bernhard Berghaus in the 1930s. Over the period 1957 to 1967, the German company Gesellschaft zur Förderung der Glimmentledungforschung, funded by the Regional Government of Norderhein-Westfalen, undertook research into the physics, chemistry, and metallurgy of glow-discharge plasmas. IONON, a private company owned by Berghaus in Köln was responsible for the industrial exploitation of the technology generated. Following the death of Berghaus in 1965, Klockner Ionon was formed in 1967 and thus gained access to this technology which formed the basis of the international commercialization of this environmentally friendly surface heat-treatment technique (Ref 51). Emphasis has recently been placed on the requirement of the production engineer to meet surface engineering specifications in a manner increasingly influenced by environmental considerations. Advantages associated with plasma heat-treatment technology include:

- No toxic fumes or waste produced
- No risks of explosion
- No significant dirt, noise, or heat pollution
- Reduced processing times
- Reduced energy consumption
- Reduced treatment gas consumption

Physical Metallurgy of Plasma Nitrocarburizing

In respect to the tribological properties of nitrocarburized steels, evidence from gaseous and salt bath nitrocarburizing research indicates that the monophase ε structure is strongly preferred. However, plasma nitrocarburizing still faces the problem of controlling the quality and character of the compound layer structure to achieve the monophase ε carbonitride on a regular basis (Ref 52). Accordingly, with plasma nitrocarburizing the compound layer usually consists of ε and γ' phases for low-carbon level atmospheres. Equilibrium thermodynamic considerations, as discussed earlier in this article, would indicate that increasing the carbon level in the atmosphere should produce the monophase ε structure. However, under the nonequilibrium thermodynamic conditions prevailing in the glow-discharge plasma, an increase in the carbon level does not automatically produce a 100% ε structure, and yet cementite does appear above a certain limit of the carbon level (Ref 53). Laboratory studies using methane as the source of carbon in the gaseous plasma, have shown that some stabilization of the ε phase is possible, but above a certain limit (depending on the substrate materials) the cementite always appears and soot formation is difficult to prevent. The use of controlled additions of oxygen-bearing gases to reduce the activity of carbon has shown some promise in stabilizing the ε phase and the kinetics of compound layer growth are increased.

Recent laboratory experiments using 90% nitrogen/hydrogen atmospheres with controlled additions of carbon dioxide (up to 2.5%) have been carried out at 570 °C (1060 °F) for 2 h (Ref 54). It was found that:

- With pure iron, increasing the carbon dioxide stabilized the ε phase and an essentially monophase εstructure was formed at 1% carbon dioxide level (Fig. 21a and b). A further increase in carbon dioxide level to 2% led to the formation of surface oxides
- With plain carbon steel, increasing the carbon dioxide level again stabilized the ε phase, but a mixture of the ε and γ' phases was invariably present (Fig. 22a and b)
- With a low-alloy chromium-bearing steel, EN40B (0.20-0.28% C, 0.10-0.35% Si, 0.45-0.70% Mn, 3.0-3.5% Cr, 0.45-0.65% Mo), the γ' phase was suppressed by even 0.5% carbon dioxide, but cementite compounds

were invariably formed (Fig. 23a and b)

These controlled laboratory experiments clearly illustrate the lack of tolerance of the plasma nitrocarburizing process to minor variations in atmosphere condition. Accordingly, current industrial plasma nitrocarburizing practice, although meeting engineering mechanical property specifications, can be anticipated to show variations in microstructural characteristics.

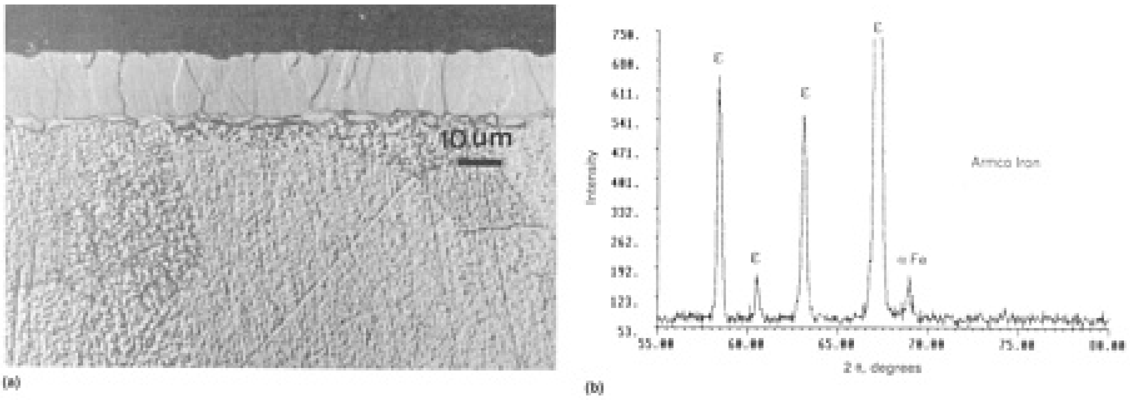

Fig. 21 Microstructure (a) of Armco iron plasma nitrocarburized at 570 °C (1060 °F) for 3 h at a gas pressure of 3.5 mbar. Gas mixture: 90 vol% N_2, 1 vol% CO_2, 9 vol% H_2. Etched in 1 mL mix of hydrochloric acid (HCl) and ethanol (1 part concentrated HCl + 10 parts ethanol) plus 99 mL 5% nital. (b) X-ray diffraction pattern of the compound layer of the sample

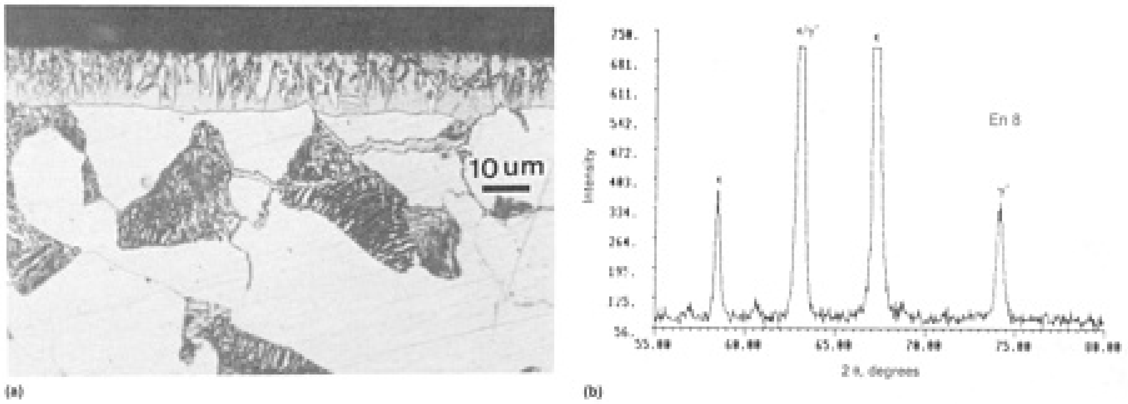

Fig. 22 Microstructure (a) of a plasma nitrocarburized EN8 steel sample with (b) the corresponding x-ray diffraction pattern. See Fig. 21 for processing details.

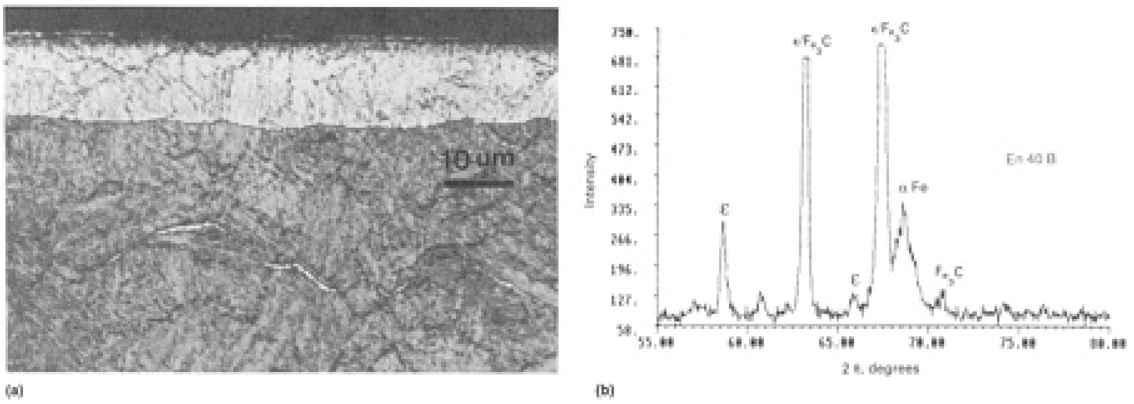

Fig. 23 Microstructure (a) of a plasma nitrocarburized EN40B steel sample with (b) the corresponding x-ray diffraction pattern. See Fig. 21 for processing details.

Industrial Plasma Nitrocarburizing

The maturity of plasma nitriding and nitrocarburizing equipment is reflected by the ability of suppliers to respond to the high reliability requirements of the automotive sector through the introduction of microprocessor-controlled modular units, such as that shown schematically in Fig. 24. As can be seen, the plasma-processing equipment has the following modules:

- Vacuum furnace
- Vacuum system
- Gas supply with gas mixing and pressure control system
- Electric power supply unit
- Microprocessor control unit

The total engineering and design of such equipment and the wide range of functions available in the microprocessor software gives high production reliability and makes it very easy for the operator to set the processing conditions. In a typical plasma nitrocarburizing unit, up to 24 programs can be stored for different applications and the equipment can be integrated in series in a manufacturing production line. In the equipment illustrated in Fig. 25, loads of 3000 automotive seat slider rails have been nitrocarburized automatically for more than 5 yr without any significant technical or metallurgical problems. Mixtures of hydrogen, nitrogen, and a carbon-bearing gas, such as methane or carbon dioxide are used for the nitrocarburizing process, which is carried out at 570 °C (1060 °F) to produce a compound layer of >5 μm and a surface hardness of ≥ 350 HV (Ref 56). The micro-processor-controlled unit ensures that the treatment schedules are undertaken in the correct sequence. Following nitrocarburizing, the workpieces are allowed to cool under controlled vacuum conditions.

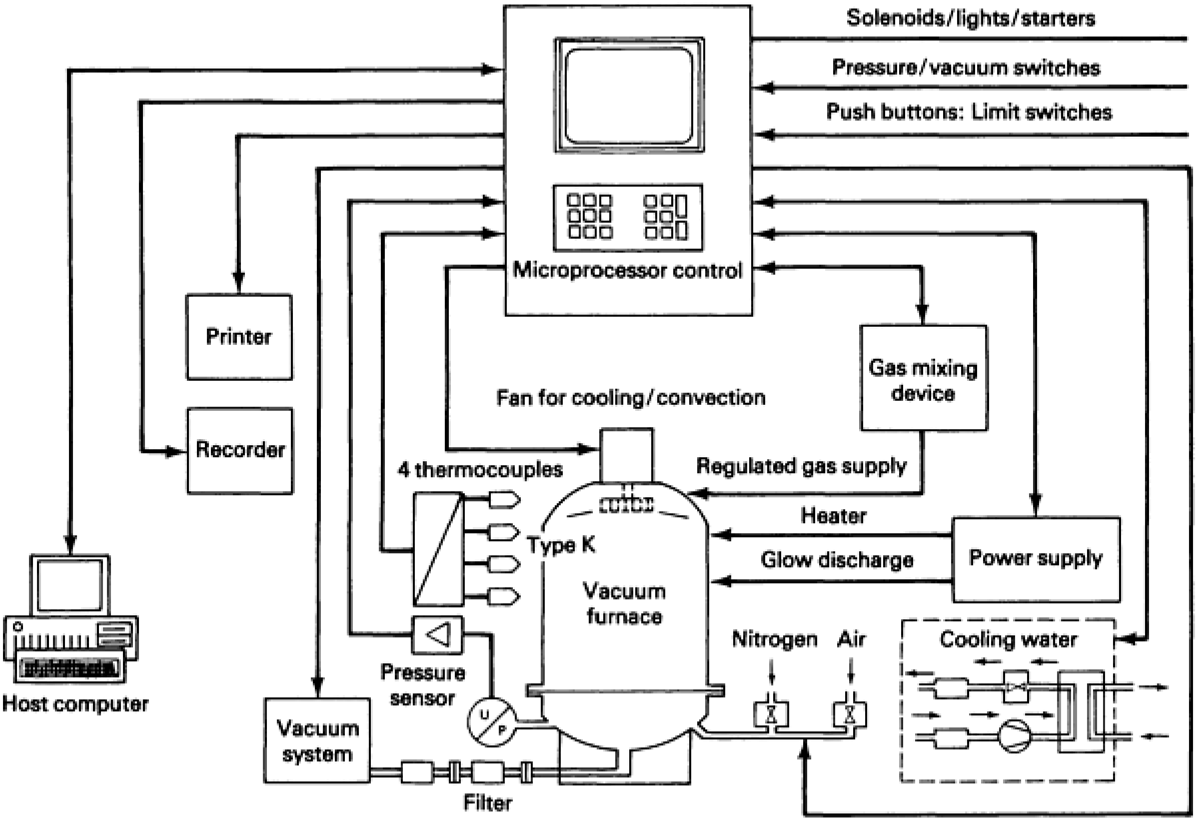

Fig. 24 Schematic of a multifunctional plasma nitriding installation. Source: Klockner IONON GmbH and Ref 55

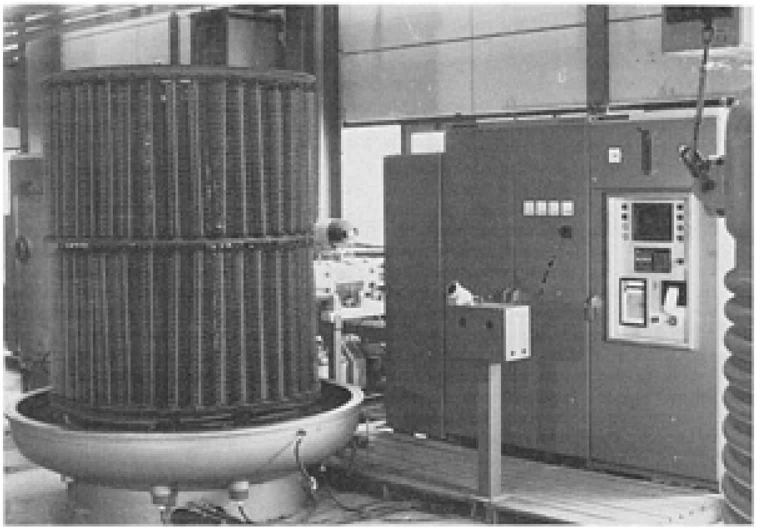

Fig. 25 Plasma nitrocarburizing installation for heat treating a load of 3000 automotive seat rails. Source: Klockner IONON GmbH and Ref 56

As a direct consequence of increased legislation designed to protect the environment, there is significantly growing interest in the plasma nitrocarburizing of sintered powder metallurgy (P/M) components. Traditionally, P/M components have been nitrocarburized using salt bath technology. This technique usually results in salt entrapment within the pores of the metallic structure. Frequently, these salts are highly toxic, and consequently there are handling problems and safe working procedures have to be employed.

A technical argument against the use of plasma nitrocarburizing has been the effect of retained lubricant on the character and stability of the glow-discharge plasma, thus effecting the reliability of the plasma technology when applied to sintered parts. Lubricants are added to powdered products in order to achieve optimum pressing conditions by the final forming operation after sintering. A method by which the lubricant can be satisfactorily removed prior to the P/M parts entering the vacuum chamber of the plasma unit is described in Ref 56. Using this method, it is now routinely possible to plasma nitrocarburize in one batch up to 4500 components, such as chain gear wheels, that have been manufactured by P/M (Ref 57). The microstructure of such a plasma nitrocarburized component is shown in Fig. 26. It is interesting to note that detailed examination shows that pores within the material, but close to the surface, also show the presence of the compound layer. The extent of the depth of such nitrocarburized pores is a function of the degree of interconnected porosity of the component, which is, in turn, a function of the pressing conditions. Such interconnected pores are capable of retaining lubricant and thus considerably enhance the reduction in wear rate of the treated components. Chain gear wheels have been plasma nitrocarburized to produce a compound layer with a typical thickness of 6 μm in a bell-type plasma furnace like that shown in Fig. 27. The chain gear wheels are stacked one on top of each other along an internal pipe that acts as an easy-to-handle jigging system (Fig. 28). Just the teeth area needs to be plasma nitrocarburized, and a simple masking arrangement ensures that the internal part of the gears remains untreated, as is required in the design specification.

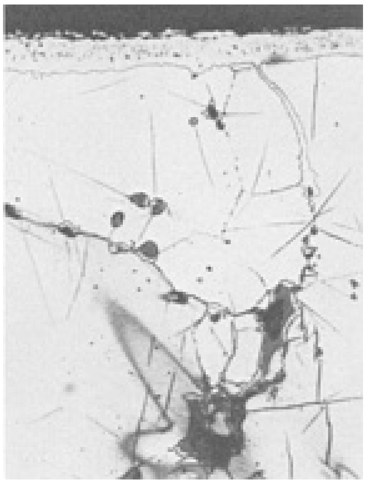

Fig. 26 Microstructure of a plasma nitrocarburized P/M steel (SINT-D35) with a compound layer thickness of 10 μm. Source: Klockner IONON GmbH and Ref 56

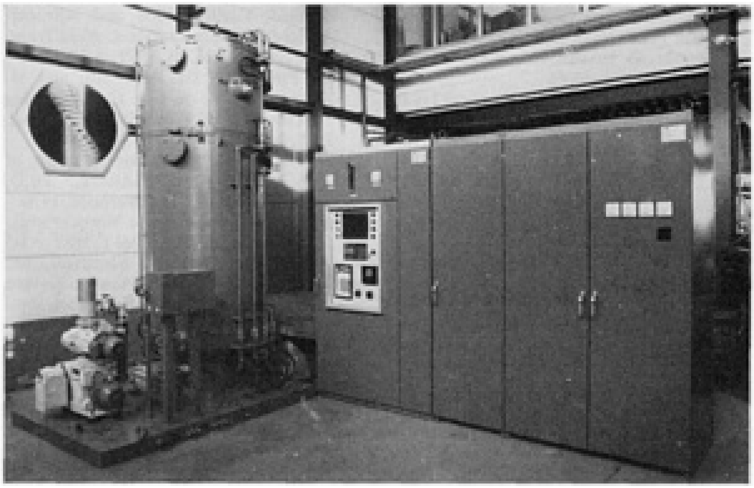

Fig. 27 Bell-type plasma installation 600 by 2200 mm diam for the processing of P/M chain gear wheels. Source: Klockner IONON GmbH and Ref 56

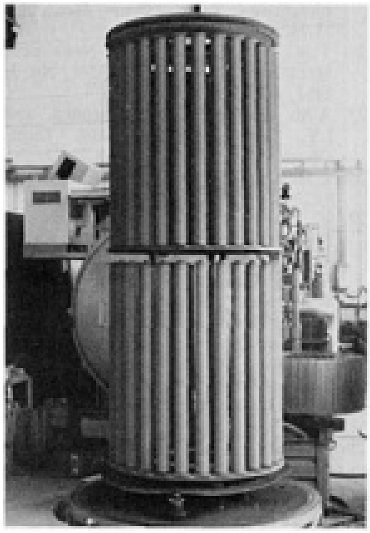

Fig. 28 Load of approximately 4500 P/M steel chain gear wheels after plasma nitrocarburizing. Source: Klockner IONON GmbH and Ref 56

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Boriding (Boronizing) of Steels

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Introduction

BORIDING, or boronizing, is a thermo-chemical surface hardening process that can be applied to a wide variety of ferrous, nonferrous, and cermet materials. The process involves heating well-cleaned material in the range of 700 to 1000 °C (1300 to 1830 °F), preferably for 1 to 12 h, in contact with a boronaceous solid powder (boronizing compound), paste, liquid, or gaseous medium. Other developments in thermochemical boriding include gas boriding techniques such as plasma boriding and fluidized bed boriding. There is a current trend toward the use of multicomponent boriding.

This article presents mainly the various media used for thermochemical boriding, their advantages, limitations, and applications. Physical and chemical vapor deposition (PVD and CVD), plasma spraying, and ion implantation are alternative nonthermo-chemical surface-coating processes for the deposition of boron or codeposition of boron and metallic element(s) onto a suitable metallic or nonmetallic substrate material. This article briefly describes the CVD process, which has emerged to be dominant among the metal boride deposition processes.

Characteristic Features of Boride Layers

During boriding, the diffusion and subsequent absorption of boron atoms into the metallic lattice of the component surface form interstitial boron compounds (Ref 1, 2, 3, 4, 5). The resulting layer may consist of either a single-phase boride or a polyphase boride layer. The morphology (Fig. 1), growth, and phase composition of the boride layer can be influenced by the alloying elements in the base material. The microhardness of the borided layer also depends strongly on the composition and structure of the boride layer and the composition of the base material (Table 1).

Table 1 Melting point and microhardness of different boride phases formed during boriding of different substrate materials

Substrate	Constituent phases in the boride layer	Microhardness of layer, HV or kg/mm^2	Melting point	
			°C	°F
Fe	FeB	1900-2100	1390	2535
	Fe_2B	1800-2000	. . .	. . .
Co	CoB	1850	. . .	. . .
	Co_2B	1500-l600	. . .	. . .
	Co_3B	700-800	. . .	. . .
Co-27.5 Cr	CoB	2200 (100 g)[a]	. . .	. . .
	Co_2B	~l550 (100 g)[a]	. . .	. . .
	Co_3B (?)	700-800	. . .	. . .
Ni	Ni_4B_3	1600	. . .	. . .
	Ni_2B	1500	. . .	. . .
	Ni_3B	900	. . .	. . .
Inco 100	. . .	1700 (200 g)[b]	. . .	. . .
Mo	Mo_2B	1660	2000	3630
	MoB_2	2330	~2100	~3810
	Mo_2B_5	2400-2700	2100	3810
W	W_2B_5	2600	2300	4170
Ti	TiB	2500	~1900	3450
	TiB_2	3370	2980	5395
Ti-6Al-4V	TiB		. . .	. . .
	TiB_2	3000 (100 g)[a]	. . .	. . .
Nb	NbB_2	2200	3050	5520
	NbB_4		. . .	. . .
Ta	Ta_2B		3200-3500	5790-6330
	TaB_2	2500	3200	5790
Hf	HfB_2	2900	3250	5880
Zr	ZrB_2	2250	3040	5500

(a) 100 g load.

(b) 200 g load. Sources: Ref 3, 7, 8

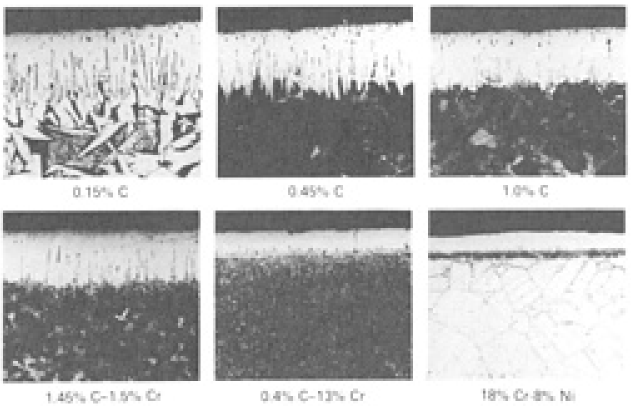


Fig. 1 Fig. 1Effect of steel composition on the morphology and thickness of the boride layer. Source: Ref 6

Advantages. Boride layers possess a number of characteristic features with special advantages over conventional case-hardened layers. One basic advantage is that boride layers have extremely high hardness values (between 1450 and 5000 HV) with high melting points of the constituent phases (Table 1). The typical surface hardness values of borided steels compared with other treatments and other hard materials are listed in Table 2. This clearly illustrates that the hardness of boride layers produced on carbon steels is much greater than that produced by any other conventional surface (hardening) treatments; it exceeds that of the hardened tool steel, hard chrome electroplate, and is equivalent to that of tungsten carbide.

Table 2 Typical surface hardness of borided steels compared with other treatments and hard materials

Material	Microhardness kg/mm^2 or HV
Boride mild steel	1600
Borided AISI H13 die steel	1800
Borided AISI A2 steel	1900
Quenched steel	900
Hardened and tempered H13 die steel	540-600
Hardened and tempered A2 die steel	630-700
High-speed steel BM42	900-9l0
Nitrided steels	650-1700
Carburized low-alloy steels	650-950
Hard chromium plating	1000-1200
Cemented carbides, WC + Co	1160-1820 (30 kg)
Al_2O_3 + ZrO_2 ceramic	1483(30 kg)
Al_2O_3 + TiC + ZrO_2 ceramic	1738 (30 kg)
Sialon ceramic	1569 (30 kg)
TiN	2000
TiC	3500
SiC	4000
B_4C	5000
Diamond	>10,000

Source: Ref 3

The combination of a high surface hardness and a low surface coefficient of friction of the borided layer also makes a significant contribution in combating the main wear mechanisms: adhesion, tribooxidation, abrasion, and surface fatigue (Ref 4, 9). This fact has enabled the mold makers to substitute easier-to-machine steels for the base metal and to still obtain wear resistance and antigalling properties superior to those of the original material (Ref 10). Figure 2 shows the effect of boriding on abrasive wear resistance of borided C45 steel, titanium, and tantalum as a function of number of revolutions (or stressing period) based on Faville test. Figure 3 shows the influence of steel composition on abrasive wear resistance.

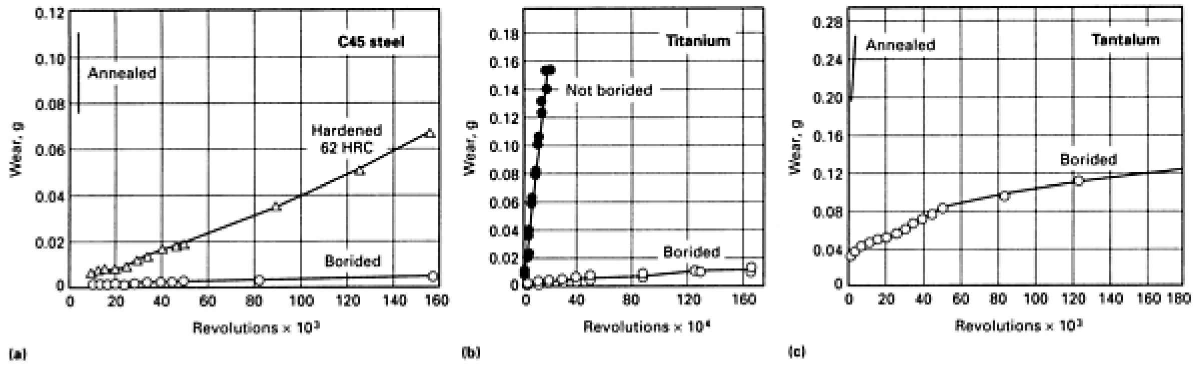


Fig. 2 Effect of boriding on the wear resistance (Faville test). (a) 0.45% C (C45) steel borided at 900 °C (1650 °F) for 3 h. (b) Titanium borided at 1000 °C (1830 °F) for 24 h. (c) Tantalum borided at 1000 °C (1830 °F) for 8 h. Source: Ref 11

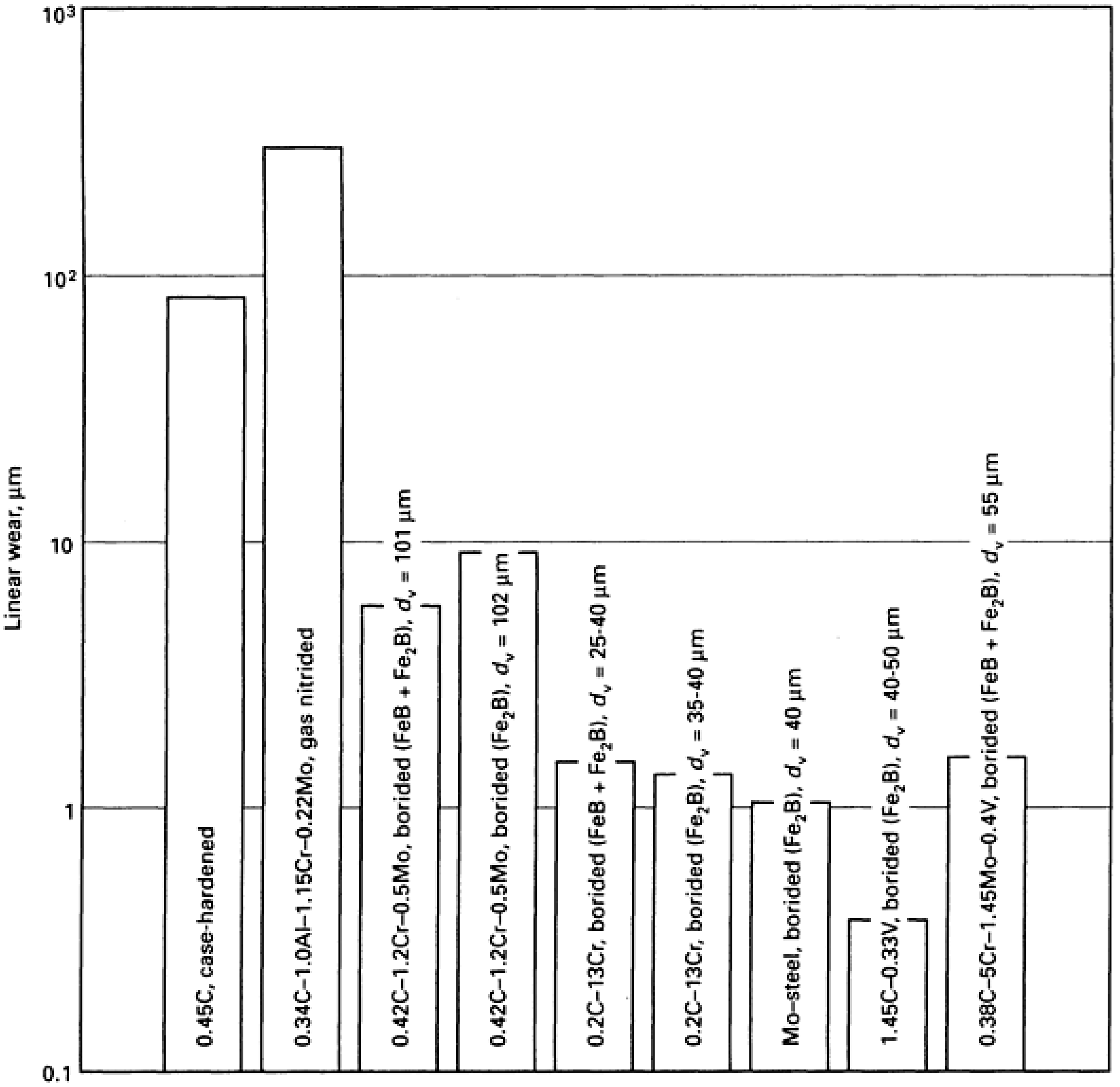
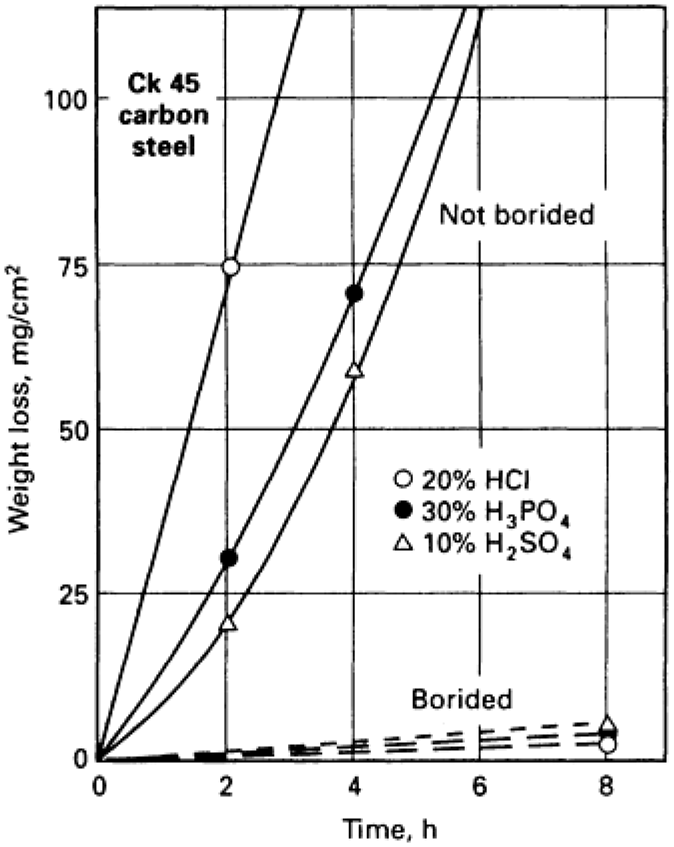


Fig. 3 Effect of steel composition (nominal values in wt%) on wear resistance under abrasive wear (d_v = thickness of the boride layer). Test conditions: DP-U grinding tester, SiC paper 220, testing time 6 min. Source: Ref 6, 9

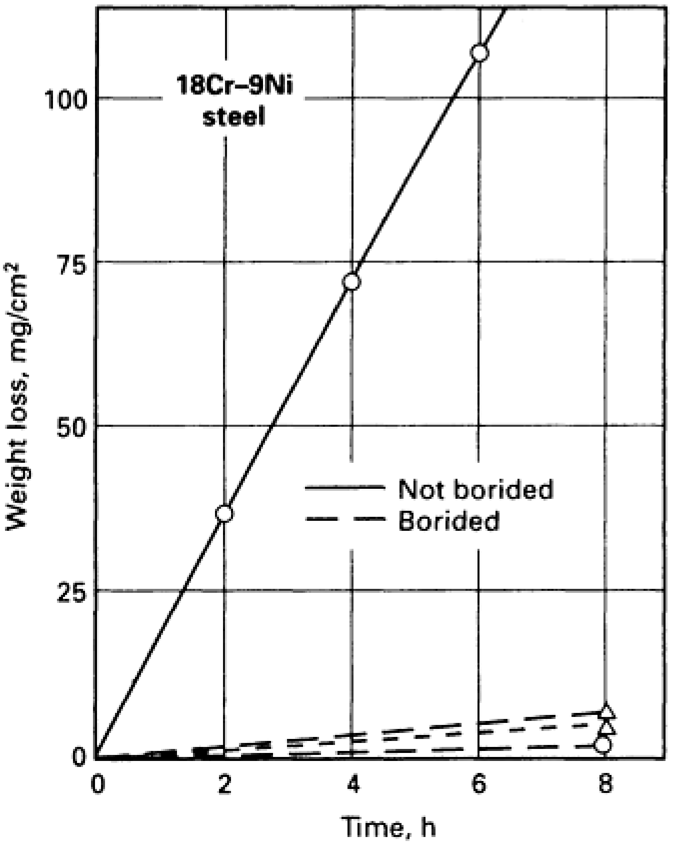
Other advantages of boriding include:

- Hardness of the boride layer can be retained at higher temperatures than, for example, that of nitrided cases

- A wide variety of steels, including through-hardenable steels, are compatible with the processes (Ref 12)
- Boriding, which can considerably enhance the corrosion-erosion resistance of ferrous materials in nonoxidizing dilute acids (Fig. 4) and alkali media, is increasingly used to this advantage in many industrial applications (Ref 4)
- Borided surfaces have moderate oxidation resistance (up to 850 °C, or 1550 °F) and are quite resistant to attack by molten metals
- Borided parts have an increased fatigue life and service performance under oxidizing and corrosive environments



(a)



(b)

Fig. 4 Corroding effect of mineral acids on boronized and nonboronized (a) 0.45% C (Ck 45) steel and (b) l8Cr-9Ni (X10CrNiTi18 9) steel at 56 °C (130 °F). Source: Ref 4, 13

Disadvantages of boronizing treatments are:

- The techniques are inflexible and rather labor intensive, making the process less cost effective than other thermochemical surface hardening treatments such as gas carburizing and plasma nitriding. Both gas carburizing and plasma nitriding have the advantage over boronizing because those two processes are flexible systems, offer reduced operating and maintenance costs, require shorter processing times, and are relatively easy to operate. It is, therefore, suited to engineering components that need high hardness and outstanding wear and corrosion resistance of the boride layers, and/or where cheaper labor is available (Ref 3)
- The growth (that is, the increase in volume) resulting from boronizing is 5 to 25% of the layer thickness (for example, a 25 μm, or 1000 μin., layer would have a growth of 1.25 to 6.25 μm, or 50 to 250 μin.); its magnitude depends on the base material composition but remains consistent for a given combination of material and treatment cycle. However, it can be predicted for a given part geometry and boronizing treatment. For treatment of precision parts, where little stock removal is permitted, an allowance of ~20 to 25% dimensional increase of the final boride layer thickness must be provided
- Partial removal of the boride layer for closer tolerance requirements is made possible only by a subsequent diamond lapping because conventional grinding causes fracture of the layer. Thus, precise boronizing is mostly practiced for components with a large cross-sectional area (Ref 3)
- Boriding of most steels provides a marginal increase, if any, in the bending fatigue endurance limit, although some improvement in the corrosion-fatigue strength has been noticed
- In general, the rolling contact fatigue properties of borided alloy steel parts are very poor compared to carburized and nitrided steels at high contact loads (2000 N, or 450 lbf). This is why boronizing treatments of gears are limited to those screw designs where transverse loading of gear teeth is minimized (Ref 3)
- There is frequently a need to harden and temper the tool after boriding (Ref 14), which requires a vacuum or inert atmosphere to preserve the integrity of the boride layer

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Boriding of Ferrous Materials

Unlike carburizing treatment on ferrous materials, where there is a gradual decrease in composition from the carbon-rich surface to the substrate, the boriding of ferrous materials results in the formation of either a single-phase or double-phase layer of borides with definite compositions. The single-phase boride layer consists of Fe_2B, while the double-phase layer consists of an outer dark-etching phase of FeB and an inner bright-etching phase of Fe_2B. The formation of either a single or double phase depends on the availability of boron (Ref 15).

Characteristics of FeB and Fe_2B Layers. The formation of a single Fe_2B phase (with a sawtooth morphology due to preferred diffusion direction) is more desirable than a double-phase layer with FeB. The boron-rich FeB phase is considered undesirable, in part, because FeB is more brittle than the iron subboride Fe_2B layer. Also, because FeB and Fe_2B are formed under tensile and compressive residual stresses, respectively, crack formation is often observed at or in the neighborhood of the FeB/Fe_2B interface of a double-phase layer. These cracks may lead to flaking and spalling when a mechanical strain is applied (Ref 5) or even separation (Fig. 5) when a component is undergoing a thermal and/or mechanical shock. Therefore, the boron-rich FeB phase should be avoided or minimized in the boride layer (Ref 5).

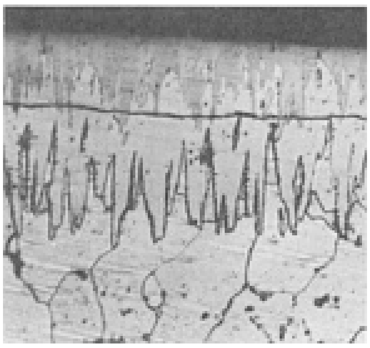

Fig. 5 Separation of two-phase boride layer on a low-carbon (St 37) steel (borided at 900 °C, or 1650 °F, for 4 h) caused by grinding with a cutting-off disk. 200×. Source: Ref 13

It has also been reported that the tribological properties depend on the microstructure of the boride layer. The dual-phase FeB-Fe_2B layers are not inferior to those of monophase Fe_2B layers, provided that the porous surface zone directly beneath the surface is removed (Ref 16). Alternatively, a thinner layer is favored because of less development of brittle and porous surface-zone formation and flaking.

Typical properties of the FeB phase are:

- Microhardness of about 19 to 21 GPa (2.7×10^6 to 3.0×10^6 psi)
- Modulus of elasticity of 590 GPa (85×10^6 psi)
- Density of 6.75 g/cm^3 (0.244 lb/in.^{3})
- Thermal expansion coefficient of 23 ppm/°C (13 ppm/°F) between 200 and 600 °C (400 and 1100 °F) (Ref 6 and 17)
- Composition with 16.23 wt% boron
- Orthorhombic crystal structure with 4 iron and 4 boron atoms per unit cell
- Lattice parameters: a = 4.053 Å, b = 5.495 Å, and c = 2.946 Å

Layers of Fe_2B. The formation of single-phase Fe_2B layers with a sawtooth morphology is desirable in the boriding of ferrous materials (Ref 18). A single Fe_2B phase can be obtained from a double FeB-Fe_2B phase by a subsequent vacuum or salt bath treatment for several hours above 800 °C (1470 °F), which may be followed by oil quenching to increase substrate properties (Ref 19).

Typical properties of Fe_2B are:

- Microhardness of about 18 to 20 GPa (2.6×10^6 to 2.9×10^6 psi)
- Modulus of elasticity of 285 to 295 GPa (41×10^6 to 43×10^6 psi)
- Thermal expansion coefficient of 7.65 ppm/°C (4.25 ppm/°F) and 9.2 ppm/°C (5.1 ppm/°F) in the range of 200 to 600 °C (400 to 1100 °F) and 100 to 800 °C (200 to 1500 °F), respectively (Ref 6 and 17)
- Density of 7.43 g/cm^3 (0.268 lb/in.^{3})

- Composition with 8.83 wt% boron
- Body-centered tetragonal structure with 12 atoms per unit cell
- Lattice parameters: a = 5.078 Å and c = 4.249 Å

The solubility of boron in ferrite and austenite is very small (<0.008% at 900 °C, or 1650 °F) according to the Fe-B phase diagram (Ref 20). According to Brown *et al.* (Ref 21) and Nicholson (Ref 22), the phase diagram exhibits an $\alpha/\gamma/Fe_2B$ peritectoid reaction at about 912 °C (1674 °F), based on their findings of higher solubility of boron in ferrite than in austenite at the reaction temperature. However, later work revealed a higher solubility of boron in austenite compared to that in ferrite, thereby suggesting the reaction is eutectoid in nature (Ref 23).

The boriding process consists of two types of reaction (Ref 6). The first reaction takes place between the boron-yielding substance and the component surface. The nucleation rate of the particles at the surface is a function of the boriding time and temperature. This produces a thin, compact boride layer.

The subsequent second reaction is diffusion controlled, and the total thickness of the boride layer growth at a particular temperature can be calculated by the simple formula:

$$d=k\sqrt{t} \qquad \textbf{(Eq 1)}$$

where d is the boride layer thickness in centimeters; k is a constant, depending on the temperature; and t is the time in seconds at a given temperature. The diffusivity of boron at 950 °C (1740 °F) is 1.82×10^{-8} cm^2/s for the boride layer and 1.53×10^{-7} cm^2/s for the diffusion zone. As a result, the boron-containing diffusion zone extends more than 7 times the depth of boride layer thickness into the substrate (Ref 24). It has been proposed that a concentration gradient provides the driving force for diffusion-controlled boride laver growth (Ref 25).

Diffusion case thicknesses range to approximately 0.13 mm (0.005 in.) for ferrous alloys, depending on alloy compositions and configurations. A lower case depth is required for the high-carbon and/or high-alloy tool steels, whereas higher case depths may be needed for the low- or medium-carbon steels. When case depth is about 320 to 350 μm, subsequent heat treatment is not performed.

Ferrous Materials for Boriding. With the exception of aluminum- and silicon-bearing steels, industrial boriding can be carried out on most ferrous materials such as structural steels; case-hardened, tempered, tool, and stainless steels; cast steels; Armco (commercially pure) iron; gray and ductile cast irons; and sintered iron and steel (Ref 26). Because boriding is conducted in the austenitic range, air-hardening steels can be simultaneously hardened and borided. Water-hardening grades are not borided because of the susceptibility of the boride layer to thermal shock. Similarly, resulfurized and leaded steels should not be used because they have a tendency toward case spalling and case cracking. Nitrided steels should not be used because of their sensitivity to cracking (Ref 27).

Influence of Alloying Elements. The mechanical properties of the borided alloys depend strongly on the composition and structure of the boride layers. The characteristic sawtooth configuration of the boride layer is dominant with pure iron, unalloyed low-carbon steels, and low-alloy steels. As the alloying element and/or carbon content of the substrate steel is increased, the development of a jagged boride/substrate interface is suppressed, and for high-alloy steels a smooth interface is formed (Ref 28 and Fig. 1). Alloying elements mainly retard the boride layer thickness (or growth) caused by restricted diffusion of boron into the steel because of the formation of a diffusion barrier. Figure 6 shows the effect of alloying additions in steel on boride layer thickness (Ref 29, 30).

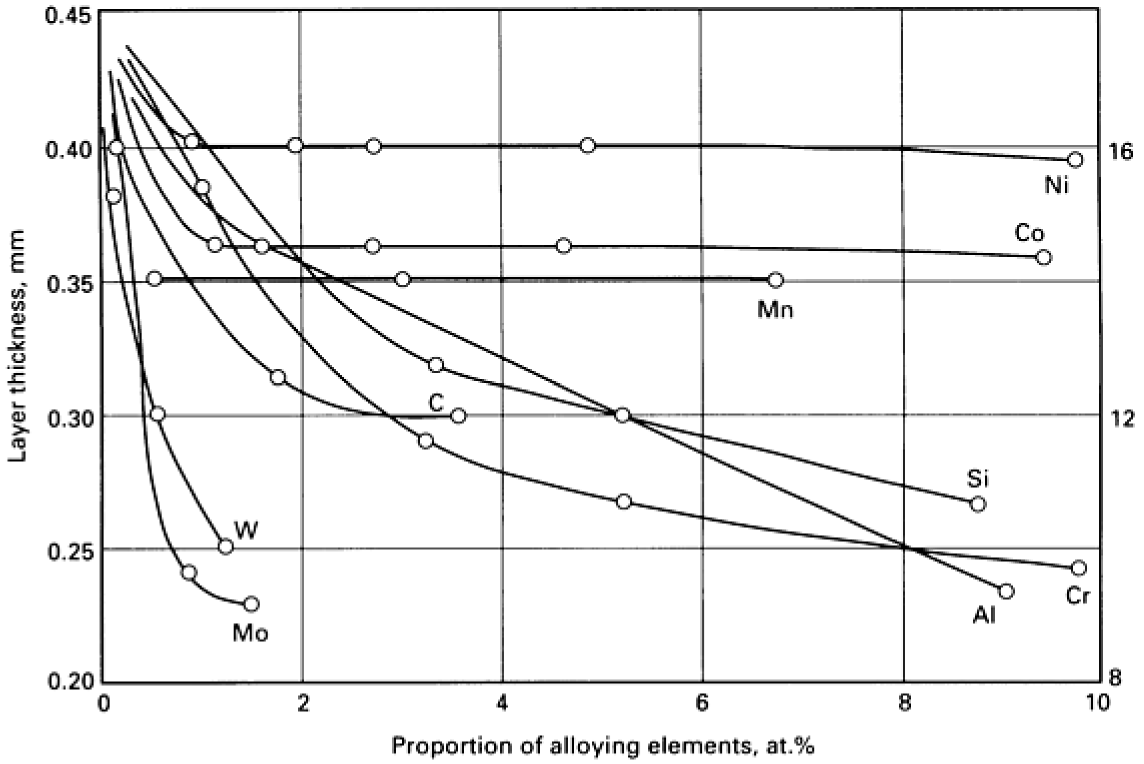

Fig. 6 Effect of alloying elements in steel on boride layer thickness. Source: Ref 29, 30

Carbon does not dissolve significantly in the boride layer and does not diffuse through the boride layer. During boriding carbon is driven (or diffused away) from the boride layer to the matrix and forms, together with boron, borocementite $Fe_3(B,C)$ [or more appropriately, $Fe_3(B_{0.67}\ C_{0.33})$ in the case of Fe-0.08% C steel] as a separate layer between Fe_2B and the matrix (Ref 31, 32).

Like carbon, silicon and aluminum are not soluble in the boride layer, and these elements are pushed from the surface by boron and are displaced ahead of the boride layer into the substrate, forming iron silicoborides--$FeSi_{0.4}B_{0.6}$ and Fe_5SiB_2--underneath the Fe_2B layer. Steels containing high contents of these ferrite-forming elements should not be used for boriding because they reduce the wear resistance of normal boride layer (Ref 1); they produce a substantially softer ferrite zone beneath the boride layer than that of the core (Ref 33). At higher surface pressure, this type of layer buildup results in the so-called egg shell effect, that is, at greater thicknesses extremely hard and brittle boride layer penetrates into the softer intermediate layer and is consequently destroyed (Ref 34).

A reduction in both the degree of interlocking tooth structure and of boride depth can occur with high-nickel-containing steels. Nickel has been found to concentrate below the boride layer; it enters the Fe_2B layer and in some instances promotes the precipitation of Ni_3B from the FeB layer (Ref 9, 35, 36, 37). It also segregates strongly to the surface from the underlying zone corresponding to the Fe_2B layer. This is quite pronounced in both Fe-14Ni and austenitic stainless steels. Consequently, gas boronizing of austenitic stainless steels appears to be a more appropriate treatment for producing a low-porosity, homogeneous, single-phase Fe_2B layer because of the lower boron activity of the gaseous mixture (Ref 37).

Chromium considerably modifies the structure and properties of iron borides. As the chromium content in the base material increases, progressive improvements in the following effects are observed: formation of boron-rich reaction products, decrease in boride depth, and flattening or smoothening of the coating/substrate interface (Ref 38). A reduction of boride thickness has also been noticed in ternary Fe-l2Cr-C steels with increasing carbon content (Ref 37). Manganese, tungsten, molybdenum, and vanadium also reduce the boride layer thickness and flatten out the tooth-shaped morphology in carbon steel. The distribution of titanium, cobalt, sulfur, and phosphorus in the boride layer has not been well established.

Heat Treatment after Boriding. Borided parts can be quench hardened in air, oil, salt bath, or polymer quenchant and subsequently tempered. Heating to the hardening temperature should be carried out in an oxygen-free protective atmosphere or in a neutral salt bath (Ref 6).

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Boriding of Nonferrous Materials

Nonferrous materials such as nickel-, cobalt-, and molybdenum-base alloys, as well as refractory metals and their alloys and cemented carbides can be borided. Copper cannot; therefore, it provides a good stopping-off material. Of special interest is the boriding of nickel alloys and titanium and its alloys. Usually, boriding of nickel plate is done in gaseous BCl_3-H_2-Ar mixture in the temperature range of 500 to 1000 °C (930 to 1830 °F) (Ref 7), whereas Permalloy is pack

borided with 85% B_4C and 15% Na_2CO_3, or 95% B_4C and 5% $Na_2B_4O_7$ powder mixture at 1000 °C (1830 °F) for 6 h in H_2 atmosphere.

Boriding of titanium and its alloys is carried out preferably between 1000 and 1200 °C (1830 and 2200 °F) Here pack boriding in oxygen-free amorphous boron in combination with high-vacuum (0.0013 Pa, or 10^{-5} torr) and high-purity argon atmosphere or gas boriding with H_2-BCl_3-Ar gas mixture is preferred. The microhardness readings of boride layers formed on titanium and refractory metals are very high compared to those formed on cobalt and nickel (see Table 1). The wear properties of sintered carbides can be increased by boriding because of the acceptance of boron by soft cobalt and nickel binders (Ref 27).

Boride layers formed on tantalum, niobium, tungsten, molybdenum, and nickel do not exhibit tooth-shaped morphology as with titanium. When cemented carbides (such as WC-Co wire-drawing dies) are commercially pack borided with a powder mixture containing 40% B_4C, 45% SiC, and 5% KBF_4, three distinct zones are found to be formed in the boride layer comprising the exterior (zone I), intermediate (zone II), and interior (zone III) regions (Table 3).

Table 3 Three distinct zones formed in borided cemented carbide materials

Zone	Reference 38	Reference 7
I	CoB, W_2B_5, WC	CoB, WC
II	W_2CoB_2, WCoB, WC	Co_2B, WC
III	$W_2Co_2B_6$, WC, Co	Co_3B, WC

(a) Sources: Ref 3, 8, 39

Effects of Alloying Elements. As in iron and steel, suitable alloying additions raise the hardness of the boride layer formed on these metals; this is presumably caused by the formation of solid-solution borides.

Additions of alloying elements in nickel, cobalt, and titanium retard the rate of boride layer growth, and in the case of multiphase layers, the proportion of boride layer with high boron content (for example, TiB_2 in titanium) increases. The tooth-shaped morphologies in the cases of cobalt and titanium are also retarded with alloying addition, and the layers appear more uniform (Ref 11).

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Thermochemical Boriding Techniques

Because extensive investigations have been carried out on boriding of ferrous materials, the techniques described below focus mainly on the boriding of ferrous materials.

Pack boriding (Ref 40, 41, 42) is the most widely used boriding process because of its relative ease of handling, safety, and the possibility of changing the composition of the powder mix, the need for limited equipment, and the resultant economic Savings (Ref 1). The process involves packing the annealed, cleaned, smooth parts in a boriding powder mixture contained in a 3 to 5 mm (0.1 to 0.2 in.) thick, heat-resistant steel box so that surfaces to be borided are covered with an approximately 10 to 20 mm (0.4 to 0.8 in.) thick layer. Many different boriding compounds have been used for pack boriding. They include solid boron-yielding substances, diluents, and activators.

The common boron-yielding substances are boron carbide (B_4C), ferroboron, and amorphous boron; the last two have greater boron potential, provide a thicker layer, and are more expensive than B_4C (Ref 42). Silicon carbide (SiC) and alumina (Al_2O_3) serve as diluents, and they do not take part in the reaction. However, SIC controls the amount of boron and prevents caking of the boronizing agent. $NaBF_4$, KBF_4, $(NH_4)_3BF_4$, NH_4Cl, Na_2CO_3, BaF_2, and $Na_2B_4O_7$ are the boriding activators. There are special proprietary brands of boriding compounds, such as different grades of Ekabor, available on the market that can be used with confidence.

Typical compositions of commercial solid boriding powder mixtures are:

- 5% B_4C, 90% SiC, 5% KBF_4
- 50% B_4C, 45% SiC, 5% KBF_4
- 85% B_4C, 15% Na_2CO_3
- 95% B_4C, 5% $Na_2B_4O_7$
- 84% B_4C, 16% $Na_2B_4O_7$
- Amorphous boron (containing 95 to 97% B)
- 95% amorphous boron, 5% KBF_4

The parts conforming to the shape of the container are packed (Fig. 7), covered with a lid, which rests inside the container and is weighted with an iron slug or stone to ensure an even trickling of the boriding agent during the boriding treatment. It is then heated to the boriding temperature in an electrically heated box or pit furnace with open or covered heating coils or a muffle furnace for a specified time. The container should not exceed 60% of the furnace chamber volume. In principle, boriding should be accomplished in such a way that high internal stresses are relieved, which in turn, eliminates cracks or spalling. With the packing process, the powder may be reused by blending with 20 to 50 wt% of fresh powder mixture. In this case, the powder should be discarded after 5 or 6 cycles.

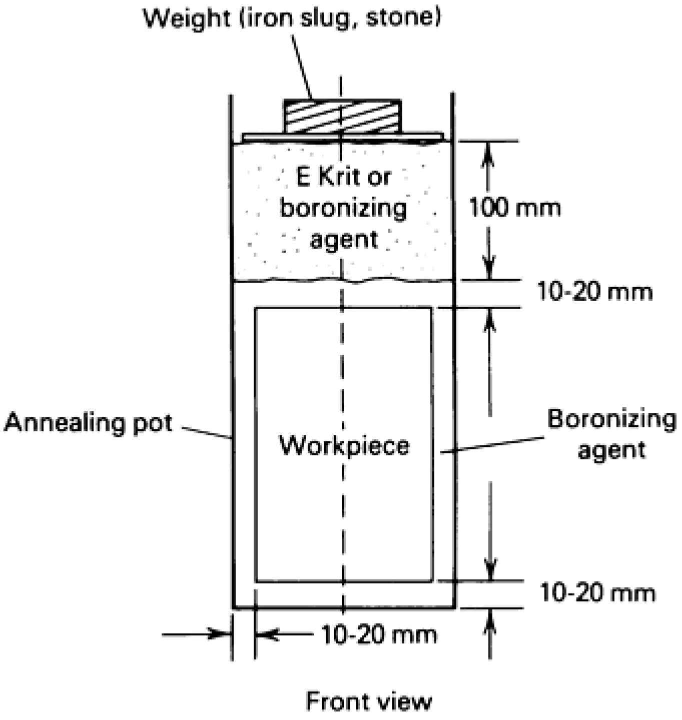

Fig. 7 Diagram of the packing of a single geometrical part in a pack boriding box. Source: Ref 1

Case Depth. The thickness of the boride layer depends on the substrate material being processed, boron potential of the boronizing compound (Fig. 8), boronizing temperature, and time (Fig. 9). In ferrous materials, the heating rate especially between 700 °C (1300 °F) and the boriding temperature (800 to 1000 °C, or 1470 to 1830 °F) should be high in order to minimize the formation of FeB (Ref 6).

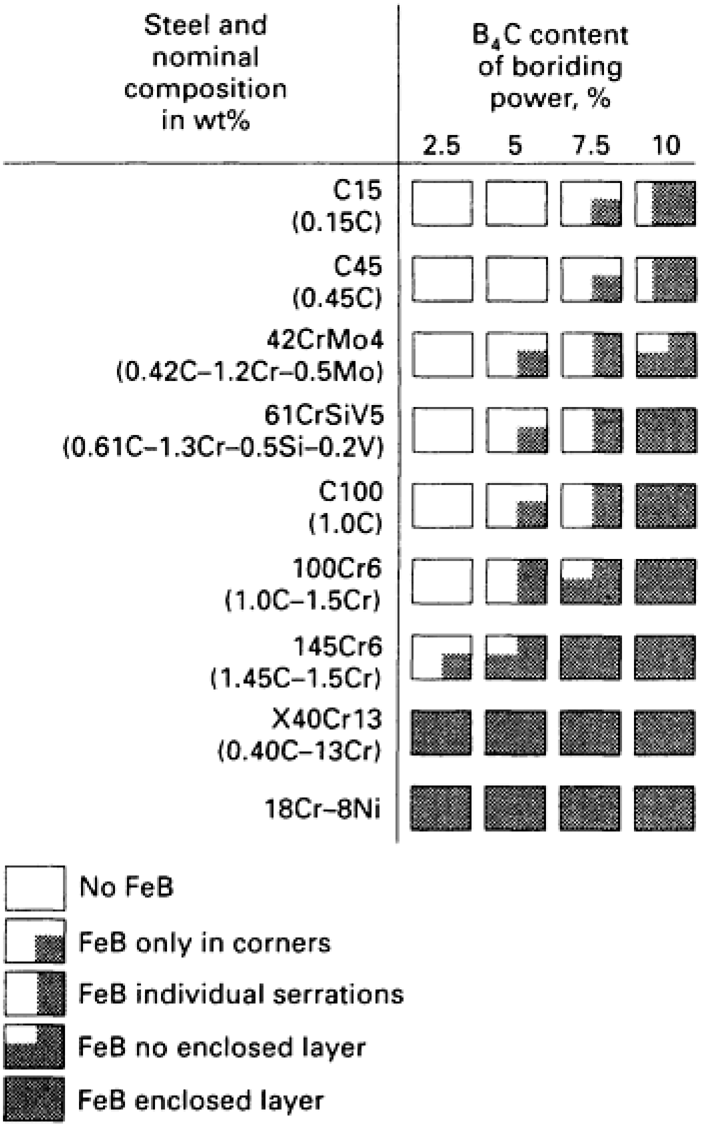

Fig. 8 Diagram showing the influence of the B_4C content of the boriding powder on the proportion of FeB phase in the boride layer of various steels borided with pack powder at 900n °C (1650 °F) for 5 h. Source: Ref 11

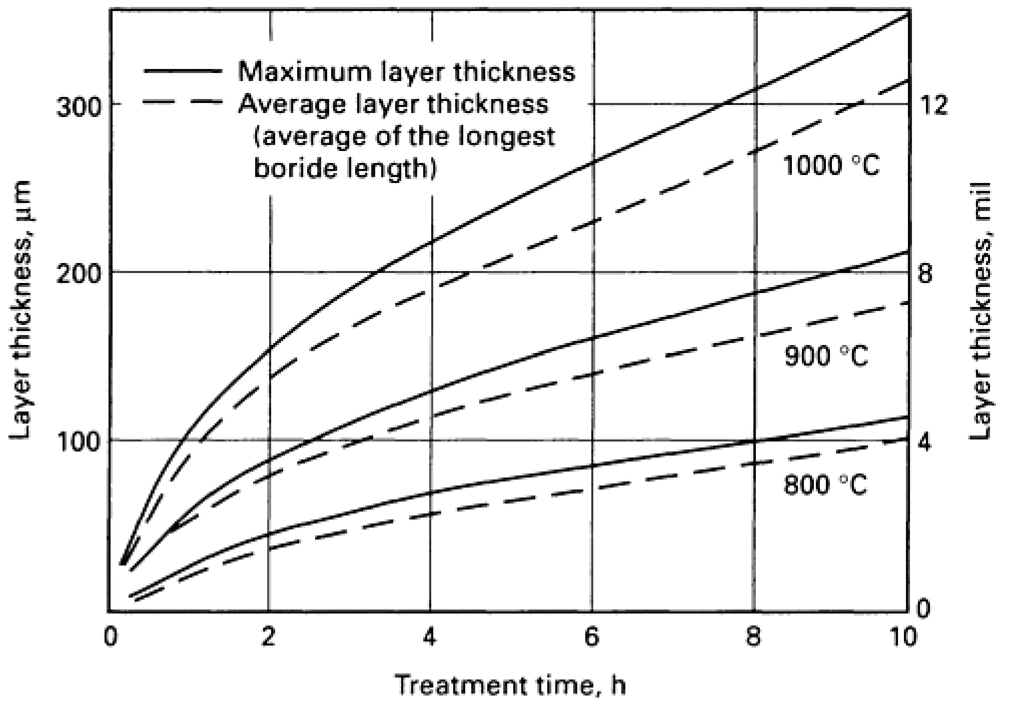

Fig. 9 Effect of pack boriding temperature and time on the boride layer thickness in a low-carbon (Ck 45) steel.

Source: Ref 26

It is usual practice to match the case depth with the intended application and base material. As a rule, thin layers (for example, 15 to 20 μm) are used for protection against adhesive wear (such as chipless shaping and metal-stamping dies and tools), whereas thick layers are recommended to combat erosive wear (for example, extrusion tooling for plastics with abrasive fillers and pressing tools for the ceramic industry). The commonly produced case depths are 0.05 to 0.25 mm (0.002 to 0.01 in.) for low-alloy and low-carbon steels and 0.025 to 0.076 mm (0.001 to 0.003 in.) for high-alloy steels. However, case depths >0.089 mm (>0.0035 in.) are uneconomical for highly alloyed materials such as stainless steels and some tool steels (Ref 27).

Borudif Process. In another modified pack boriding treatment, called the Borudif process, steel parts are packed in a 1:4 mixture of B_4C-SiC, and the moderate activator, BF_3 plus $(BOF)_3$ gas (formed by passing BF_3 through silica heated to above 450 °C, or 840 °F), is passed through the pack at 850 to 1100 °C (1560 to 2000 °F) for 4 h (Ref 43). The process offers a wide range of boriding potential because of the easy control of $(BOF)_3$ gas concentration that facilitates the treatment of a wide variety of substrate materials (Ref 43).

Paste boriding is used commercially when pack boronizing is difficult, more expensive, or time consuming. In this process, a paste of 45% B_4C (grain size 200 to 240 μm) and 55% cryolite (Na_3AlF_6, flux additive, Ref 5), or conventional boronizing powder mixture (B_4C-SiC-KBF_4) in a good binding agent (such as nitrocellulose dissolved in butyl acetate, aqueous solution of methyl cellulose, or hydrolyzed ethyl silicate) is repeatedly applied (that is, brushed or sprayed) at intervals over the entire or selected portion of parts until, after drying, a layer about 1 to 2 mm (0.04 to 0.08 in.) thick is obtained. Subsequently, the ferrous materials are heated (say at 900 °C, or 1650 °F, for 4 h) inductively, resistively, or in a conventional furnace to 800 to 1000 °C (1470 to 1830 °F) for 5 h. In this process, a protective atmosphere (for example, argon, cracked NH_3, or N_2) is necessary. A layer in excess of 50 μm thickness may be obtained after inductively or resistively heating to 1000 °C (1830 °F) for 20 min (Fig. 10). This process is of special interest for large components or for those requiring partial (or selective) boriding (Ref 6).

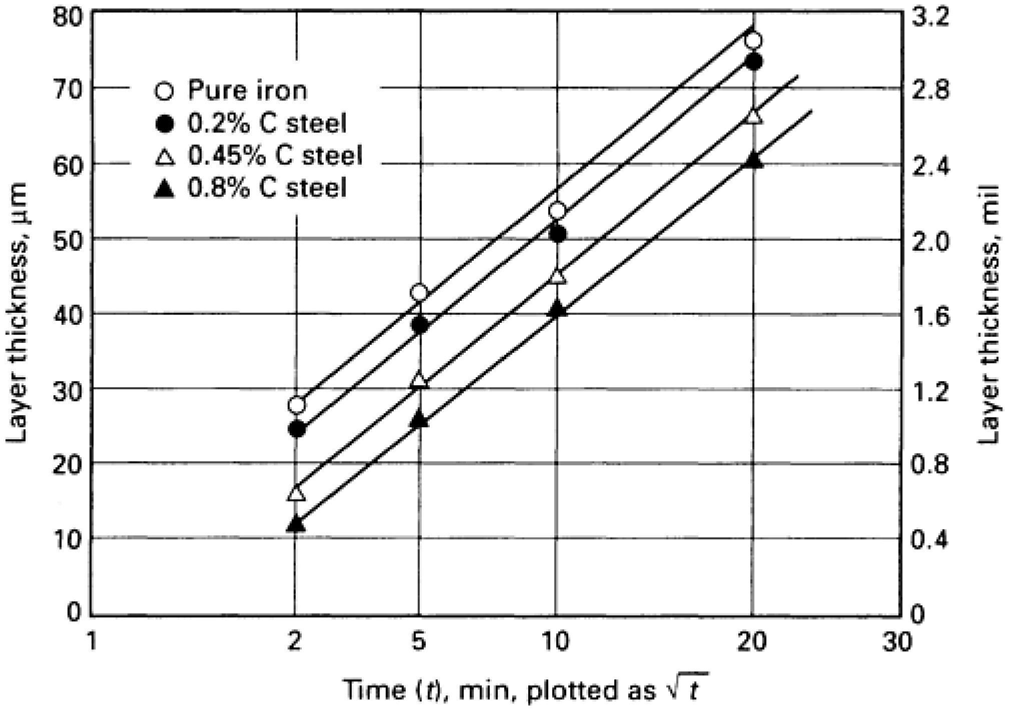

Fig. 10 A linear relationship between boride layer thickness and $\sqrt{time}$ for iron and steel boronized with B_4C-$Na_2B_4O_7$-Na_3AlF_6-based paste at 1000 °C (1830 °F). Source: Ref 40

Liquid boriding is grouped into electroless and electrolytic salt bath processes. These processes have several disadvantages:

- Removal of excess salt and unreacted boron is essential after the treatment; this step may prove to be expensive and time consuming
- To achieve boronizing reproducibility, bath viscosity is not allowed to increase. This is done by

recharging with salt, which involves high maintenance costs

- In some situations protection from corrosive fumes may be required

Electroless salt bath boriding of ferrous materials is carried out in a borax-based melt at about 900 to 950 °C (1650 to 1750 °F), to which about 30 wt% B_4C is added (Ref 44). The boronizing action can be further improved by replacing up to 20 wt% B_4C with ferroaluminum because it is a more effective reductant. However, superior results have been found by using a salt bath mixture containing 55% borax, 40 to 50% ferroboron, and 4 to 5% ferroaluminum (Ref 45). It has also been shown that 75:25 KBF_4-KF salt bath can be used at temperature below 670 °C (1240 °F) for boronizing nickel alloys, and at higher temperatures for ferrous alloys, to develop the desired boride layer thickness.

Electrolytic Salt Bath Boriding. In this process, the ferrous part acting as the cathode and a graphite anode are immersed in the electrolytic molten borax at 940 °C (1720 °F) for 4 h using a current density of about 0.15 A/cm^2 (Ref 46). The parts are then air cooled. In general, the parts are rotated during the treatment to obtain a uniform layer. A high current density produces a thin coating on low-alloy steels in a short time. For high-alloy steels of greater thickness, lower current densities are required for a longer time (Ref 47).

In the fused state tetraborate decomposes into boric acid and nascent oxygen.

$$B_4O_7 + 2e = 2B_2O_3 + O \qquad \textbf{(Eq 2)}$$

Simultaneously, sodium ions, after being neutralized in the vicinity of cathode, react with boric acid to liberate boron.

$$6\ Na + B_2O_3 = 3\ Na_2O + 2B \qquad \textbf{(Eq 3)}$$

In this manner, a high boriding potential is established near the cathode region. Other satisfactory electrolytic salt bath compositions include:

- KBF_4-LiF-NaF-KF mixture for parts to be treated at 600 to 900 °C (1100 to 1650 °F) (Ref 47)
- 20KF-30NaF-50LiF-0.7BF_2 mixture (by mole %) at 800 to 900 °C (1470 to 1650 °F) in 90N_2-10H_2 atmosphere
- 9:1 (KF-LiF)-KBF_4 mixture under argon atmosphere (Ref 48)
- KBF_4-NaCl mixture at 650 °C (1200 °F) (Ref 49)
- 90(30LiF + 70KF)-10KBF_4 mixture at 700 to 850 °C (1300 to 1560 °F)
- 80$Na_2B_4O_7$-20NaCl at 800 to 900 °C (1470 to 1650 °F) (Ref 50)

Gas boriding may be accomplished with:

- Diborane (B_2H_6)-H_2 mixture
- Boron halide-H_2/or (75:25 N_2-H_2) gas mixture
- Organic boron compounds such as $(CH_3)_3B$ and $(C_2H_5)_3B$

Boronizing with B_2H_6-H_2 mixture is not commercially viable due to the high toxic and explosive nature of diborane (Ref 1, 3). When organic boron compounds are used, carbide and boride layers form simultaneously. Because BBr_3 is expensive and is difficult to handle (with violent reactions with water), and because BF_3 requires high reduction temperature (due to its greater stability) and produces HF fumes, BCl_3 remains the attractive choice for gas boriding.

When parts are gas borided in a dilute (1:15) BCl_3-H_2 gas mixture at a temperature of 700 to 950 °C (1300 to 1740 °F) and a pressure up to 67 kPa (0.67 bar), a boride layer 120 to 150 μm thick is reported to be produced at 920 °C (1690 °F) in 2 h (Ref 51). Recent work has suggested the use of 75:25 N_2-H_2 gas mixture instead of H_2 gas for its better performance because of the production of boride layers with minimum FeB content. The latter phase can be easily

eliminated during the subsequent diffusion treatment before hardening (Ref 52). This process can be applied to titanium and its alloys as well.

Plasma Boriding. Both mixtures of B_2H_6-H_2 and BCl_3-H_2-Ar may be used successfully in plasma boronizing (Ref 53, 54). However, the former gas mixture can be applied to produce boride layer on various steels at relatively low temperatures such as 600 °C (1100 °F), which is impossible with a pack or liquid boronizing process (Ref 55). It has been claimed that plasma boriding in a mixture of BCl_3-H_2-Ar gases shows good features such as better control of BCl_3 concentration, reduction of the discharge voltage, and higher microhardness of the boride films (Ref 56). Figure 11 shows a schematic layout of a plasma boriding facility.

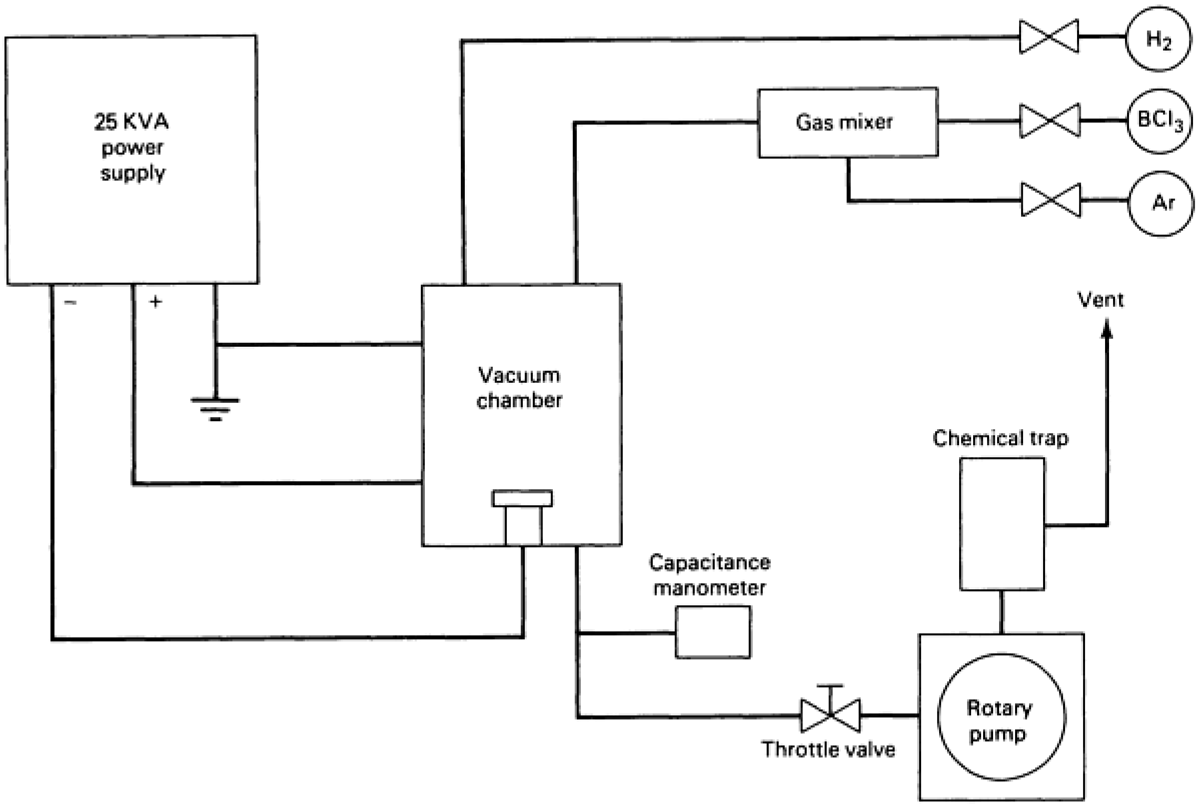

Fig. 11 Layout of plasma boronizing facility. Source: Ref 19

The dual-phase layer is characterized by visible porosity, occasionally associated with a black boron deposit. This porosity, however, can be minimized by increasing the BCl_3 concentration. Boride layers up to 200 μm in thickness can be produced in steels after 6 h treatment at a temperature of 700 to 850 °C (1300 to 1560 °F) and a pressure of 270 to 800 Pa (2 to 6 torr) (Ref 57).

Advantages of this process are:

- Control of composition and depth of the borided layer
- Increased boron potential compared to conventional pack boronizing
- Finer plasma-treated boride layers
- Reduction in temperature and duration of treatment
- Elimination of high-temperature furnaces and their accessories
- Savings in energy and gas consumption

The only disadvantage of the process is the extreme toxicity of the atmosphere employed. As a result, this process has not gained commercial acceptance. To avoid the above shortcoming, boriding from paste (containing a mixture of 60% amorphous boron and 40% liquid borax) in a glow discharge at the impregnating temperature has been recently developed, which is found to greatly increase the formation of the surface boride layer (Ref 58).

Fluidized Bed Boriding A recent innovation is boriding in fluidized beds (Fig. 12), which involves bed material of coarse-grained silicon carbide particles, a special boriding powder such as Ekabor WB, and an oxygen-free gas such as N_2-H_2 mixture (Ref 59). When electricity is used as the heat source, the bed serves as a faster heat-transfer medium. This is usually equipped with quench and tempering furnaces.

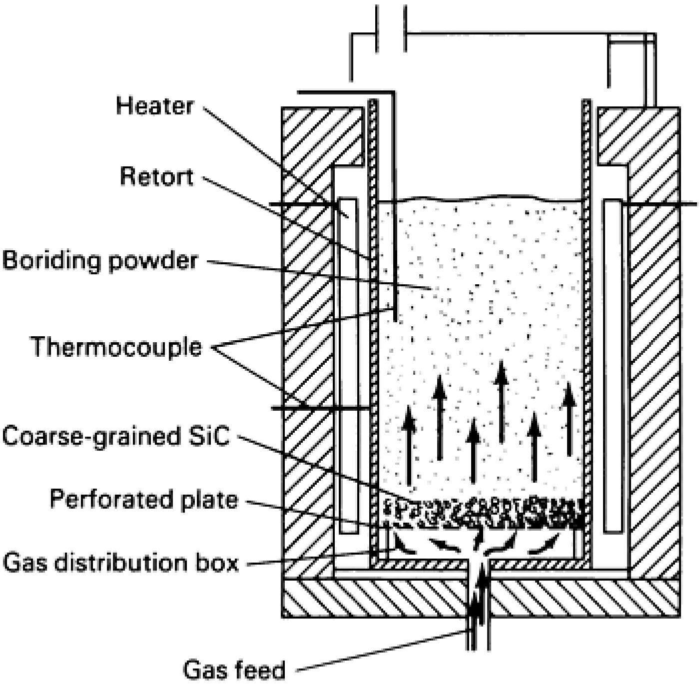

Fig. 12 Diagram of a fluidized bed for boriding. Source: Ref 4

This process offers such advantages as:

- High rates of heating and flow, as well as direct withdrawal of the parts, provide shorter operating cycle times (that is, rapid boronizing)
- Temperature uniformity with low capital cost and flexibility is ensured
- A fluidized furnace is very tight because of upward pressure of the gas
- This process produces reproducibility, close tolerances, and a very uniform finish on mass-produced parts
- This process can be adaptable to continuous production and can lend itself to automation as the parts are charged and withdrawn intermittently
- Quenching (and subsequent tempering) of the parts directly after this treatment is possible
- Low operating cost (due to reduced processing time and energy consumption) for mass production of boronized parts

An important disadvantage lies in the continuous flushing of the boriding agent within the retort by the inert gas. The exhaust gases containing enriched fluorine compounds must be cleaned absolutely, for example, in an absorber filled with dry $CaCO_3$ chips to avoid environmental problems (Ref 34). Alternatively pulsed fluidizing process can considerably decrease the amount of exhaust gases (Ref 34).

Multicomponent boriding is a thermochemical treatment involving consecutive diffusion of boron and one or more metallic elements such as aluminum, silicon, chromium, vanadium, and titanium into the component surface. This process is carried out at 850 to 1050 °C (1560 to 1920 °F) and involves two steps:

1. Boriding by conventional methods--notably pack, paste, and electrolytic salt bath methods (Ref 60). Here, the presence of FeB is tolerated, and, in some cases, may prove beneficial. Among these methods, much work has been done on pack method (Table 4 and Ref 2, 60, 61, 62), which produces a compact layer at least 30 μm (1 mil) thick
2. Diffusing metallic elements through the powder mixture or borax-based melt into the borided surface. If

the pack method is used, Sintering of particles can be avoided by passing argon or H_2 gas into the reaction chamber

There are six multicomponent boronizing methods (Ref 3, 60): boroaluminizing, boro-siliconizing, borochromizing, borochromtitanizing, borochromvanadizing, and borovanadizing.

Table 4 Multicomponent boriding treatments

Reference	Multicomponent boriding technique	Media type	Media composition[(a)], wt%	Process steps investigated[(a)]	Substrate(s) treated	Temperature, °C (°F)
61	Boroaluminizing	Electrolytic salt bath	3-20% Al_2O_3 in borax	S	Plain carbon steels	900 (1650)
62	Boroaluminizing	Pack	84% B_4C + 16% borax 97% ferroaluminium + 3% NH_4Cl	S B-Al Al-B	Plain carbon steels	1050 (1920)
2	Borochromizing	Pack	5% B_4C + 5% KBF_4 + 90% SiC (Ekabor II) 78% ferrochrome + 20% Al_2O_3 + 2% NH_4Cl	S B-Cr Cr-B	Plain carbon steels	Borided at 900 (1650) Chromized at 1000 (1830)
2	Borosiliconizing	Pack	5% B_4C + 5% KBF_4 + 90% SiC (Ekabor II) 100% Si	B-Si Si-B	0.4% C steel	900-1000 (1650-1830)
2	Borovanadizing	Pack	5% B_4C + 5% KBF_4 + 90% SIC (Ekabor II) 60% ferrovanadium + 37% Al_2O_3 + 3% NH_4Cl	B-V	1.0% C steel	Borided at 900 (1650) Vanadized at 1000 (1830)

Source: Ref 3

(a) S, simultaneous boriding and metallizing; B-Si, borided and then siliconized; Al-B, aluminized and then borided

Boroaluminizing. When boroaluminizing involves boriding followed by aluminizing, the compact layer formed in steel parts provides good wear and corrosion resistance, especially in humid environments (Ref 6, 30, 60).

Borosiliconizing results in the formation of FeSi in the surface layer, which enhances the corrosion-fatigue strength of treated parts (Ref 62).

Borochromizing (involving chromizing after boriding) provides better oxidation resistance than boroaluminizing, the most uniform layer (probably comprising a solid-solution boride containing iron and chromium), improved wear resistance compared with traditionally borided steel, and enhanced corrosion-fatigue strength. In this case, a post-heat-treatment operation can be safely accomplished without a protective atmosphere (Ref 2, 63, 64).

Borochromtitanized structural alloy steel provides high resistance to abrasive wear and corrosion as well as extremely high surface hardness 5000 HV (15 g load) (Ref 60). Figure 13 shows the microstructure of the case of a borochromtitanized constructional alloy steel part exhibiting titanium boride in the outer layer and iron-chromium boride beneath it.

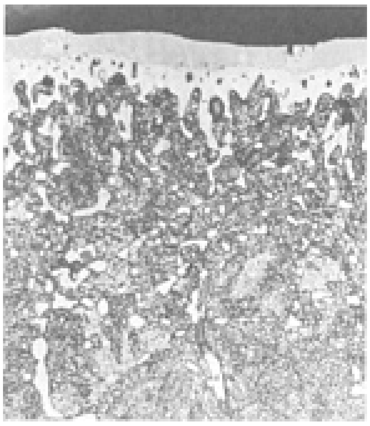

Fig. 13 Microstructure of the case of a borochromtitanized construction alloy steel. Source: Ref 6, 60

Borovanadized and borochromvanadized layers are quite ductile with their hardnesses exceeding 3000 HV (15 g load). This reduces drastically the danger of spalling under impact loading conditions (Ref 60).

Applications of Thermochemical Boriding. Presently borided parts have been used in a wide variety of industrial applications (Table 5) because of the numerous advantageous properties of boride layers. In sliding and adhesive wear situations, boriding is applied to:

- Spinning steel rings, steel rope, and steel thread guide bushings (made of DIN St 37 steel)
- Grooved gray cast iron drums (thread guides) for textile machinery
- Four-holed feed Water regulating valves (made from DIN 1.4571, or AISI 316 Ti steel)
- Burner nozzles, swirl elements, and injector tops for steel oil burners in the chemical industry (Ref 4)
- Drive, worm, and helically toothed steel gears in various high-performance vehicle and stationary engines (Ref 3)

Table 5 Proven applications for borided ferrous materials

Substrate material			Application
AISI	BSI	DIN	
		St37	Bushes, bolts, nozzles, conveyer tubes, base plates, runners, blades, thread guides
1020	. . .	C15 (Ck15)	Gear drives, pump shafts
1043	. . .	C45	Pins, guide rings, grinding disks, bolts
		St50-1	Casting inserts, nozzles, handles
1138	. . .	45S20	Shaft protection sleeves, mandrels
1042	. . .	Ck45	Swirl elements, nozzles (for oil bumers), rollers, bolts, gate plates
		C45W3	Gate plates
W1	. . .	C60W3	Clamping chucks, guide bars
D3	. . .	X210Cr12	Bushes, press tools, plates, mandrels, punches, dies
C2	. . .	115CrV3	Drawing dies, ejectors, guides, insert pins
		40CrMnMo7	Gate plates. bending dies
H11	BH11	X38CrMoV51	Plungers, injection cylinders, sprue
H13	. . .	X40CrMoV51	Orifices, ingot molds. upper and lower dies and matrices for hot forming, disks
H10	. . .	X32CrMoV33	Injection molding dies, fillers, upper and lower dies and matrices for hot forming
D2	. . .	X155CrVMo121	Threaded rollers, shaping and pressing rollers, pressing dies and matrices
		105WCr6	Engraving rollers
D6	. . .	X210CrW12	Straightening rollers
S1	~BS1	60WCrV7	Press and drawing matrices, mandrels, liners, dies, necking rings
D2		X165CrVMo12	Drawing dies, rollers for cold mills
L6	BS224	56NiCrMoV7	Extrusion dies, bolts, casting inserts, forging dies, drop forges
		X45NiCrMo4	Embossing dies, pressure pad and dies
02	~BO2	90MnCrV8	Molds, bending dies, press tools, engraving rollers, bushes, drawing dies, guide bars, disks, piercing punches
E52100	. . .	100Cr6	Balls, rollers, guide bars, guides
		Ni36	Parts for nonferrous metal casting equipment
		X50CrMnNiV229	Parts for unmagnetizable tools (heat treatable)
4140	708A42	42CrMo4	Press tools and dies, extruder screws, rollers, extruder barrels, non-return valves

	(En19C)		
4150	~708A42(CDS-l5)	50CrMo4	Nozzle base plates
4317	. . .	17CrNiMo6	Bevel gears, screw and wheel gears, shafts, chain components
5115	. . .	16MnCr5	Helical gear wheels, guide bars, guiding columns
6152	. . .	50CrV4	Thrust plates, clamping devices, valve springs, spring contacts
302	302S25 (EN58A)	XI2CrNi188	Screw cases, bushes
316	~316S16 (EN58J)	X5CrNiMo1810	Perforated or slotted hole screens, parts for the textile and rubber industries
		G-X10CrNiMo189	Valve plugs, parts for the textile and chemical industries
410	410S21 (En56A)	X10Cr13	Valve components, fittings
420	~420S45 (EN56D)	X40Cr13	Valve components, plunger rods, fittings, guides, parts for chemical plants
		X35CrMo17	Shafts, spindles, valves
Gray and ductile cast iron			Parts for textile machinery, mandrels, molds, sleeves

(a) Sources: Ref 4, 26

As abrasive Wear-resistance materials, borided stainless steels are used for parts such as screw cases and bushings, perforated and slotted hole screens, rollers, valve components, fittings, guides, shafts, and spindles, and borided Ti-6Al-4V for parts such as leading edge rotor blade cladding for helicopter applications. Other applications in this category include:

- Nozzles of bag filling equipment
- Extrusion screws, cylinders, nozzles, and reverse-current blocks in plastic production machinery (extruder and injection molding machinery) (Ref 1)
- Bends and baffle plates for conveying equipment for mineral-filled plastic granules in the plastics industry
- Punching dies (for making perforations in accessory parts for cars), press and drawing matrices, and necking rings (made from S1 tool steel)
- Press dies, cutting templates, punched plate screens (made of DIN St 37 steel)
- Screw and wheel gears, bevel gears (from AISI 4317 steel)
- Steel molds (for the manufacture of ceramic bricks and crucibles in the ceramics industry), extruder barrels, plungers and rings (from 4140 steel)
- Extruder tips, nonreturn valves and cylinders (for extrusion of abrasive minerals or glass fiber-filled plastics, from 4150 steel)
- Casting fillers for processing nonferrous metals (from AISI H11 steel)
- Transport belts for lignite coal briquettes

Borided parts also find applications in die-casting molds; bending blocks; wire draw blocks; pipe clips; pressing and shaping rollers, straightening rollers, engraving rollers, rollers for cold mills; mandrels; press tools; bushings; guide bars; discs; casting inserts; various types of dies including cold heading, bending, extrusion, stamping, pressing, punching, thread rolling, hot forming, injection molding, hot forging, drawing, embossing, and so on in A2, A6, D2, D6, H10, H11, 02, and other tool steels (Ref 42).

Borided steel parts have also been used as transport pipe for molten nonferrous metals such as aluminum, zinc, and tin alloys (made from DIN St 37), corrosion-resistant transport pipe elbows for vinyl chloride monomer, grinding discs (made from DIN Ck 45), die-casting components, air foil erosion-resistant cladding, data printout components (for example, magnetic hammers, wire printers), and engine tappets (Ref 12).

Boronized Permalloy is used for magnetic head applications. Boronized cemented carbides are used as drawing dies, guiding parts, and dimensional measurement parts. Some examples of multicomponent boriding include: improving the wear resistance of austenitic steels (borochromizing), of parts for plastics processing machines (borochromtitanizing), and of dies used in the ceramics industry (borochromizing) (Ref 60).

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Chemical Vapor Deposition

Metal boride coatings or deposition via chemical vapor deposition (CVD) of TiB_2, ZrB_2, rare earth borides, and so forth on steel, refractory metals, and alloys have been made using the following chloride reaction:

$$MCl_4\ (g) + 2BCl_3\ (g) + 5H_2\ (g) = MB_2\ (s) + 10\ HCl\ (g) \qquad \textbf{(Eq 4)}$$

Good deposition of some borides is obtained under the conditions listed in Table 6. Among these boride coatings, much research work has been directed toward the deposition of TiB_2.

Table 6 Chemical vapor deposition (CVD) conditions for some borides

Boride	Precursors	Temperature		Pressure		After
		°C	°F	kPa	torr	
HfB_2	$HfCl_4$-BCl_3-H_2	1400	2550	0.4	3	Gebhardt and Cree (1965)
NbB_2	$NbBr_5$-BBr_3	850-1750	1560-3180	0.003-0.025	0.025-0.2	Armas *et al.* (1976)
Ni-B	$Ni(CO)_4$-B_2H_6-CO	150	300	87	650	Mullendore and Pope (1987)
SiB_4	SiH_4-BCl_3-H_2	800-1400	1470-2500	6.5-80	50-600	Dirkx and Spear (1984)
SiB_x	$SiBr_4$-BBr_3	975-1375	1790-2500	0.007	0.05	Armas and Combescure (1977)
TaB_2	$TaBr_5$-BBr_3	850-1750	1560-3180	0.003-0.025	0.025-0.2	Armas *et al.* (1976)
	$TaCl_5$-B_2H_6	500-1025	930-1875	100	760	Randich (1980)
TiB_2	$TiCl_4$-BCl_3-H_2	1200-1415	2200-2580	0.4-2	3-15	Gebhardt and Cree (1965)
	$TiCl_4$-B_2H_6	600-900	1100-1650	100	760	Pierson and Mullendore (1980)
	$TiCl_4$-BCl_3-H_2	750-1050	1380-1920	100	760	Caputo *et al.* (1985)
	$TiCl_4$-BCl_3-H_2	1200	2200	6.5	50	Desmaison *et al.* (1987)
ZrB_2	$ZrCl_4$-BCl_3-H_2	1400	2550	0.4-0.8	3-6	Gebhardt and Cree (1965)

The CVD process for the deposition of TiB_2 or ZrB_2 coatings on various substrate materials is carried out by passing a mixture of $TiCl_4$ (or $ZrCl_4$) and BCl_3-H_2 gas mixture over a heated part placed in a vacuum chamber where the gas decomposition into atomic boron and titanium (or zirconium) and subsequent deposition of TiB_2 (or ZrB_2) occurs at the component surface when the appropriate deposition temperature and gas pressure are maintained (Table 6). It is necessary to adjust the gas flow so that the atomic ratios are:

- B/Ti = 1 to 2 and H/Cl = 6 to 10 for TiB_2
- B/Zr = 1.0, and H/Cl = 20.0 for ZrB_2

It is further noticed that when B/(B + Cl) = ~0.4, the TiB_2 deposit becomes dense with a {1010} or {1120} preferred orientation, which is often associated with a columnar appearance (Ref 66) and microhardness values of about 3300 to 4500 HV (50 g load).For a good adherent deposit of TiB_2 on steel and cemented carbides, it is desirable to precoat the substrate with corrosion-resistant layers of cobalt and TIC, respectively (Ref 66, 67, 68).

Advantages and Applications. This process has several advantages such as the high purity of the deposit, a relatively high rate of deposition; close chemical composition control; high resistance to thermal shock, erosion, and/or corrosion at elevated temperatures; and large economic savings for the mass production of small parts. As a result, TiB_2 coatings are variously used on cemented carbide cutting inserts (Ref 68), on graphite electrodes in aluminum reduction cells, and on letdown valves in coal conversion reactors (Ref 69, 70). $ZrBr_2$ coatings on graphite are sometimes used as a spectrally selective surface at elevated temperatures (Ref 71).

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Thermoreactive Deposition/Diffusion Process for Surface Hardening of Steels

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Introduction

THE THERMOREACTIVE DEPOSITION/DIFFUSION PROCESS (TRD) is a method of coating steels with a hard, wear-resistant layer of carbides, nitrides, or carbonitrides. In the TRD process, the carbon and nitrogen in the steel substrate diffuse into a deposited layer with a carbide-forming or nitride-forming element such as vanadium, niobium, tantalum, chromium, molybdenum, or tungsten. The diffused carbon or nitrogen reacts with the carbide- and nitride-forming elements in the deposited coating so as to form a dense and metallurgically bonded carbide or nitride coating at the substrate surface.

The TRD process is unlike conventional case-hardening methods, where the specific elements (carbon and nitrogen) in a treating agent diffuse into the substrate for hardening. Unlike conventional diffusion methods, the TRD method also results in an intentional buildup of a coating at the substrate surface. These TRD coatings, which have thicknesses of about 5 to 15 μm (0.2 to 0.6 mil), have applications similar to those of coatings produced by chemical vapor deposition (CVD) or physical vapor deposition (PVD). In comparison, the thickness of typical CVD coatings (usually less than 25 μm, or 1 mil) has about the same range as TRD coatings.

Process Characteristics

The hard alloy carbide, nitride, and carbonitride coatings in the TRD method can be applied to steels by means of salt bath processing (Ref 1, 2, 3, 4) or fluidized beds (Ref 5). The carbide coating by salt bath immersion was first developed in Japan and used industrially almost 20 years ago under the name of the Toyota Diffusion (TD) coating process (Ref 1, 2). The TD method uses molten borax with additions of carbide-forming elements such as vanadium, niobium, titanium, or chromium, which combine with carbon from the substrate steel to produce alloy carbide layers. Because the growth of the layers is dependent on carbon diffusion, the process requires a relatively high temperature, from 800 to 1250 °C (1470 to 2280 °F), to maintain adequate coating rates. Carbide coating thicknesses of 4 to 7 μm are produced in 10 min to 8 h, depending on bath temperature and type of steel. The coated steels may be cooled and reheated for hardening, or the bath temperature may be selected to correspond to the steel austenitizing temperature, permitting the steel to be quenched directly after coating.

Salt bath temperatures can also be lowered to the tempering range of steel (Ref 3). In order to lower salt bath deposition temperatures, techniques to produce alloy carbonitride coatings are used. Such coatings are applied to hardened and nitrided steels in vanadium-containing chloride baths at temperatures of 550 to 600 °C (1020 to 1110 °F). This section deals exclusively with coating at a high temperature.

Coating Procedure and Mechanism of Coating Formation. The high-temperature salt bath TRD process is performed in a molten borax bath at 850 to 1050 °C (1560 to 1920 °F). Immersion time ranges from 0.5 to 10 h to obtain an optimum carbide layer thickness of 5 to 15 μm (0.2 to 0.6 mil) for most applications. This temperature range is suitable for quench hardening many grades of low-alloy steels, carburized steels, and tool steels.

Before parts are TRD processed they are first preheated to minimize distortion and to lower the TRD processing time. They are then TRD processed at the austenitizing temperature for the particular grade of steel. After TRD processing, the parts are quenched in air, salt, or oil to produce a hardened substrate. After quenching, tempering is carried out. Figure 1 shows a schematic of a typical cycle. High-speed steels and other steels that have austenitizing temperatures greater than 1050 °C (1920 °F) may be post-TRD heat treated in vacuum, gas, or protective salt to achieve full substrate hardness.

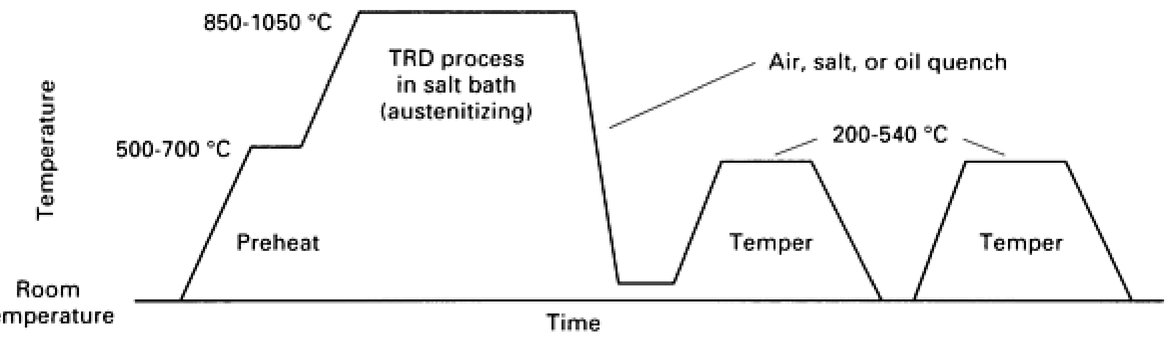

Fig. 1 Schematic of typical TRD processing cycle

When substrate materials containing carbon and nitrogen are kept in contact with treating agents at appropriately elevated temperatures, carbon and nitrogen chemically combine with the carbide- and nitride-forming elements of the treating agent due to their small free energies for carbide and nitride formation. This formation of carbides, carbonitrides, and nitrides on the substrate results in the growth of a layer, as shown in Fig. 2 for vanadium carbide and chromium carbide coatings. Carbide layers are formed in the following steps:

- Carbide-forming elements dissolve into borax from added powders
- Carbon in steel combines with the carbide-forming elements to produce a carbide layer on the surface
- The carbide layer grows at the surface front through reaction between carbide-forming elements and carbon atoms successively supplied from the substrate

Vanadium and chromium diffuse into the steel substrate to form iron-chromium or iron-vanadium solid-solution layers beneath the carbide layer. The solid-solution layers were formed on low-carbon steel at high treating temperature.

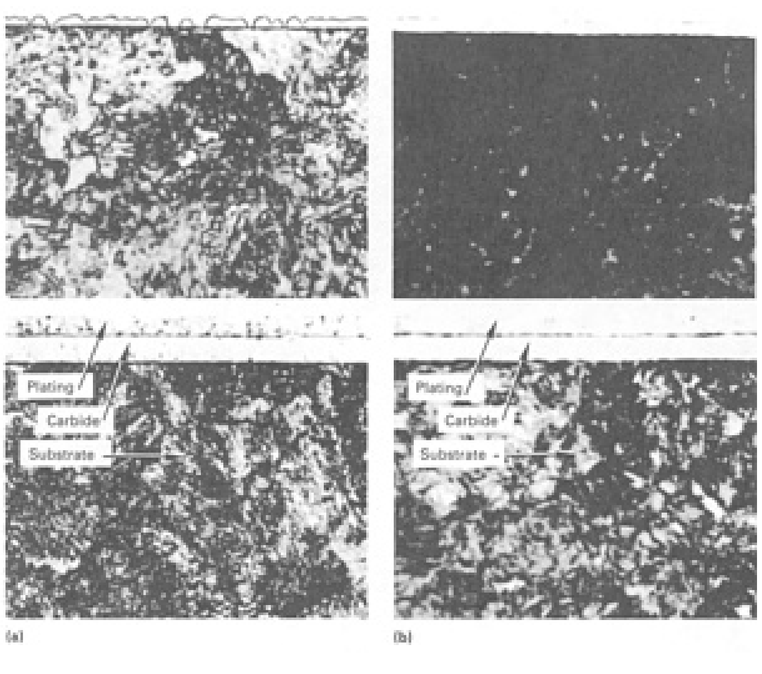

Fig. 2 Carbide coating grown during TRD process. Substrate, W1 steel; temperature, 900 °C (1650 °F). Salt: borax, V_2O_5 and B_4C borax and chromium. (a) Vanadium carbide coating. Upper, 5 min; lower, 30 min. (b) Chromium carbide coating. Upper, 5 min; lower, 30 min

Reagents Used. The carbide-forming elements (CFE) and the nitride-forming elements (NFE) must be in an active state to combine with carbon and nitrogen. Typical reagents have the CFE and NFE dissolved into molten salt in the salt bath immersion method and those in halide vapor produced through reaction between CFE- and NFE-containing powders and halide at elevated temperatures in the powder-pack and fluidized-bed methods. Therefore, borax with additions of CFE and NFE contained in ferroalloy powder or with oxides of CFE and NFE and their reducing agents, such as boron carbide and aluminum, are successfully used as bath agents. Mixtures of ferroalloy powder containing CFE and NFE and halide powder, such as ammonium chloride, often added with alumina powder, are used in packed boxes (Ref 6 and 7) or in a fluidized bed (Ref 5).

Substrate Materials. Most carbon-containing materials such as steels, cast iron, cobalt alloys, cemented carbides, carbide-metal cermets, carbide ceramics (Ref 8), and carbon may be used as the substrates for carbide coating. Carbon-deficient metals, for example, iron and nickel alloys, can be used after carburization prior to application of the carbide coating. Carbonitride coating is applicable to preliminarily nitrided steel. A nitride coating can be formed on nitride ceramics (Ref 8).

Various tool steels are most frequently used for tooling. Low- or medium-carbon constructural steels are used for machine components. The composition and properties of the coatings are almost independent of the substrate materials. Therefore, inexpensive and easily machinable materials should be used.

Effect of Treating Parameters. The coating growth rate is determined by the number of carbon atoms and nitrogen atoms that can be supplied to the coating from the substrate by diffusion, if the treating reagents can supply CFE and NFE in excess of the critical amount required to combine with the carbon and nitrogen supply from the substrate. Excess amounts of material containing CFE and NFE (for example, more than 10 wt% Fe-V, or 20 wt% V_2O_5 and 5 wt% B_4C in molten borax for vanadium carbide coating, or more than 10 wt% Cr and 1 wt% NH_4Cl in a fluidized bed for chromium carbide coating) are usually added to maintain this requirement. Therefore, the coating growth rate is determined by factors that affect only the amount of CFE and NFE required for coating: temperature, time, type of substrate, and type of coating.

As in many diffusion treatments, the effect of temperature and time on coating thickness (d) is expressed by the following equation:

$$d^2/t = K = K_o \exp(-Q/RT) \qquad \textbf{(Eq 1)}$$

where d is the thickness of coating (cm), t is time (s), K is the growth rate constant (cm^2/s), K_o is the constant term of K (cm^2/s), Q is the activation energy (KJ/mol), T is absolute temperature (K), and R is the gas constant. Figure 3 shows the relation between the thickness of the vanadium carbide layer formed on W1 steel versus salt bath temperature and immersion time in the molten salt bath immersion method. The temperature is usually selected around the hardening temperature of steels, that is, 800 to 1250 °C (1475 to 2285 °F).

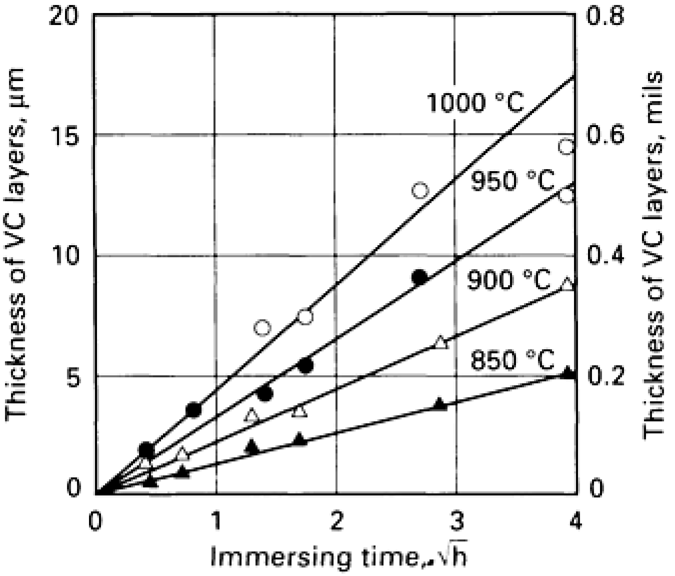

Fig. 3 Effect of temperature and time on thickness of vanadium carbide layer in a borax bath containing 20 wt% Fe-V powder

The carbon and nitrogen content in the substrate has a positive effect on the growth rate. However, the total content in the substrate does not have a direct effect. For example, in steels the carbon content in the austenite matrix, not the total carbon content, is nearly linear in relation to the thickness of the carbide coating. This is shown in Fig. 4 for the salt bath immersion process (Ref 1, 2). In the case of alloyed steels, an increase of temperature increases the carbon content in the matrix phase, as well as the diffusion rate of carbon in the carbide layer and in the substrate, resulting in a considerable increase of coating thickness. Figure 5 exemplifies the relation between bath temperature and immersion time needed for producing a 4 μm and 7 μm thick VC coating on four types of steel. In the case of cemented carbides, not only the carbon content but also the amount of cobalt matrix has a large effect on the thickness. The diffusion rate and its temperature dependence in relation to the carbon and nitrogen content are different between coatings. However, the difference in thickness among vanadium carbide (VC), niobium carbide (NbC), chromium carbide (Cr_7C_3, $Cr_{23}C_6$), and titanium carbide (TiC) is negligibly small.

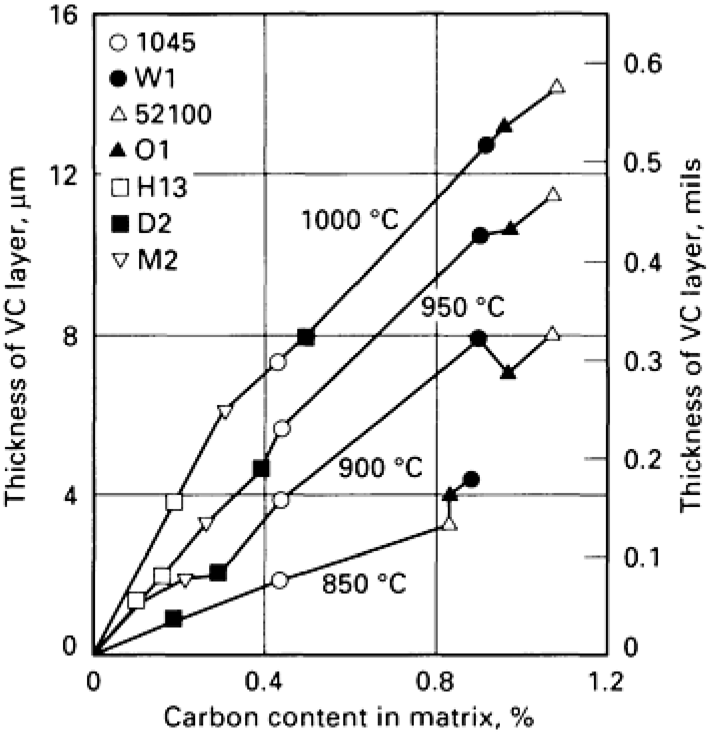

Fig. 4 Effect of carbon content in matrix phase on thickness of vanadium carbide layer in a borax bath containing 20 wt% Fe-V powder. Immersion time, 4 h

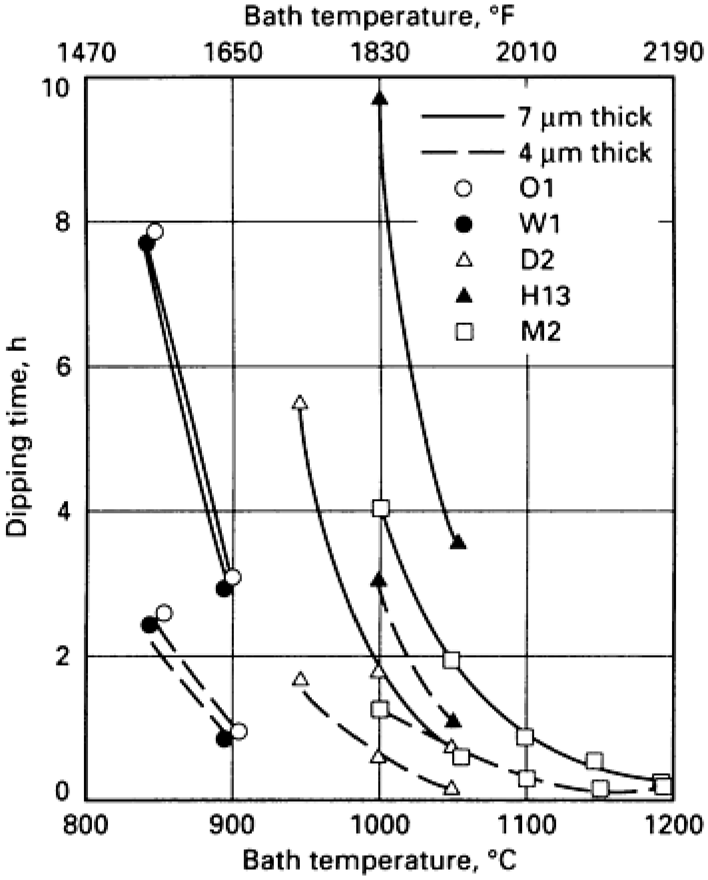

Fig. 5 Effect of bath temperature and substrate steel on the immersion time required to form a 7 μm and 4 μm thick vanadium carbide layer in a borax bath

Control of Distortion. The possibility of distortion is present with the high-temperature process. Distortion entails dimensional change and deformation. Dimensional change is due to phase transitions in heat treatment of the base steel and to formation of the carbide layer. Deformation is a change in shape.

TRD processing usually hardens a material. Therefore, to minimize dimensional change, it is best to start with a part that has been hardened and finish ground. Even then, there will be some dimensional change due to differences in the amount of retained austenite. Cemented carbide is not hardened in the process, therefore it has very little dimensional change.

The amount of retained austenite before TRD processing should equal the amount after processing. The easiest method of controlling retained austenite is to reduce it to 0% before and after the TRD process. This can be achieved in D2 tool steel by tempering at 520 to 535 °C (975 to 1000 °F) to decompose the retained austenite. Sub-zero treatment is another method of decomposing retained austenite.

Deformation is caused by thermal stresses, transformation stresses, creep during heating, anisotropy of the substrate structure, and residual stresses. The following are steps that can be taken to minimize deformation:

- Minimize variations in cross-sectional area
- Use air-hardening grades of tool steel, which can be slow cooled
- Machine tools so that critical dimensions are transverse of the rolling direction of the raw material
- Use powder metal steels
- Relieve residual stresses caused by machining and grinding

In making new tooling, it is recommended to leave stock on nonworking surfaces and finish only the working surfaces. The non-working surfaces may then be finished after TRD processing.

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TRD Carbide Coatings

General Characteristics. Carbide coatings that are available with the high-temperature salt bath process include vanadium carbide, niobium carbide, and chromium carbide. Vanadium carbide and niobium carbide have high surface hardness and resistance to wear, seizure, and corrosion. Chromium carbide has light wear resistance and high resistance to oxidation. The surface hardness and wear, seizure, corrosion, and oxidation resistance in relation to other surface-hardening processes is shown in Fig. 6, 7, 8, 9, and 10.

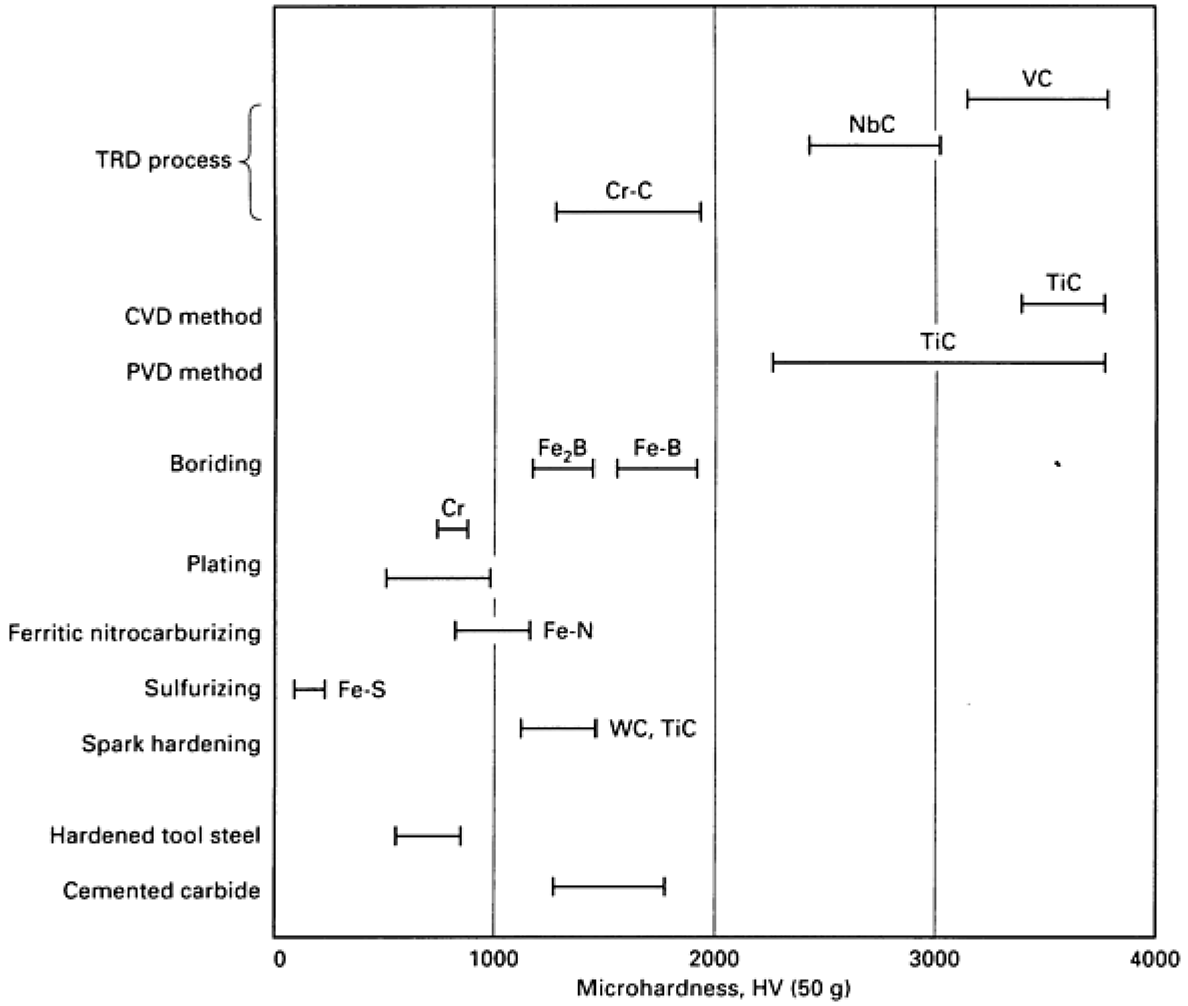

Fig. 6 Surface hardness of carbide layers by TRD process in relation to other surface-hardening processes

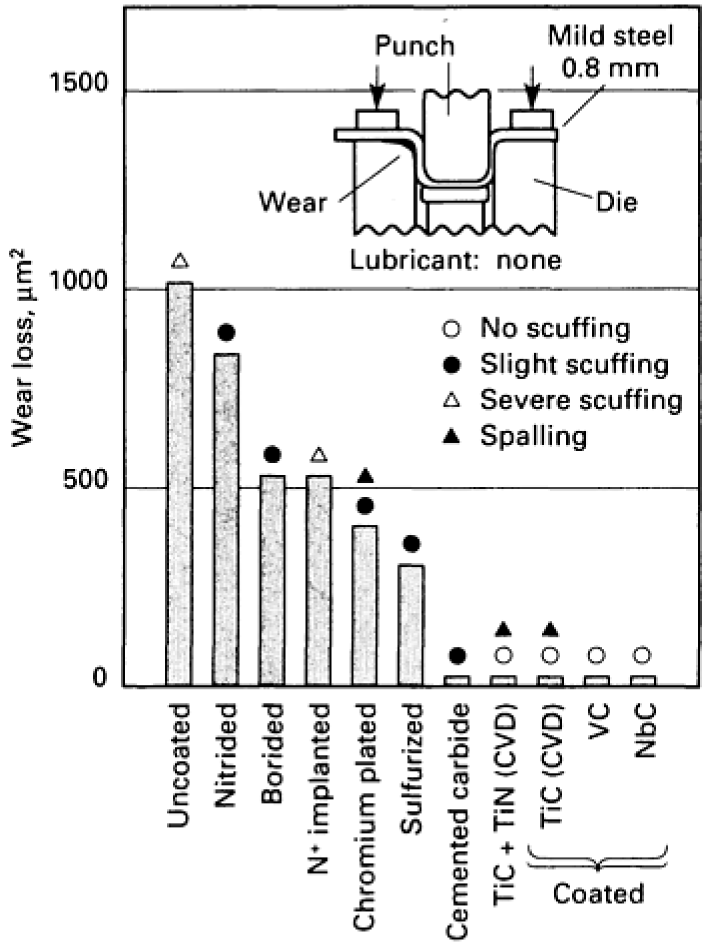

Fig. 7 Comparative cross-sectional area of wear, scuffing, and spalling on a die radius in a sheet steel-bending test

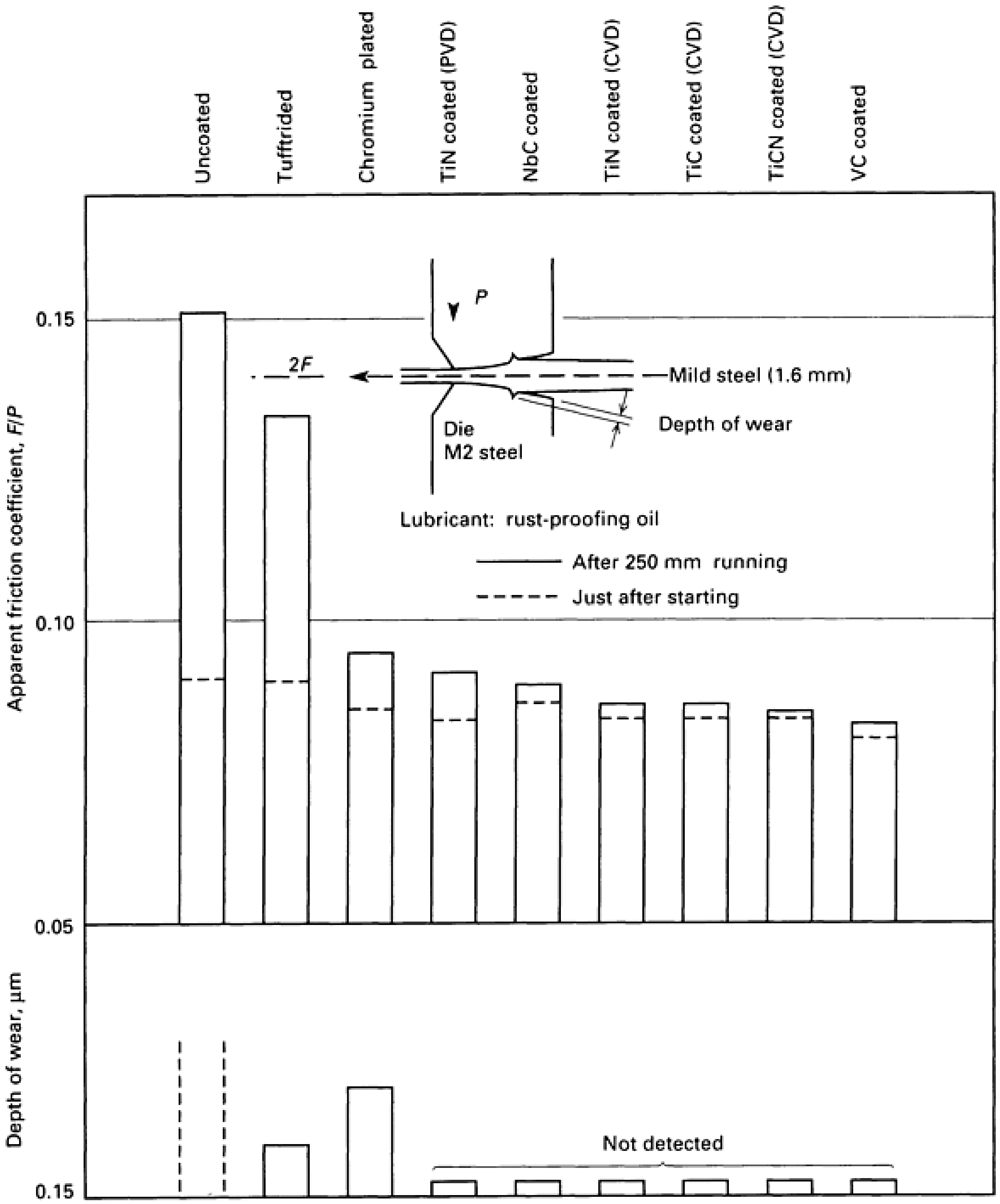

Fig. 8 Comparative friction coefficient and depth of wear on dies in a sheet steel-ironing test

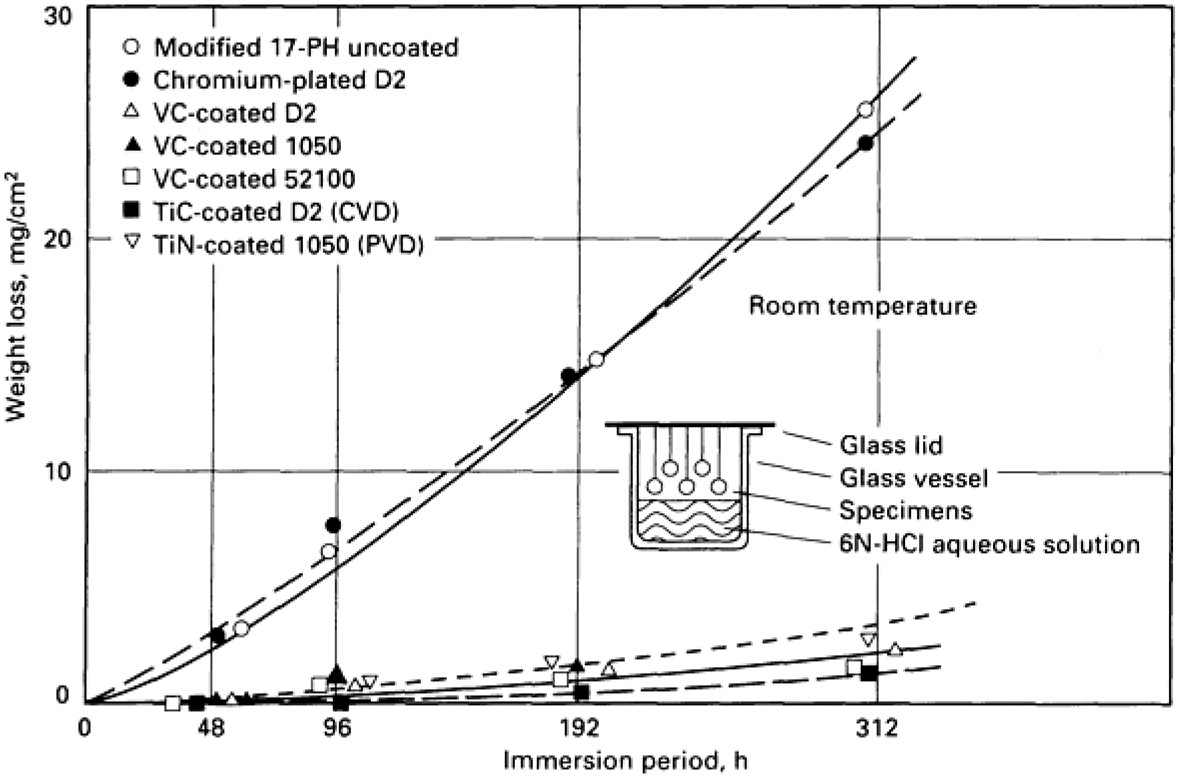

Fig. 9 Comparative weight loss by corrosion in hydrochloric acid vapor

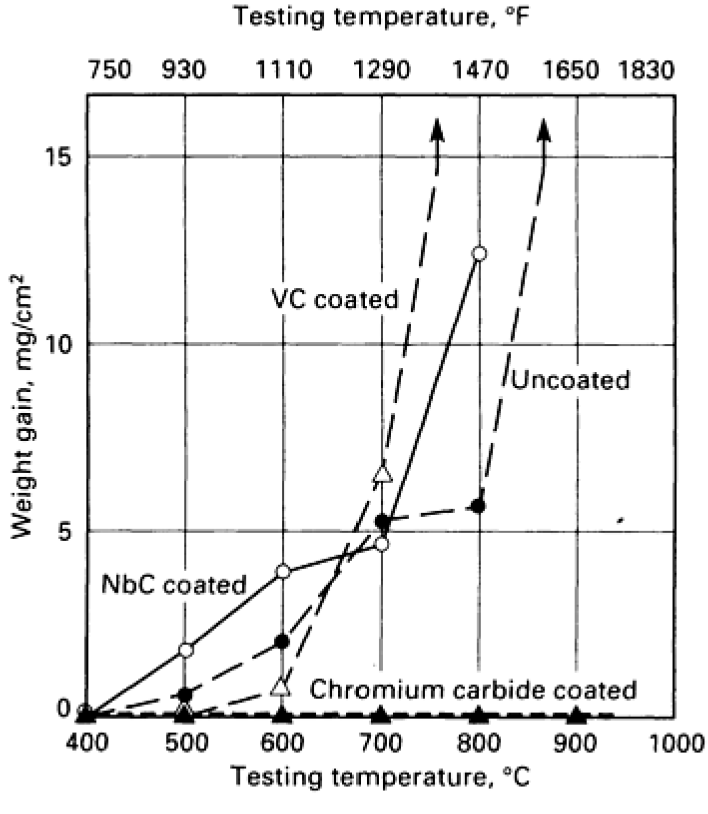

Fig. 10 Comparative weight gain in a high-temperature oxidation test. Substrate, D2; testing period, 40 h

The spalling resistance of the carbide layers is very good. Figure 11 shows the spalling resistance of vanadium carbide in relation to other coating processes. In applications with cyclic stresses, the fatigue resistance of steels is often slightly deteriorated by tensile residual stress induced on the base metal, as shown in Fig. 12. The residual stress initiates cracks in the base metal. The problem can be solved by proper TRD processing and soaking after TRD treatment to decrease the tensile stress, if necessary. The toughness is usually not affected by the process, as shown in Fig. 13.

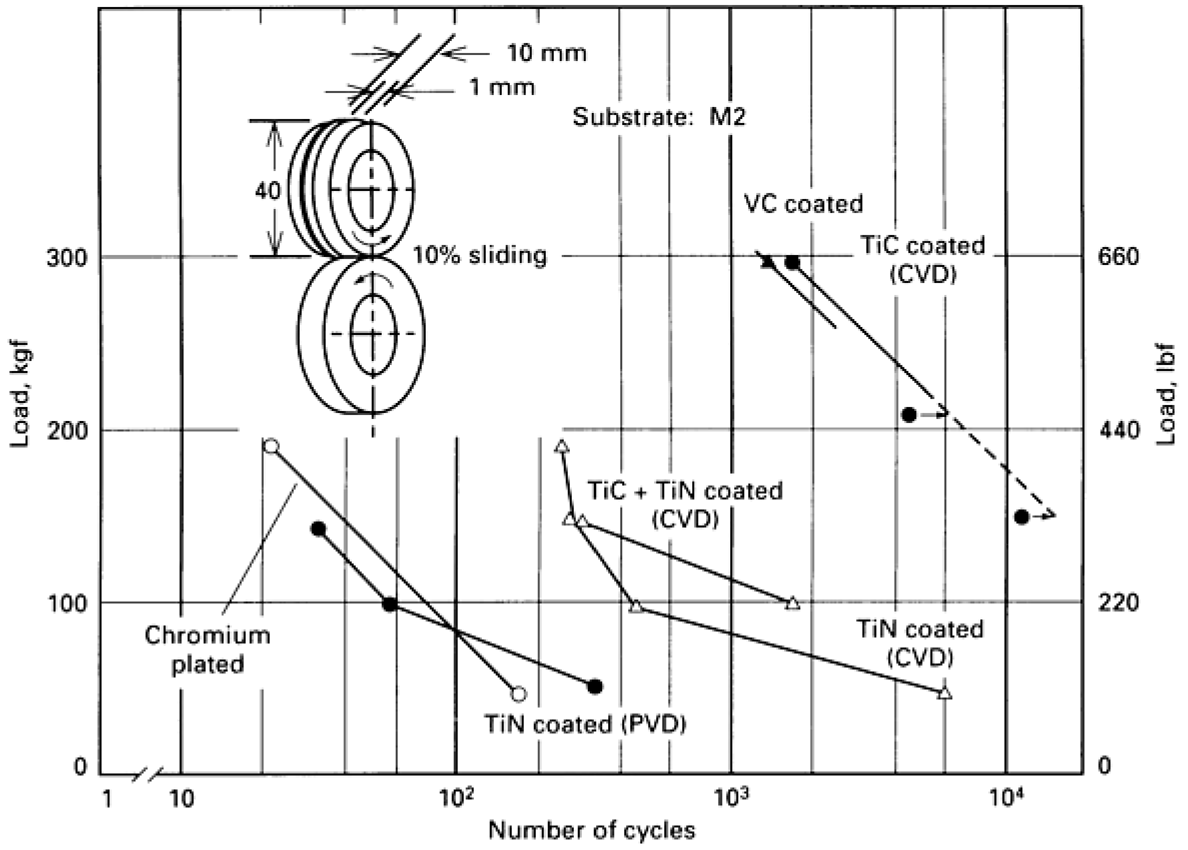

Fig. 11 Comparative number of cycles at which spalling of layer occurred in a rolling test with 10% sliding

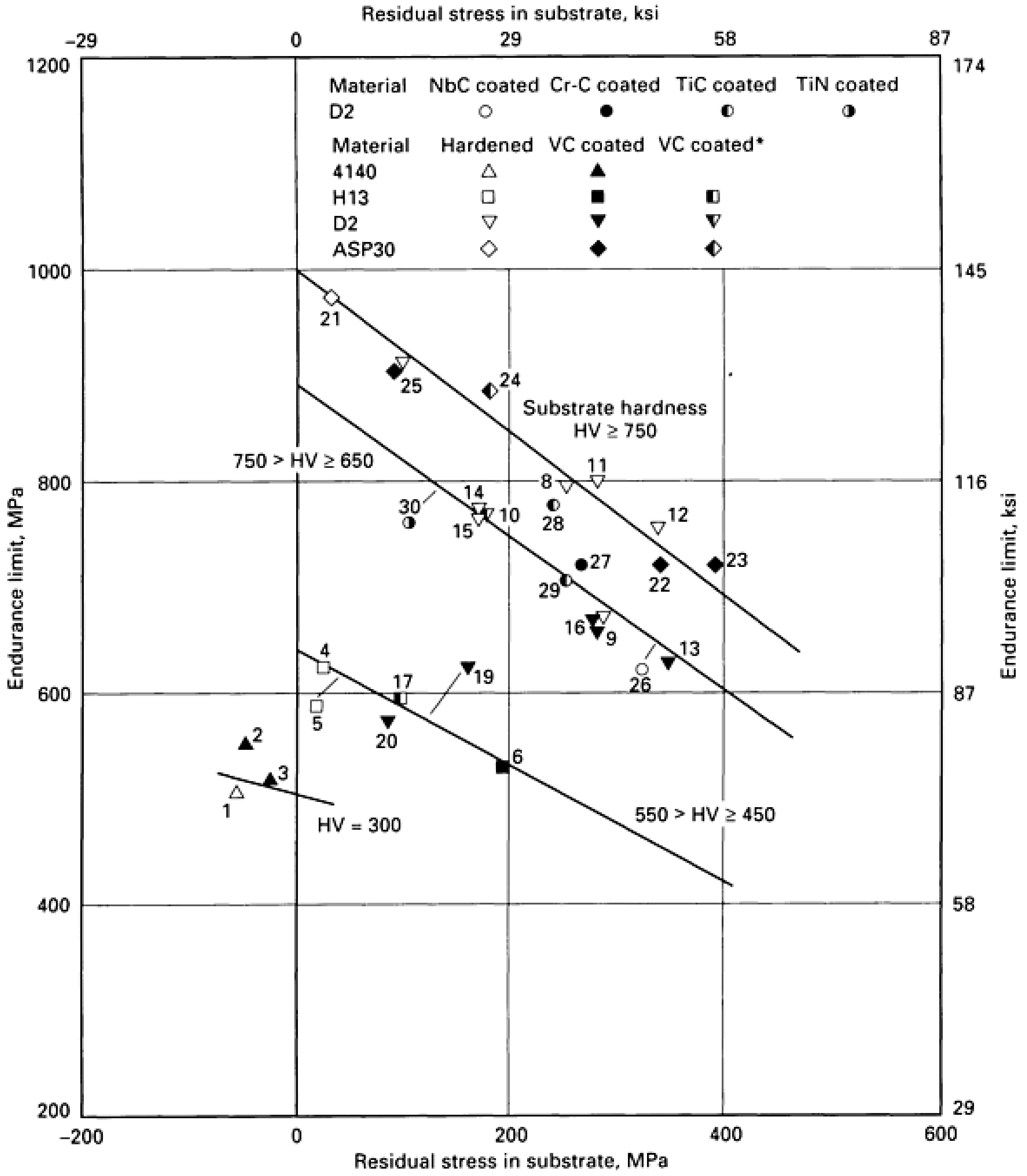

Fig. 12 Relation between endurance limit in fatigue test and residual stress in substrate and substrate hardness (in HV). Sample numbers for data included in figure

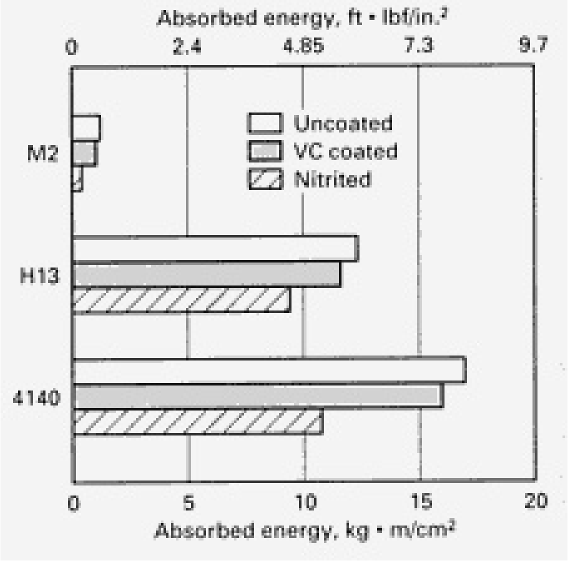

Fig. 13 Comparative absorbed energy in a dynamic bending toughness test

Tooling Applications. Tool steels that contain 0.3% or greater carbon may be TRD processed. This includes most cold- and hot-work steels, high-speed steels, and some martensitic stainless steels. To achieve full substrate hardness in high-speed steel, it must be rehardened after TRD processing. Cemented carbide is frequently used as the substrate for tooling.

The best applications for TRD are tools that have high wear and galling problems. This includes many types of forming and cutting tools, and die components, as shown in Table 1. Mild steel, high-strength steel, plated steel, stainless steel, nonferrous metal, plastics, and rubber are some of the materials that can be worked.

Table 1 Applications of TRD-processed tooling

Application	Tool
Sheet metal working	Draw die, bending die, pierce punch, form roll, embossing punch, coining punch, shave punch, seam roll, shear blade, stripper guide pin and bushing, pilot pin, and so on
Pipe and tube manufacturing	Draw die, squeeze roll, breakdown roll, idler roll, guide roll, and so on
Pipe and tube working	Bending die, pressure die, mandrel, expand punch, swaging die, shear blade, feed guide, and so on
Wire manufacturing	Draw die, straightening roll, descaling roll, feed roll, guide roll, cutting blade
Wire working	Bending die, guide plate, guide roll, feed roll, shear blade
Cold forging and warm forging	Extrusion punch and die, draw die, upsetting punch and die, coining punch and die, rolling die, quill cutter, and so on
Hot forging	Press-forging die, rolling die, upsetting die, rotary swaging die, closed-forging die, and so on
Casting (aluminum, zinc)	Gravity-casting core pin, die-casting core pin, core, sleeve, and so on
Rubber forming	Form die, extrusion die, extrusion screw, torpedo, cylinder sleeve, piston, nozzle, and so on
Plastic forming	Form die, injection screw, sleeve, plunger, cylinder, nozzle, gate, and so on
Glass forming	Form die, plunger, blast nozzle, machine parts, and so on
Powder compacting	Form die, core rod, extrusion die, screw, and so on
Cutting and grinding	Cutting tool, cutting knife, drill, tap, gage pin, tool holder, guide plate, and so on

The substrate hardness may be the same or lower than normal in some applications. In applications where tool chipping or breakage is the problem, a lower substrate hardness with increased toughness can be used. The hard carbide coating provides the surface wear resistance. Underhardened high-speed steel could be used to provide needed substrate toughness.

In applications with high surface pressures, such as extrude dies and cold-forging dies, the carbide layer has to be supported by a hard substrate. High-speed steels should be post-TRD hardened. Some powdered high-speed steels that contain cobalt can be treated at the maximum TRD processing temperature of 1050 °C (1920 °F) to give hardnesses of 60 to 65 HRC. The hardest substrate available is cemented carbide, which can be TRD treated very successfully.

Edge preparation of cutting and piercing tools is important. An edge that is too sharp or that contains burrs will break. The cutting edge should be rounded to a radius of 0.05 to 0.25 mm (0.002 to 0.010 in.) with a stone or emery paper. A worn cutting edge may be resharpened. This is not detrimental because performance is governed by the carbide layer on the side surface of the cutting edge.

The surface finish and polishing direction of a forming die prior to TRD processing is very important. Due to the high-hardness carbide layer, a TRD processed tool that has a rough surface finish will perform worse than a regular uncoated tool. This is shown in Fig. 14. The surface should be finished to a maximum peak-to-valley roughness height (R_{max}) of 3 μm (120 μin.). All large scratches and machining marks should be removed. When plated steel, stainless steel, high-strength steels, and aluminum are the materials being processed, a finish of 0.5 to 1 μm (20 to 40 μin.) for R_{max} is recommended on the tool being used. The polishing lines should be parallel to the metal flow. The characteristic white layer that is produced in electrical discharge machining should be removed before TRD processing.

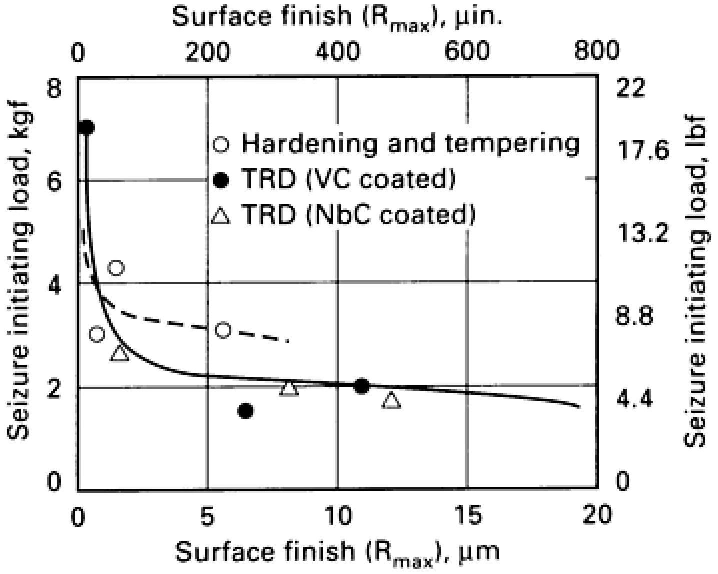

Fig. 14 Influence of tool surface finish on seizure-initiating load for a TRD-coated tool and uncoated tool. Mating material, SUS304; speed, 2.6 m/s (8.5 ft/s); lubricant, none

Tools processed by TRD may be re-treated by TRD. Some tools have been re-treated eight times. After the worn areas are refinished, tools can be re-treated without removing the sound carbide. The difference in layer thicknesses will be insignificant, due to the slower growth rate of the carbide layer on the previously coated areas.

Other TRD Product Applications. The TRD process is very useful for products as well as for tools because the carbide coating formed provides high resistance to abrasive wear, adhesive wear, fretting wear, corrosion, and oxidation, which cannot be provided by other conventional surface treatments. The following are examples of application:

- *Components used in high-performance machines:* roller chain for racing bicycles, motorcycles, and automobiles; traveller rings used under extremely high-velocity spinning; and pump plungers used under extremely high pressure
- *Components used in corrosive or adverse operating conditions:* vanes in vane pumps, spraying nozzles that work with corrosive liquids, and liquids in which abrasive particles exist; link components in glass-molding machines; and automobile components that are susceptible to oxidation and corrosion by exhaust gas

Structural steels such as 10*xx* series carbon steel, and 41*xx* series low-alloyed steel are widely used for these applications. Low-carbon steels are often carburized prior to TRD processing. Substrate hardening is done during cooling in TRD treatment or by reaustenitizing hardening, if it is necessary. Attention should be paid to surface finishing and edge preparation for components used in severe conditions. Barrel finishing is often used for surface finishing of small components in large volume.

Methods of Measuring Case Depth in Steels

Revised by Christopher M. Klaren, John Deere, Waterloo Works; and James Nelson, Buehler Ltd.

Introduction

CASE HARDENING may be defined as a process by which a ferrous material is hardened so that the surface layer, known as the case, becomes substantially harder than the remaining material, known as the core. Case-hardening processes include carburizing, nitriding, carbonitriding, cyaniding, and induction and flame hardening. Each of these methods increases the surface hardness of ferrous materials.

An accurate and repeatable method of measuring case depth is essential for quality control of the case-hardening process and for evaluation of workpieces for conformance with specifications, such as might be done during a failure analysis. This article describes various methods for measuring case depth as outlined in SAE specification J423 (Ref 1). Nondestructive eddy current measurement of case depth is also discussed. Each method has its own area of application established through proven practice, and no single method is recommended for all purposes. The methods employed for measuring case depth are chemical, mechanical, visual with an acid etch, or nondestructive. The mechanical method is the most widely used technique for case depth measurement.

Reference

1. "Methods of Measuring Case Depth," J423 (revised 1983), *SAE Handbook,* Vol 1, Society of Automotive Engineers, 1990

Measurement Specifications

Case depths determined by the different methods can vary extensively, depending on case characteristics, parent-steel composition, and quenching conditions. The various methods also take measurements at different locations in a case, which can result in variations in hardness. For example, typical hardness surveys taken on cross sections at the pitch line, root fillet, and root land of a tooth in a carburized and hardened gear made of 8620H steel are shown in Fig. 1. These data illustrate the importance of well-defined specifications by showing that there are variations in effective case depth even among three areas of the same gear tooth.

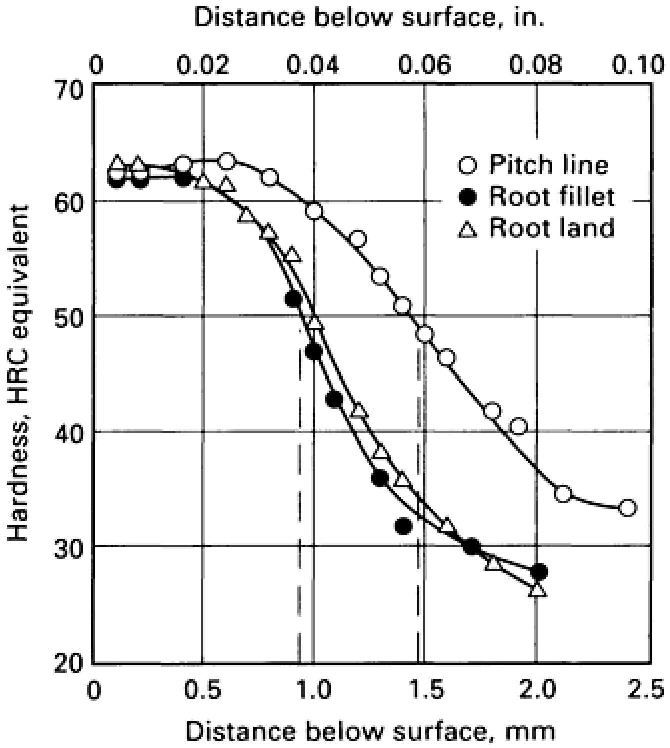

Fig. 1 Variation in hardness with distance below surface for a carburized and hardened 8620H steel gear. Effective case depths to 50 HRC: 0.94 mm (0.037 in.) at root fillet, 1.02 mm (0.040 in.) at root land, 1.45 mm (0.057 in.) at pitch line

It is also important to distinguish between total case depth and effective case depth. Measurements are reported as either effective or total case depth for hardened specimens, and as either total case depth or equivalent effective case depth for unhardened specimens used in the chemical method. Specific descriptions, such as total case depth, effective case depth to 50 HRC, and case depth to 0.40 wt% C will help to avoid misunderstandings.

Effective case depth is the perpendicular distance from the surface of a hardened case to the deepest point at which a specified level of hardness is reached. The hardness criterion, except when otherwise specified, is 50 HRC. The effective case depth is typically about two-thirds to three-fourths the total case depth.

Total case depth may be defined as the perpendicular distance from the surface of a hardened or unhardened case to the point at which differences in chemical or physical properties of the case and core can no longer be distinguished. Total case depth sometimes is considered to be the distance from the surface to the deepest point at which the carbon content is 0.04% higher than the carbon content of the core.

Chemical Method

The chemical method of measuring case depth generally is used only for carburized cases but may be used for cyanided or carbonitrided cases as well. This method consists of determining the carbon content (and, when applicable, the nitrogen content) by chemical analysis at incremental depths below the surface. The chemical method is considered to be the most accurate method of measuring total case depth. Two common methods used for analyzing carbon content are combustion analysis or spectrographic analysis. Combustion carbon analysis is the most widely employed.

Procedure for Carburized Cases. If test specimens are used, they should be of the same grade of steel, but not necessarily the same heat, as that of the parts being carburized. Specimens may be actual parts, rings, or bars, and the carburized surface should be flat or otherwise suitable for accurate machining to obtain chips for subsequent carbon analysis. To ensure maximum uniformity of the carburizing process among various types of furnaces, large heat-treatment facilities often use test specimens. These specimens are often standardized with respect to alloy and configuration to establish carburizing schedules for various case depths and to ensure maximum uniformity among various furnaces. Case depths of actual parts then can be correlated to the standard test specimen.

Test specimens should be carburized with actual parts, but in some cases a simulation procedure is used in a manner representative of the procedure to be used for actual parts. However, simulation is not recommended because the furnace

load containing the test specimens should approximate actual production conditions in terms of load density, configuration, and surface area to be carburized. These three variables affect atmosphere flow, temperature uniformity, and carbon demand. Differences in these conditions between production loads and the load that contains the specimens can lead to errors in the correlation of case depths.

In cooling of test specimens after carburizing, care should be exercised to avoid distortion and decarburization. When parts and test specimens are quenched after being carburized, they should be tempered at approximately 165 to 190 °C (325 to 375 °F). After removal of a sample from the test specimen for case depth determination, the remainder should be tempered at 595 to 650 °C (1100 to 1200 °F). Time at temperature should be minimized to avoid excessive carbon diffusion. The parts and specimens should be straightened to 0.038 mm (0.0015 in.) maximum total indicator reading (TIR) before machining is attempted.

Test specimens must have clean surfaces and should be machined dry, taking the necessary precautions to avoid burning. Predetermined increments of depth from 0.05 to 0.25 mm (0.002 to 0.010 in.) are chosen, depending on desired accuracy and expected case depth. A typical procedure for obtaining specimens for carbon analysis is:

1. Prepare a bar of suitable material in the configuration shown in Fig. 2. Identify the bar in some manner, such as by stamping a number on the end
2. Carburize and then quench or cool the bar as required. If the bar is slowly cooled, steps 3 through 7 can be omitted
3. Wash bar with soap and water. Rinse with methanol, and dry
4. Cut a section from the 25 mm (1 in.) diam end for examination of micro-structure
5. Record the as-quenched surface hardness of the large-diameter end
6. Temper the bar for the time and at the temperature specified for the part with which the test bar was carburized. Record the as-tempered hardness of the large-diameter end
7. Temper for $1\frac{1}{2}$ h at 650 °C (1200 °F)
8. Grit blast lightly, clean centers, and straighten bar to 0.038 mm (0.0015 in.) TIR taken in three places
9. Wash bar with soap and water. Rinse with methanol, and dry
10. For case depths less than 5.10 mm (0.200 in.), machine approximately 3.8 mm (0.15 in.) from the 25 mm (1 in.) diam end to a depth of 5.0 mm (0.20 in.), to ensure that the case on the end does not contaminate the specimens for carbon analysis. An alternative is to just perform a plunge cut in the center section of the turn bar, in order to preclude any machining at the ends of the bar
11. Machine the bar. Before each machining operation, record the diameter of the bar as measured with a micrometer. Maximum allowable taper of machined area is 0.03 mm (0.001 in.) on the radius. Machine a maximum of 0.05 mm (0.002 in.) from the radius to clean the surface. Save the chips for analysis. Next, machine the radius in increments ranging from 0.05 to 0.25 mm (0.002 to 0.010 in.), depending on the desired accuracy and expected case depth. Machine the radius in increments to a depth of 0.25 mm (0.010 in.) below the maximum expected case depth. Take three more increments of 0.25 mm (0.010 in.) from the radius or make three cuts at the expected case-depth break (0.40 wt% C). Save chips from each increment for separate analysis. Take precautions to ensure that chips from each cut are not burned or contaminated by dirt, paper, oil, or chips from preceding cuts
12. Analyze chips or turnings
13. Calculate and plot the carbon-gradient curve. A sample data sheet and a carbon-gradient curve are presented in Table 1 and Fig. 3, respectively

Table 1 Sample data sheet for computing case-depth values for a carbon-gradient plot

Data are for 8620H steel, carburized at 925 °C (1700 °F) in a 19-tray continuous pusher furnace with infrared control of carbon dioxide content in zones 2, 3, and 4. See text for explanation of procedure, and see Fig. 3 for plot of carbon gradient.

Cut No.	Dimensional factor, mm									Carbon, %
	D_L [a]	D_R [a]	A_L [b]	A_R [b]	C_L [c]	C_R [c]	X [d]	M [e]	P [f]	
0	25.35	25.36	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
1	25.20	25.23	0.15	0.13	0.15	0.13	0.07	0.03	0.03	0.987
2	24.98	24.99	0.22	0.24	0.37	0.37	0.18	0.06	0.13	0.953
3	24.76	24.76	0.22	0.23	0.59	0.60	0.30	0.06	0.24	0.918

4	24.49	24.47	0.27	0.29	0.86	0.89	0.44	0.07	0.37	0.871
5	24.22	24.22	0.27	0.25	1.13	1.14	0.57	0.06	0.50	0.818
6	23.94	23.91	0.28	0.31	1.41	1.45	0.71	0.07	0.64	0.787
7	23.69	23.65	0.25	0.26	1.66	1.71	0.84	0.06	0.77	0.717
8	23.41	23.38	0.28	0.27	1.94	1.98	0.98	0.07	0.91	0.675
9	23.10	23.10	0.31	0.28	2.25	2.26	1.13	0.07	1.05	0.627
10	22.80	22.78	0.30	0.32	2.55	2.58	1.28	0.08	1.21	0.583
11	22.49	22.48	0.31	0.30	2.86	2.88	1.43	0.08	1.36	0.540
12	22.19	22.17	0.30	0.31	3.16	3.19	1.59	0.08	1.51	0.483
13	21.87	21.87	0.32	0.30	3.48	3.49	1.74	0.08	1.67	0.444
14	21.59	21.56	0.28	0.31	3.76	3.80	1.89	0.07	1.81	0.401
15	21.25	21.27	0.34	0.29	4.10	4.09	2.05	0.08	1.97	0.365
16	20.80	20.75	0.45	0.52	4.55	4.61	2.29	0.12	2.17	0.328
17	20.27	20.24	0.53	0.51	5.08	5.12	2.55	0.13	2.42	0.283
18	19.72	19.68	0.55	0.56	5.63	5.68	2.83	0.14	2.69	0.245

(a) D_R, D_L = Diameters of left and right ends of turned bar, respectively. $D_{L, 0}$, $D_{R, 0}$ are diameters before turning; $D_{L, n}$, $D_{R, n}$ are diameters measured after each cut.

(b) A_L, A_R = Material removed from diameter as measured from preceding cut; $A_{L, n} = D_{R, n-1} - D_{L, n}$, $A_{R, n} = D_{R, n-1} - D_{R, n}$, n > 0.

(c) C_L, C_R = Total diametrical depth of material removed, measured from case-hardened bar surface; $C_{L, n} = D_{L, n} - D_{L, 0}$, $C_{R, n} = D_{R, n} - D_{R, 0}$, n > 0.

(d) X = Average total radial depth of material removed from case-hardened bar surface; $X_n = (C_{L, n} + C_{R, n})/4$, n > 0.

(e) M = Average radial midpoint of current depth of cut as measured from preceding depth; $M_n = (X_n - X_{n-1})/2$, n > 0.

(f) P = Plotted depth from surface of bar corresponding to chemical analysis of turnings from this depth; $P_n = X_{n-1} + M_n$, n > 0

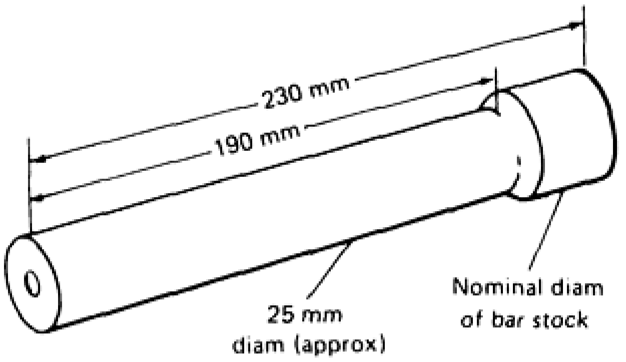

Fig. 2 Nominal configuration of standard test bar used for chemical method of case depth measurement. The 25 mm (1 in.) diam end is finished with 80 grit sandpaper.

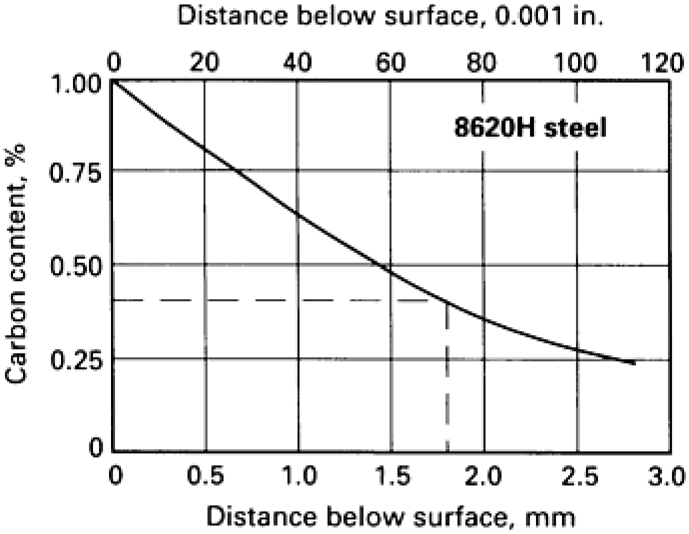

Fig. 3 Carbon gradient for carburized test bar of 8620H steel. A test bar similar to the one shown in Fig. 2 was carburized at 925 °C (1700 °F) in a 19-tray continuous pusher furnace with infrared control of carbon dioxide content in zones 2, 3, and 4. Effective case depth to 0.40% C is 1.82 mm (0.0715 in.) (indicated by broken lines). See text for explanation of procedure for calculating plot points and Table 1 for sample data sheet for this figure.

Spectrographic Analysis. Carbon content may be determined accurately by spectrographic analysis. This method makes use of a vacuum spectrometer, which permits measurement of spectral lines in the ultra-violet region where air would ordinarily absorb much of the emitted radiation.

Many critical items must be assessed for carbon content to ensure uniform properties after heat treatment. The spectrographic carbon method normally uses flat test specimens that can be taper ground, step ground, or reground incrementally after each carbon determination. A very small amount of material is ground from the surface (to remove oxides). Successive cuts are made and analyses are performed after each cut. Each test takes less than 2 min.

Special care must be taken for accurate measurement of the depth corresponding to each carbon determination. Case depth determined on flat or round test specimens will often be different from case depth determined directly on workpieces because of the difference in shape.

Whereas carbon determination by the combustion method provides an average carbon content for the amount of material removed by machining, the spectrograph determines the local carbon content of the specimen to a depth of 0.03 mm (0.001 in.). A comparison of carbon values obtained from five specimens by spectrographic methods is presented in Table 2.

Table 2 Carbon contents of shim stock and of surfaces of workpieces concurrently processed, as determined by spectrographic and combustion analysis

Both shim stock and workpieces were heat treated in a continuous-belt furnace with an endothermic-base atmosphere (class 301; dew point, -9 to -1 °C, or 15 to 30 °F).

Specimen No.	Carbon present, %		
	Shim stock		Workpiece surface (spectrographic analysis)
	Spectrographic analysis	Combustion analysis	
1	0.36	0.36	0.38
2	0.24	0.27	0.25
3	0.22	0.24	0.225
4	0.35	0.35	0.34

Mechanical Method

In the mechanical method of measuring case depth, hardness traverses are taken on the case and core of a specimen that has been prepared by one of three procedures. The mechanical method is the most widely used method and is considered the most accurate method of measuring effective case depth (depth to 50 HRC). This method is also preferred for measuring total depth of thin cases (≤ 0.25 mm, or 0.01 in.).

For measurement of effective case depth, read to the point of specified hardness, which is 50 HRC (or approved equivalent) except for selectively hardened cases, for which the values recommended are:

Carbon content, %	Case hardness, HRC
0.28-0.32	35
0.33-0.42	40
0.43-0.52	45
0.53 and over	50

Microhardness testers that produce small, shallow impressions should be used for all of the following procedures so that the hardness values obtained will be representative of the surface or area being tested. Testers that produce Vickers or Knoop microhardness numbers with loads of 0.2 to 1.0 kg are recommended.

Considerable care should be exercised during the preparation of specimens for case depth determination by the mechanical method to prevent cutting or grinding temper burns. The use of an etchant for burn detection is recommended

as a general precaution because of the serious error that can be introduced by the presence of metal whose metallurgical condition has been altered during specimen preparation by temper burning. However, a heavy application of etchant could affect hardness values and should be avoided.

Cross-Section Procedure. Cut specimens perpendicular to the hardened surface at a near central-length location, being careful to avoid any cutting or grinding practice that would affect the original hardness.

Grind and polish the specimen. The surface of the area to be traversed should be polished finely enough so that hardness impressions are unaffected (the lighter the indenter load, the finer the polish necessary). A 6 μm maximum final polish is recommended.

The procedure illustrated in Fig. 4 is recommended for the measurement of light and medium cases. The alternative procedure shown in Fig. 5 is recommended for the measurement of medium and heavier cases (>0.38 mm, or 0.015 in. case depth).

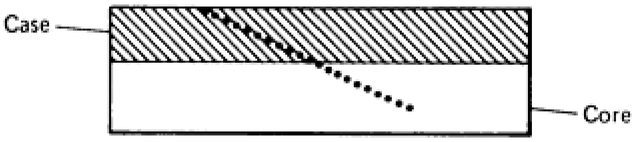

Fig. 4 Cross-sectioned specimen for hardness-traverse method of measuring depth of light and medium cases. Dots show locations of hardness-indenter impressions.

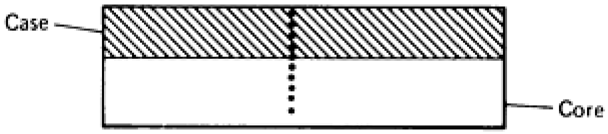

Fig. 5 Cross-sectioned specimen for hardness-traverse method of measuring depth of medium and heavy cases. Dots show locations of hardness-indenter impressions.

The hardness traverse should be started far enough below the surface (0.13 mm, or 0.005 in., with a 500 g load at 58 HRC or greater hardness) to ensure proper support from the metal between the center of the impression and the surface. Subsequent impressions are spaced far enough apart so that the hardness test impressions are not distorted. The distance from the surface to the center of the impression is measured on a calibrated optical instrument, micrometer stage, or other suitable measuring device.

Taper-Grind Procedure. This procedure, illustrated in Fig. 6, sometimes is used for the measurement of light and medium cases. A shallow taper is ground through the case, and hardness measurements are made along the surface thus prepared. The angle is chosen so that equidistant readings will represent the hardnesses at the desired increments below the surface of the case. This procedure is difficult and therefore not recommended.

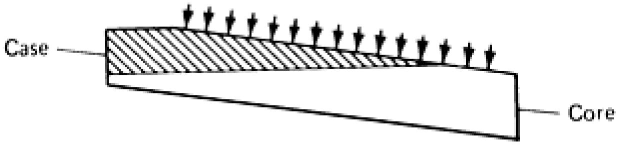

Fig. 6 Taper-ground specimen for hardness-traverse method of measuring depth of light and medium cases. Arrows show locations of hardness-indenter impressions.

Step-Grind Procedure. This procedure, shown in Fig. 7, is recommended for the measurement of medium and heavy cases. It is essentially the same as the taper-grind procedure, with the exception that hardness readings are made on steps that are known distances below the surface. Like the taper-grind procedure, the step-grind procedure is not generally recommended.

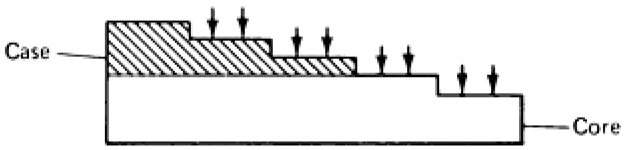

Fig. 7 Step-ground specimen for hardness-traverse method of measuring depth of medium and heavy cases. Arrows show locations of hardness-indenter impressions.

A variation on this procedure is the step-grind method in which two predetermined depths are ground. If the hardness is greater than 50 HRC on the shallow step and less than 50 HRC on the deep step, the effective case depth to 50 HRC lies somewhere between the two steps. This variation frequently is used to ensure that the effective case depth is within specified limits.

Visual Methods

These methods employ any visual procedure, with or without the aid of magnification, for reading the depth of case produced by any of the various processes. Specimens may be prepared by combinations of fracturing, cutting (with water cooling to prevent burning), grinding, and polishing. Etching with a suitable reagent normally is required to produce a contrast between the case and the core. Nital (concentrated nitric acid in alcohol) of various strengths is frequently used as the reagent for producing this contrast.

Visual methods have been classified into two general categories: macroscopic and microscopic. In macroscopic procedures, specimens normally are ground no finer than through No. 000 metallographic emery paper (600 grit silicon carbide paper), and magnifications usually do not exceed 20 diameters. The Brinell microscope, a hand-held optical instrument with retical markings at intervals of 0.1 mm (about 0.004 in.) and 20 diam magnification, is a convenient tool for macroscopic measurement. In microscopic procedures, complete metallographic polishing and etching generally are required, and case depths normally are read at a magnification of 100 diameters.

Macroscopic Visual Procedures

Macroscopic methods for measuring case depth are recommended for routine process control, primarily because of the short time required for determinations and because of the minimum of specialized equipment and trained personnel that are needed. Although these methods normally are applied to hardened specimens, they have the additional advantage of being applicable to the measurement of unhardened cases as well. However, the accuracy of such measurements can be improved by correlation with the results of other methods. A variety of methods may be employed with equal success, but typical and widely used procedures are:

- *Fracture:* Prepare part or specimen by fracturing. Examine at a magnification not exceeding 20 diameters, with no further preparation
- *Fracture and etch:* Water quench part or specimen directly from the carburizing temperature. Fracture, then etch in 20% nitric acid in water for a time established to develop maximum contrast. Rinse in water, and read while wet
- *Fracture or cut, and rough grind:* Prepare specimen by either fracturing or cutting (with water cooling), and then rough grinding. Etch in 10% nital for a time established to provide a sharp line of demarcation between case and core. Examine at a magnification not exceeding 20 diameters (Brinell microscope), and read all of the darkened area for approximate total case depth
- *Fracture or cut, and polish or grind:* Prepare specimen by fracturing or cutting (with water cooling). Polish, or grind through No. 000 or finer metallographic emery paper (600 grit silicon carbide paper), or both. Etch in 5% nital for approximately 1 min. Rinse in two clean alcohol or water rinses. Examine at a magnification not exceeding 20 diameters (Brinell microscope) and read all of the darkened zone. After correlation, effective case depth can be determined by reading from external surface of specimen to a selected line of the darkened zone. An alternative etching procedure is to etch in 25% nital for 30 s, wash in concentrated picral, rinse in alcohol, blow dry, and read as described above
- *M_s method:* This method of case-depth measurement utilizes the fact that the martensite-start temperature (M_s point) varies with carbon content. Quenching and holding the steel for a short time at the M_s point corresponding to a given carbon content tempers the martensite formed at all lower carbon levels. Subsequent water quenching transforms austenite at all higher carbon levels to untempered martensite. Then polishing and etching of the testpiece will reveal a sharp line of demarcation between tempered and untempered martensite; this line is normally read at 20 diam magnification (Brinell microscope) to a precision of ±0.05 mm (±0.002 in.)

The case depth is not sensitive to small temperature changes in the quenching bath. The final selection of quenching temperature is usually done statistically to produce an equal plus-and-minus distribution of error about known carbon curves.

The main factors that affect the accuracy of this method are pearlite formation during quenching to the M_s point and time at M_s temperature. The specimen size should be sufficiently small to ensure that the severity of quench transforms all austenite of lower carbon levels to martensite without any formation of pearlite. (Specimen size may be critical for low-hardenability steels.) The time at M_s temperature should be short enough to preclude the formation of bainite, which interferes with the sharpness of the line of demarcation upon etching and can obliterate it completely. For additional information on the M_s technique, see Ref 2.

Microscopic Visual Procedures

Microscopic methods generally are used for laboratory measurement of case depth and require complete metallographic polishing and etching suitable for the material and the process. Measurements are made using a filar measuring microscope accessory that replaces one of the ocular viewing lenses. The most common magnification used for examination is 100 diameters.

Carburized Cases. Microscopic methods may be used for laboratory determinations of total and effective case depths of material in the hardened condition. When the specimen is annealed properly, the total case depth can be determined quite precisely. For certain applications involving alloy steels of moderate-to-high hardenability that contain 0.4 to 0.8% C, the M_s method of determining case depth to a specific carbon level has been found effective.

Procedure for hardened condition:

1. Fracture or cut specimen (water cool when cutting) at right angles to the surface
2. Prepare specimen for microscopic examination and etch in 2 to 5% nital
3. For approximation of effective case depth, read from surface to metallographic structures that have been shown to be equivalent to 50 HRC. Often, the structure that is nearly equivalent to 50 HRC consists of about 85% tempered martensite and 15% intermediate quench or mixed upper transformation products
4. For approximation of total case depth, read to the line of demarcation between the case and the core. In alloy steels that have been quenched from a high temperature, the line of demarcation is not sharp. Read all of the darkened zone that indicates a difference in carbon content from that of the uniform core structure

See Table 3 and Fig. 8 for Vickers, Brinell, Knoop, and Rockwell hardness conversions.

Table 3 Approximate equivalent hardness numbers for steel

For carbon and alloy steels in the annealed, normalized, and quenched-and-tempered conditions; less accurate for cold-worked condition and for austenitic steels. The values in **boldface type** correspond to the values in the joint SAE-ASM-ASTM hardness conversions as printed in ASTM E140, Table 1. The values in parentheses are beyond normal range and are given for information only.

HV	HK, 500 g load and greater	HRC, 150 kg load, Brale indenter	Superficial Brale indenter			HB, 3000 kg load, 10 mm ball	
			HR15N scale, 15 kg load	HR30N scale, 30 kg load	HR45N scale, 45 kg load	Standard ball	Tungsten carbide ball
940	920	**68.0**	**93.2**	**84.4**	**75.4**	. . .	. . .
920	908	**67.5**	**93.0**	**84.0**	**74.8**	. . .	. . .
900	895	**67.0**	**92.9**	**83.6**	**74.2**	. . .	. . .
880	882	**66.4**	**92.7**	**83.1**	**73.6**	. . .	(767)
860	867	**65.9**	**92.5**	**82.7**	**73.1**	. . .	(757)
840	852	**65.3**	**92.3**	**82.2**	**72.2**	. . .	**(745)**
820	837	**64.7**	**92.1**	**81.7**	**71.8**	. . .	**(733)**
800	822	**64.0**	**91.8**	**81.1**	**71.0**	. . .	**(722)**
780	806	**63.3**	**91.5**	**80.4**	**70.2**	. . .	**(710)**
760	788	**62.5**	**91.2**	**79.7**	**69.4**	. . .	**(698)**
740	772	**61.8**	**91.0**	**79.1**	**68.6**	. . .	**(684)**
720	754	**61.0**	**90.7**	**78.4**	**67.7**	. . .	**(670)**
700	735	**60.1**	**90.3**	**77.6**	**66.7**	. . .	**(656)**

690	725	**59.7**	**90.1**	**77.2**	**66.2**	. . .	**(647)**
680	716	**59.2**	**89.8**	**76.8**	**65.7**	. . .	**(638)**
670	706	**58.8**	**89.7**	**76.4**	**65.3**	. . .	**(630)**
660	697	**58.3**	**89.5**	**75.9**	**64.7**	. . .	**620**
650	687	**57.8**	**89.2**	**75.5**	**64.1**	. . .	**611**
640	677	**57.3**	**89.0**	**75.1**	**63.5**	. . .	**601**
630	667	**56.8**	**88.8**	**74.6**	**63.0**	. . .	**591**
620	657	**56.3**	**88.5**	**74.2**	**62.4**	. . .	**582**
610	646	**55.7**	**88.2**	**73.6**	**61.7**	. . .	**573**
600	636	**55.2**	**88.0**	**73.2**	**61.2**	. . .	**564**
590	625	**54.7**	**87.8**	**72.7**	**60.5**	. . .	**554**
580	615	**54.1**	**87.5**	**72.1**	**59.9**	. . .	**545**
570	604	**53.6**	**87.2**	**71.7**	**59.3**	. . .	**535**
560	594	**53.0**	**86.9**	**71.2**	**58.6**	. . .	**525**
550	583	**52.3**	**86.6**	**70.5**	**57.8**	**(505)**	**517**
540	572	**51.7**	**86.3**	**70.0**	**57.0**	**(496)**	**507**
530	561	**51.1**	**86.0**	**69.5**	**56.2**	**(488)**	**497**
520	550	**50.5**	**85.7**	**69.0**	**55.6**	**(480)**	**488**
510	539	**49.8**	**85.4**	**68.3**	**54.7**	**(473)**	**479**
500	528	**49.1**	**85.0**	**67.7**	**53.9**	**(465)**	**471**
490	517	**48.4**	**84.7**	**67.1**	**53.1**	**(456)**	**460**
480	505	**47.7**	**84.3**	**66.4**	**52.2**	**(448)**	**452**
470	494	**46.9**	**83.9**	**65.7**	**51.3**	**441**	**442**
460	482	**46.1**	**83.6**	**64.9**	**50.4**	**433**	**433**
450	471	**45.3**	**83.2**	**64.3**	**49.4**	**425**	**425**
440	459	**44.5**	**82.8**	**63.5**	**48.4**	**415**	**415**
430	447	**43.6**	**82.3**	**62.7**	**47.4**	**405**	**405**
420	435	**42.7**	**81.8**	**61.9**	**46.4**	**397**	**397**
410	423	**41.8**	**81.4**	**61.1**	**45.3**	**388**	**388**
400	412	**40.8**	**80.8**	**60.2**	**44.1**	**379**	**379**
390	400	**39.8**	**80.3**	**59.3**	**42.9**	**369**	**369**
380	389	**38.8**	**79.8**	**58.4**	**41.7**	**360**	**360**
370	378	**37.7**	**79.2**	**57.4**	**40.4**	**350**	**350**
360	367	**36.6**	**78.6**	**56.4**	**39.1**	**341**	**341**
350	356	**35.5**	**78.0**	**55.4**	**37.8**	**331**	**331**
340	346	**34.4**	**77.4**	**54.4**	**36.5**	**322**	**322**
330	337	**33.3**	**76.8**	**53.6**	**35.2**	**313**	**313**
320	328	**32.2**	**76.2**	**52.3**	**33.9**	**303**	**303**
310	318	**31.0**	**75.6**	**51.3**	**32.5**	**294**	**294**
300	309	**29.8**	**74.9**	**50.2**	**31.1**	**284**	**284**
295	305	**29.2**	**74.6**	**49.7**	**30.4**	**280**	**280**
290	300	**28.5**	**74.2**	**49.0**	**29.5**	**275**	**275**
285	296	**27.8**	**73.8**	**48.4**	**28.7**	**270**	**270**
280	291	**27.1**	**73.4**	**47.8**	**27.9**	**265**	**265**
275	286	**26.4**	**73.0**	**47.2**	**27.1**	**261**	**261**
270	282	**25.6**	**72.6**	**46.4**	**26.2**	**256**	**256**
265	277	**24.8**	**72.1**	**45.7**	**25.2**	**252**	**252**
260	272	**24.0**	**71.6**	**45.0**	**24.3**	**247**	**247**
255	267	**23.1**	**71.1**	**44.2**	**23.2**	**243**	**243**
250	262	**22.2**	**70.6**	**43.4**	**22.2**	**238**	**238**
245	258	**21.3**	**70.1**	**42.5**	**21.1**	**233**	**233**
240	253	**20.3**	**69.6**	**41.7**	**19.9**	**228**	**228**
230	243	(18.0)	. . .	. . .	. . .	219	219
220	234	(15.7)	. . .	. . .	. . .	209	209
210	226	(13.4)	. . .	. . .	. . .	200	200
200	216	(11.0)	. . .	. . .	. . .	190	190
190	206	(8.5)	. . .	. . .	. . .	181	181
180	196	(6.0)	. . .	. . .	. . .	171	171
170	185	(3.0)	. . .	. . .	. . .	162	162
160	175	(0.0)	. . .	. . .	. . .	152	152
150	164	. . .	. . .	. . .	. . .	143	143
140	154	. . .	. . .	. . .	. . .	133	133
130	143	. . .	. . .	. . .	. . .	124	124
120	133	. . .	. . .	. . .	. . .	114	114

110	123	. . .	. . .	. . .	. . .	105	105
100	112	. . .	. . .	. . .	. . .	95	95
95	107	. . .	. . .	. . .	. . .	90	90
90	102	. . .	. . .	. . .	. . .	86	86
85	97	. . .	. . .	. . .	. . .	81	81

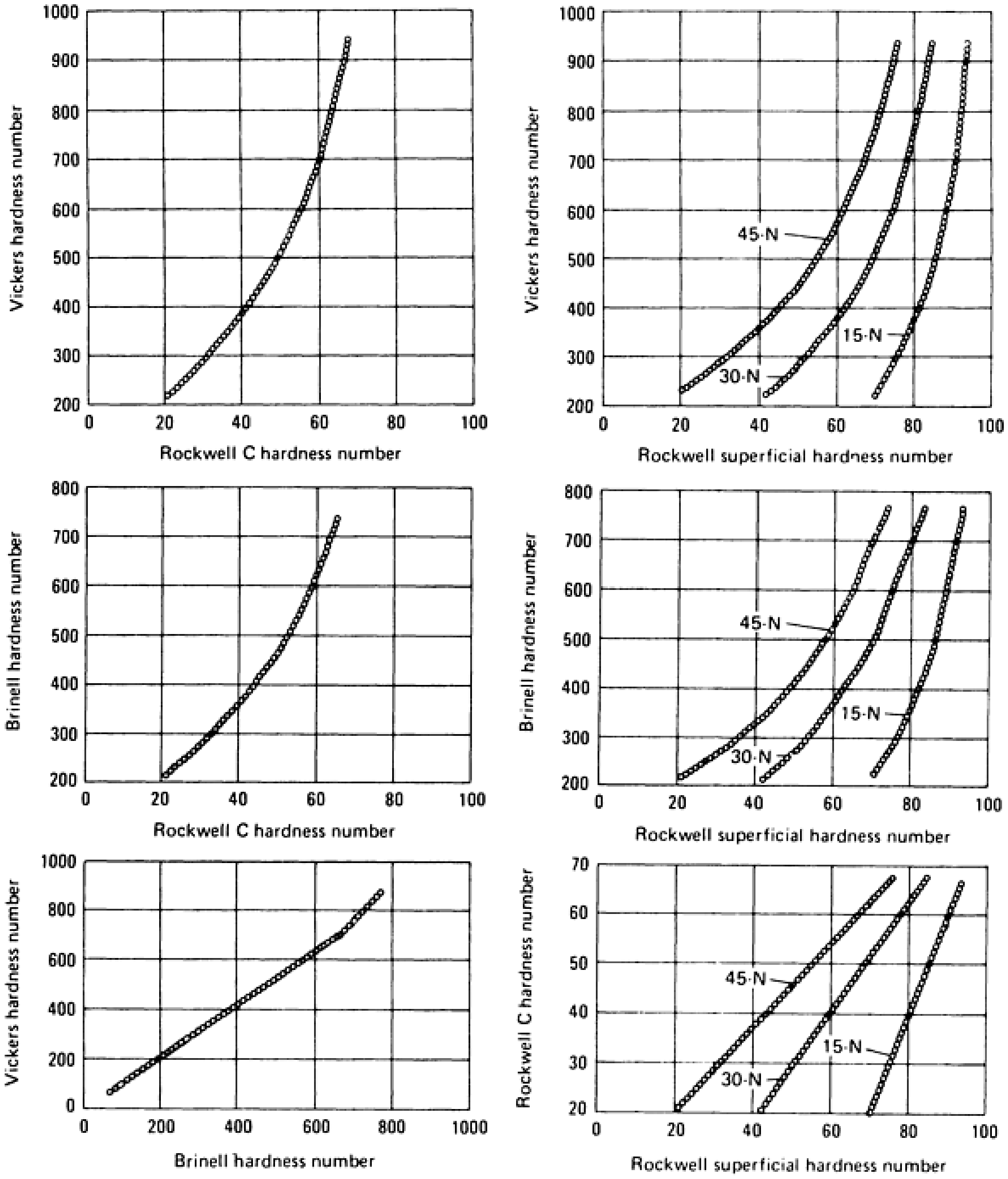

Fig. 8 Approximate equivalent hardness numbers for steel

Procedure for annealed condition (for specimens previously hardened or not cooled under controlled conditions):

1. The specimen to be annealed may be protected by copper plating or by masking with other suitable compounds for preventing carbon loss
2. Anneal specimens in a protective atmosphere (or use the outdated practice of packing specimens in a thin-walled container with a suitable material such as charcoal, spent chips, or pitch coke)
3. Heat specimens to a temperature about 30 to 55 °C (about 50 to 100 °F) above the upper critical temperature (Ac_3) for the core. (Generally, an annealing temperature of 870 to 925 °C, or 1600 to 1700 °F, is

satisfactory.) Hold specimen at temperature only long enough to transform completely to austenite; otherwise, excessive diffusion of carbon may lead to inordinately high estimates of actual total case depth
4. Cool from the annealing temperature at the following rates for carbon and alloy steels: a normally satisfactory cooling rate for most plain carbon steels such as 1010, 1015, and 1018 is 150 °C/h (270 °F/h) from the annealing temperature to 425 °C (800 °F). For high-manganese steels (1500 series), boron steels, and steels with high residual alloy contents, cooling may have to be slower. Cool as desired below 425 °C (800 °F). For most alloy steels, the best results are obtained from isothermal transformation. For some steels, however, a low cooling rate, such as 75 °C/h (135 °F/h) from the annealing temperature to 425 °C (800 °F), is satisfactory. If martensite is retained in the structure, better contrast after etching may be obtained by tempering the specimen at 540 to 595 °C (1000 to 1100 °F). Cool as desired after tempering
5. Section, prepare, and etch specimen as described under "Procedure for hardened condition"
6. For total case depth, read the depth at which no further change in microstructure occurs

Production carburizing schedules often have cooling rates similar to those described above under "Procedure for annealed condition." Specimens treated in this manner may be prepared and examined without being reheated after carburizing, and the results can be accurately correlated to a standard specimen.

Additional information is available in the articles "Gas Carburizing," "Pack Carburizing," "Vacuum Carburizing," "Plasma (Ion) Carburizing," and "Microstructures and Properties of Carburized Steels" in this Volume.

Carbonitrided cases are measured for total case depth in the hardened condition. High quenching temperatures, high alloy content of the steel, and high carbon content of the core decrease the accuracy of readings obtained by this method.

Procedure: Section, prepare, etch, and read as described above for carburized cases, under "Procedure for hardened condition" in this section.

Cyanided cases are thin, and only the microscopic method is recommended for accurate case depth measurement. The usual cyanided case contains a light-etching layer followed by a totally martensitic constituent, which in turn is followed by martensite accompanied by increasingly extensive networks of other constituents, depending on the type of steel. Cyanided cases are read in the hardened condition only, and results are reported as total case depth. Additional information is available in the article "Liquid Carburizing and Cyaniding" in this Volume.

Procedure:

1. Section, prepare, and etch specimen as already described for carburized cases under "Procedure for hardened condition"
2. Read to the line of demarcation between the case and the core. Often, optical case depth greatly exceeds effective case depth. (When a sharp line of demarcation does not exist, a hardness traverse such as that described in the section "Mechanical Method" in this article is recommended)

Nitrided Cases. For measuring the depths of nitrided cases, the microscopic method is used chiefly in those situations in which the available sample cannot readily be prepared for the more desirable hardness-traverse method.

Procedure:

1. Section and prepare specimen as described above for carburized cases under "Procedure for hardened condition"
2. Etch specimen in less than 10% nital
3. Read all of the darkened zone for total case depth

Additional information is available in the articles "Carbonitriding," "Gas Nitriding," "Liquid Nitriding," and "Plasma (Ion) Nitriding" in this Volume.

Selectively Hardened Cases. Because no compositional change occurs in selective hardening (induction hardening, for example), readings must be taken on material in the hardened or the hardened-and-tempered condition only. A procedure for reading effective case depth may be established by correlating microstructures with a hardness-traverse method. A minimum hardness of 50 HRC is commonly used, but some other value may be selected or required, for example, in lower-carbon steels that do not reach 50 HRC when fully hardened (see the in-text table correlating carbon content with effective case depth hardness under the section "Mechanical Method"). The microstructure at the selected location will vary depending on steel composition, prior treatment, and hardness level chosen.

Procedure:

1. Section, prepare, and etch specimen as described above for carburized cases under "Procedure for hardened condition"
2. For total case depth, read the entire zone containing structures hardened by the process
3. For effective case depth, read to selected microstructure correlated with specified hardness

Microhardness Testing. The most precise means of measuring effective case depth is the microhardness test. This consists of making light load indentations at specified linear intervals from a point near the edge of the surface to a point well within the core area, as shown in Fig. 9. For case depth measurements, the selection of a Knoop indenter is recommended so that the highest density of indentations may be obtained.

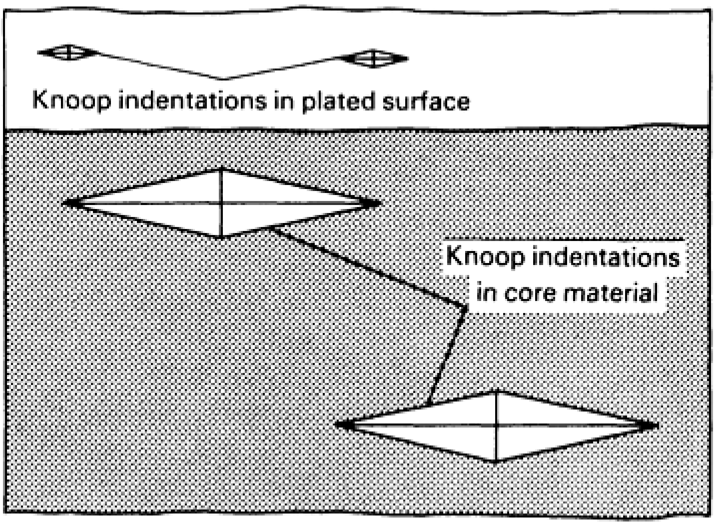

Fig. 9 Comparison of Knoop indentation using the same load in both the hardened case and soft core of a workpiece

The Knoop indenter shown in Fig. 10 uses a spheroconical diamond that produces an elongated indentation. This is especially important when measuring thin cases.

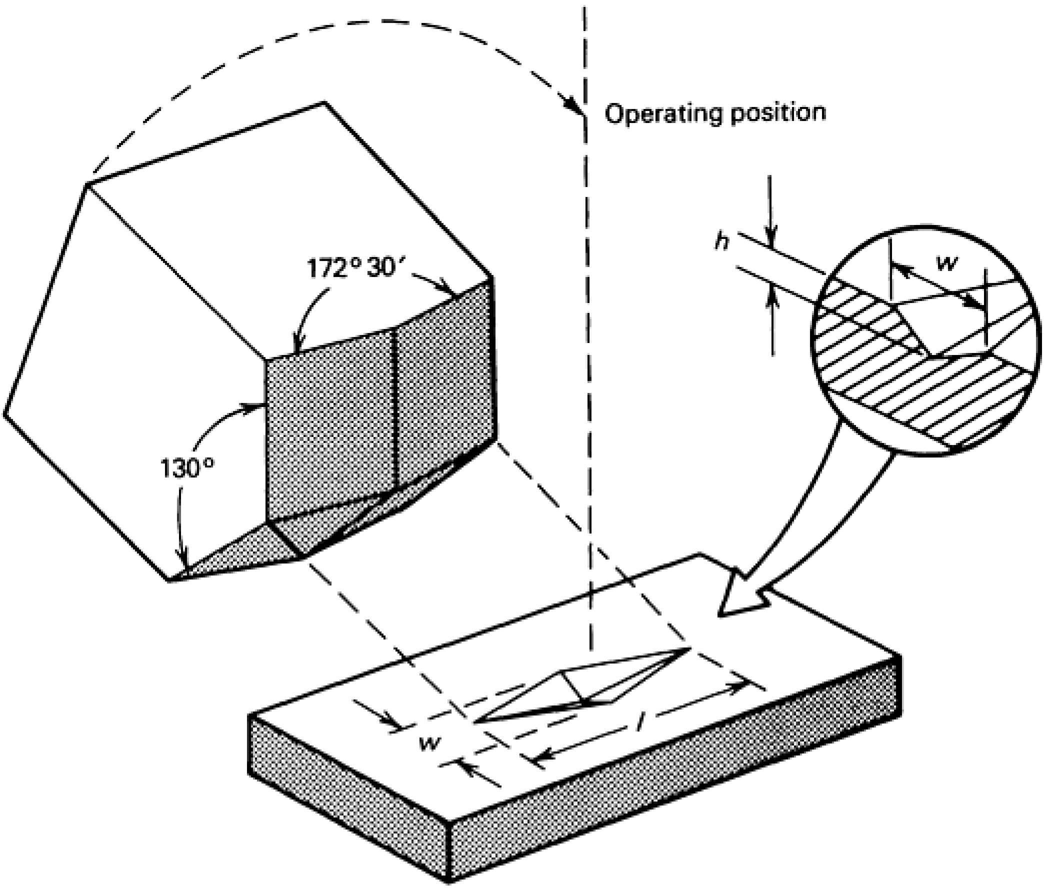

Fig. 10 Pyramidal or spheroconical Knoop indenter and resulting indentation in the workpiece

The use of the square pyramid Vickers indenter shown in Fig. 11 limits the ability to make closely spaced indentations and indentations close to the surface. To avoid error, there should always be a two-indentation-width space from the edge of the case to the first indentation and the same distance between subsequent indentations. The load selection is based on the need to have a sufficient number of indentations to obtain good reliable data and large enough indentations to be read accurately. Microhardness traverses are made using loads ranging from 100 to 1000 g.

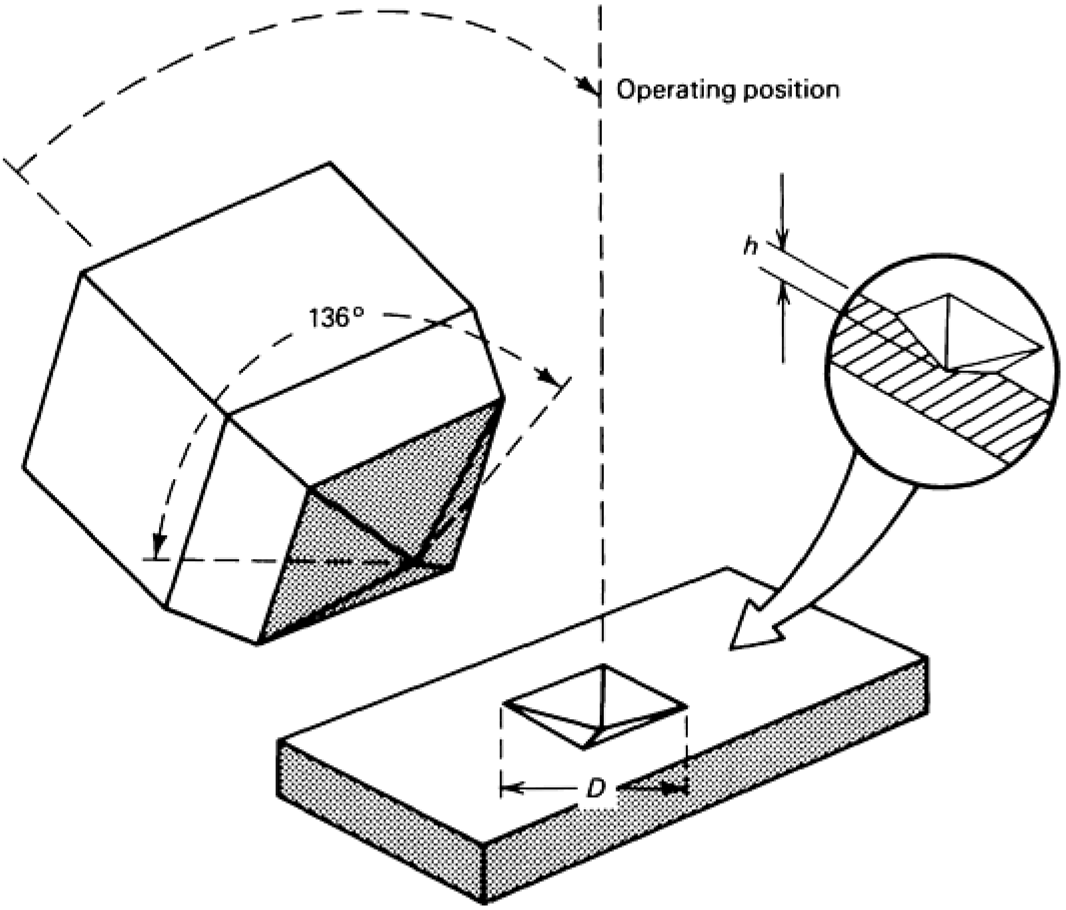

Fig. 11 Diamond pyramid indenter used for the Vickers test and resulting indentation in the workpiece. *D* is the mean diagonal of the indentation in millimeters.

Sample Preparation. The accuracy of a microhardness traverse across the case and core depends on the correct preparation of the sample to be tested. First, a representative cross section of the hardened case and adjacent core (unaffected material) must be cut from the bulk material with care to avoid altering the microstructure. The cut sample is then compression molded in a low-shrinkage thermosetting resin containing a hard filler to retain the edge of the case. The sample is ground and polished, with attention to maintaining flatness across the entire sample. To accomplish this, the same care should be taken as would be taken were the sample to be examined for microstructure. Each step must be performed thoroughly with ample lubrication to prevent microstructural deformation. The intermediate polishing step following the fine grinding sequence should be performed on a napless cloth charged with 6 μm (240 μin.) diamond abrasive compound or suspension with a suitable extender. Final polishing with 0.05 μm (2 μin.) alumina on a napped cloth should be limited to approximately 30-s duration to prevent edge rounding.

Etching. It may be necessary to etch the as-polished sample to determine the demarcation between the case and the core, but this application of the etchant must be light. A heavy etch may affect the hardness readings and also make the visual measurement of the indentations more difficult.

Accuracy. The accuracy of microhardness testers should be checked regularly using the calibration sample provided. Care must also be taken to prevent errors due to the manual conversion of ocular indentation measurements to actual hardness numbers. Some more advanced testers display actual hardness numbers, making it unnecessary to convert ocular readings.

Hardness Scale Conversions. Because the more advanced microhardness testers are equipped to convert Knoop or Vickers measurements directly into Rockwell values, the chance for error is reduced. However, it must be remembered that any conversion of hardness values from one hardness measurement system to another introduces some error.

Reference cited in this section

2. E.S. Rowland and S.R. Lyle, The Application of M_s Points to Case Depth Measurement, *Trans. ASM,* Vol

37, 1946, p 27

Nondestructive Methods

Nondestructive methods of measuring case depth make use of the changing electrical and magnetic properties of the material through the depth of a case-hardened workpiece. These property changes result from localized differences of material microstructure, hardness, and/or chemistry within the case. Eddy current tests are the most frequently used nondestructive tests in the automotive industry. Primary among their valuable characteristics is the speed with which tests can be performed; this makes them suitable for the automatic testing of high production quantities. Production nondestructive evaluations of case depths are performed on parts such as piston pins; axle, transmission, and water pump shafts; and differential and transmission gears. Measured case depths range from 0.2 to 9 mm (0.008 to 0.35 in.), with agreement with destructive techniques of 0.2 mm (0.008 in.) or less. This requires equipment specifically designed for the parts being tested.

A typical system for the production precision measurement of case depths generally requires the use of master parts of known case depth to standardize the unit. With a system developed to test cold-extruded axle shafts, measurements are made on a master shaft and stored in computer memory for later comparison with measurements from unknown production parts. Desktop computers are commonly used to control the part scanner and eddy current instrument, acquire and analyze the data, and store the results. A typical test consists of placing the part within the test machine and then sequentially applying frequencies ranging from 5 to 10 kHz to the eddy current coil located at the area of interest. The computer uses the responses at certain frequencies to estimate the case depth. Then, on the basis of the estimate, it selects algorithms to make a final calculation of case depth, based on multiple linear regressions of eddy current responses at several frequencies against case depth. The particular frequencies used depend upon the location on the part. Generally, they consist of a combination of one or more low frequencies (0.1 to 1.0 kHz) with one or more higher frequencies (5 to 10 kHz). The highest frequencies (5 to 10 kHz) are used for surface hardness measurements. Figure 12 illustrates the correlation that can be achieved between destructive and nondestructive case depth measurement methods.

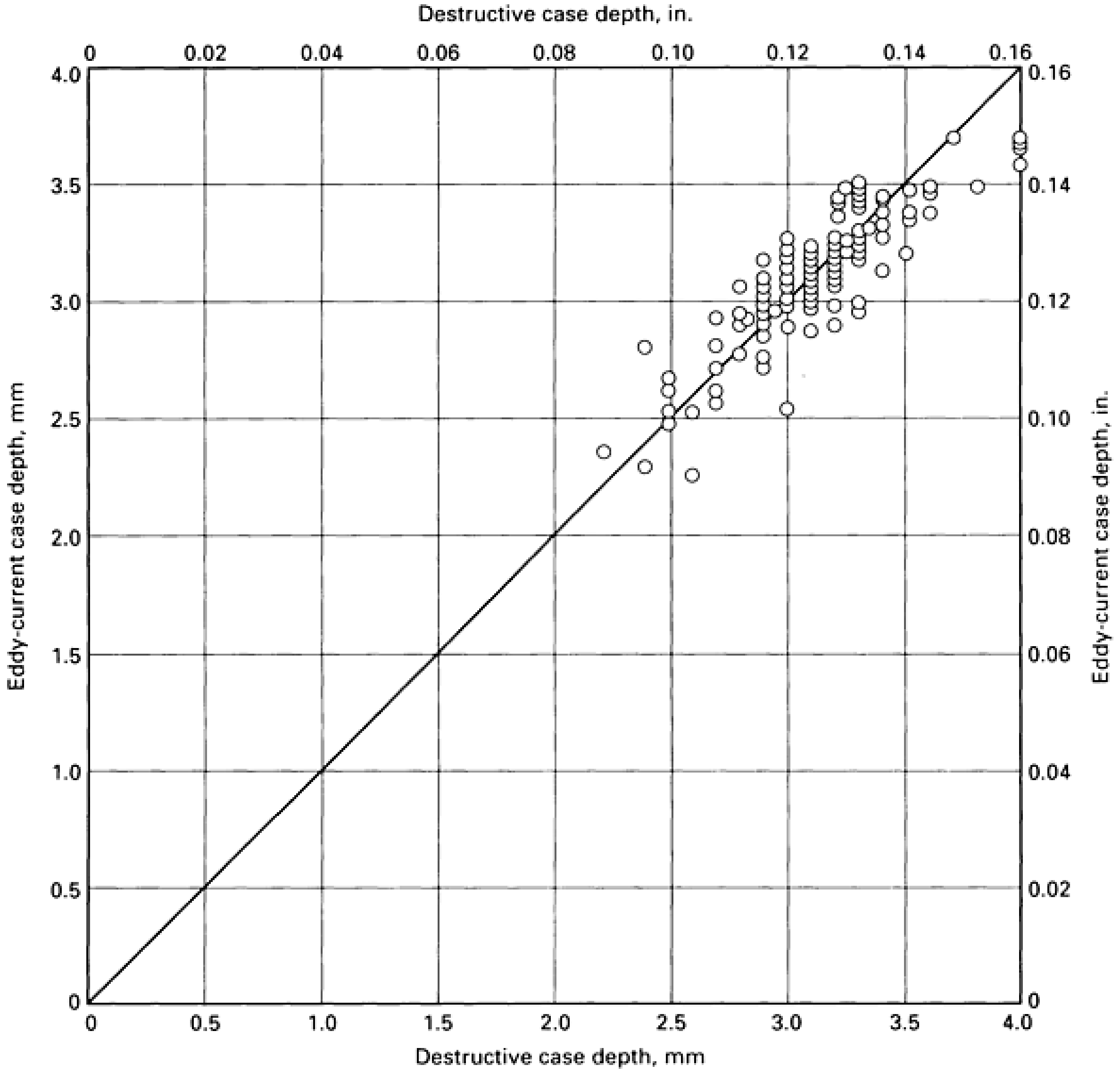

Fig. 12 Plot of axle-shaft correlation data for destructive and nondestructive case depth measurements. Source: Ref 3

The accuracy of eddy current inspection is limited by the testing conditions encountered by the instrument. Variations in workpiece temperature, material chemistry, and core microstructure can affect the impedance of the material and the resultant determination of case depth. When measuring carburized cases, varying surface carbon concentrations may introduce additional uncertainties. It is important to recognize these variables when designing and operating nondestructive measurement systems and selecting appropriate master parts.

Additional information is available in the articles "Eddy Current Inspection" and "Remote-Field Eddy Current Inspection," in *Nondestructive Evaluation and Quality Control*, Volume 17 of *ASM Handbook*, formerly 9th Edition *Metals Handbook.*

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3. Automotive Applications of Eddy Current Testing, in *Electromagnetic Testing*, Vol 4, 2nd ed., *Nondestructive Testing Handbook*, American Society of Nondestructive Testing, Inc., 1986, p 424-426

Types of Heat-Treating Furnaces

John W. Smith, Holcroft, A Division of Thermo Process Systems Inc.

Introduction

FURNACES commonly used in heat treating are classified in two broad categories, batch furnaces and continuous furnaces. In batch furnaces, workpieces normally are manually loaded and unloaded into and out of the furnace chamber. A continuous furnace has an automatic conveying system that provides a constant work load through the unit.

Batch Furnaces

The basic batch furnace normally consists of an insulated chamber with an external reinforced steel shell, a heating system for the chamber, and one or more access doors to the heated chamber. Standard batch furnaces such as box, bell, elevator, car-bottom, and pit types are most commonly used when a wide variety of heat-hold-cool temperature cycles are required. Other types of batch furnaces, discussed in separate articles of this Volume, are salt bath, vacuum, and fluidized-bed furnaces.

The use of batch equipment for heat treating usually requires considerable labor for loading, handling, and unloading of the work and work trays. High labor costs dictated by the process must always be considered in the selection of batch equipment.

Batch furnaces are normally used to heat treat low volumes of parts (in terms of weight per hour). Batch furnaces are also used to carburize parts that require heavy case depths and long cycle times. For example, integral-quench batch carburizers treat gears or rock bits, while pit-type carburizers process parts such as drill rods or bearing races. However, there is no real advantage in the use of batch methods for deep-case carburizing. Yet, very often batch furnaces are used for deep-case work because the volumes are so low that a pusher-type continuous furnace is not cost effective. Here again, the batch furnace has the advantage in terms of part volume, not case depth. Batch furnaces are also normally used:

- To handle special parts for which it would be difficult to adapt a conveying system for continuous handling (long drill rods processed in a pit furnace, for example)
- To process large parts in small numbers, for example, stress relief or annealing of large weldments or castings in a car-bottom-type furnace
- To process various parts requiring a wide range of heat-treat cycles that can readily be changed, either manually or automatically

Batch processing is especially appropriate when the work must be heated from room temperature to a maximum temperature at controlled rates, held at temperature, and cooled at controlled rates. For example, car-type furnaces are used for critical stress-relief work or carbon baking in saggers.

Box-Type Furnace. With the addition of powered work-handling systems--integral quench tanks, slow-cool chambers, and some automatic controls--the basic box-type batch furnace is upgraded to a semicontinuous batch furnace, which is a commonly used piece of heat-treating equipment. One type of semicontinuous batch furnace is shown in Fig. 1.

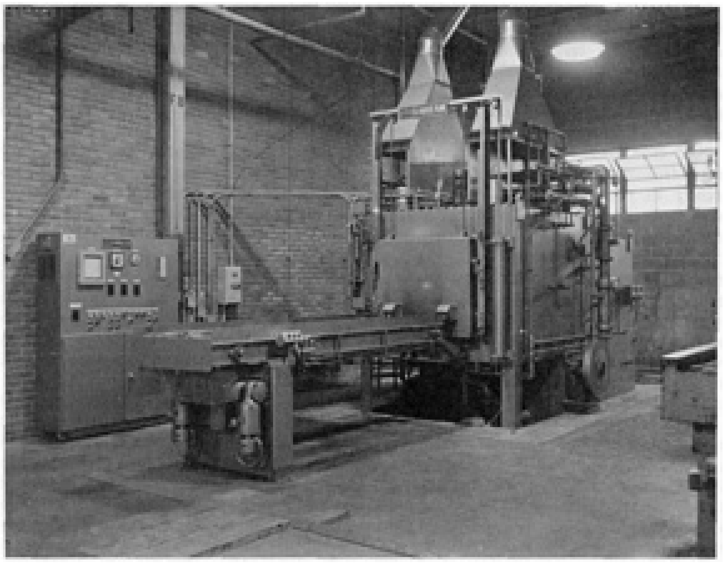


Fig. 1 Semicontinuous batch furnace with a controlled gas-heated box furnace. Courtesy of Seco/Warwick Corporation

The car furnace, also called a "bogie hearth," is normally considered an extremely large batch furnace. The bottom (or floor) of the furnace is constructed as an insulated movable car that is moved out of the furnace for loading and unloading, as shown in Fig. 2. When in position inside the furnace, the car is sealed to the furnace structure with granular-type "sand" sealing troughs or solid seals. Furnace cars can be self-propelled with the motor drive mounted on the car, or they can be moved in and out by a floor-mounted drive with a continuous chain or a rack-and-pinion drive. Most car furnaces are nonatmosphere type due mainly to the difficulty in sealing the car.

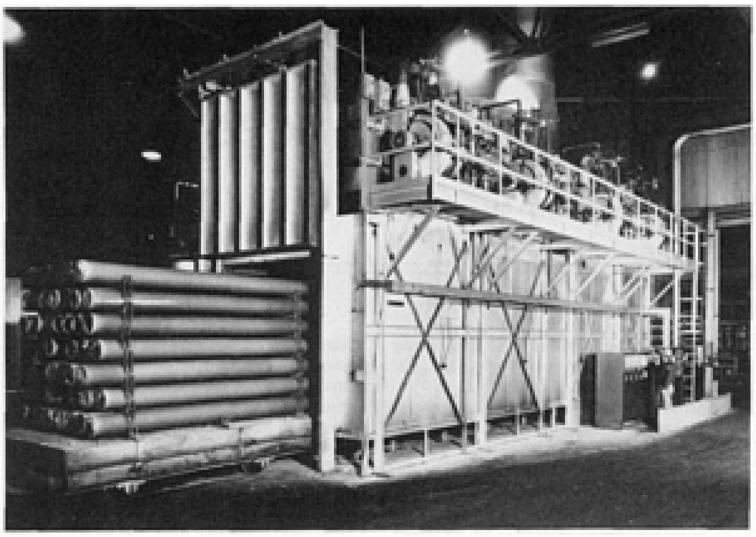


Fig. 2 Car-bottom batch furnace for homogenizing large cylindrical parts. Courtesy of Despatch Industries, Inc.

Heating systems normally are either direct fired or electrically heated with resistance elements. With direct-fired systems, it has proved advantageous to design a pressure-control system to control the flues. With the large difference in fuel burned during the heat-up portion of the cycle as compared to the soak portion of the cycle, it is extremely difficult to maintain a minimum acceptable furnace pressure with a fixed flue area. Most car furnaces are heated from room temperature with the load already in the furnace. A typical cycle would be to heat from room temperature to a control temperature at a specific rate, hold at the control temperature for a specified time, and then slow cool to discharge

temperature at a specified rate. Programmable temperature-control systems with stored menu programs are capable of performing a wide variety of heat-treat cycles, including process monitoring and recording of historical data.

The use of ceramic fiber insulation in a car furnace allows greater control of furnace temperature when following a programmed cycle. Because ceramic fiber has minimal heat storage capacity compared to hard refractories, it will heat and cool at faster rates. Also, less total heat is required to bring the furnace to the desired temperature, although the difference may be minimal because the total heat is governed more by the mass of the load. Further, continuous cyclic heating and cooling has little or minimal effect on ceramic fiber lining. Temperature limits of ceramic fiber blanketing are discussed in the article "Energy-Efficient Furnace Design and Operation" in this Volume.

Car furnaces are used from the lower stress-relieving ranges around 540 °C (1000 °F) to temperatures of over 1095 °C (2000 °F) for certain applications. Because many of the larger car furnaces are installed outdoors, increased allowances should be made for thermal holding losses caused by winds and other changes in ambient conditions.

Elevator-type furnaces are similar to car-bottom furnaces except that the car and hearth are rolled into position underneath the furnace and raised into the furnace by means of a motor-driven mechanism. Such furnaces are built to handle large, heavy loads and can be cooled rapidly by a high-velocity internal or external circulating gas system. For certain plant layouts, this type of furnace eliminates the need for crane facilities, transfer cars, and switching tracks and often saves floor space.

Elevator-type furnaces are suited for heavy work and for the precipitation-hardening nonferrous alloys, which must be quenched rapidly to retain a supersaturated solid solution. Either gas firing or electric heating is commonly used, with oil firing being employed less frequently. The temperature range for these furnaces is generally about 315 to 1200 °C (600 to 2200 °F).

Bell-type furnaces have removable retorts or covers called "bells," which are lowered over the load and hearth by crane. The inner retort is placed over the loaded hearth, sealed at the bottom, and provided with a constant supply of protective atmosphere; then the outer heating shell is lowered dover the assembly.

One bell furnace outer heating shell can take care of several retorts. For dense hearth loadings, a motor-driven fan for circulating the atmosphere inside the retort provides more rapid, uniform heating.

Pit furnaces, sometimes called pot furnaces, consist essentially of two parts: the furnace, which is placed in a pit and extends to floor level or slightly above, and a cover or lid, which extends upward from floor level. Large pit furnaces are generally installed with at least part of their heating chambers below floor level. Smaller furnaces are usually mounted on the floor. Workpieces are suspended from fixtures, held in baskets, or placed on bases in the furnaces. This type of furnace is particularly suitable for heating long parts, such as tubes, shafts, and rods suspended from a top supporting fixture or supported from the lower end and held in a vertical position. Loading in this manner gives minimal warpage.

Pit furnaces are available over a wide range of weight capacities and are well adapted to the use of devices for automatic carbon control. They are particularly suited to the processing of parts that must be cooled in the furnace. However, direct quenching is usually not feasible when large loads and large furnaces are involved.

An additional disadvantage of the pit-type furnace is that, if the work is to be direct quenched, the load must be moved from the atmosphere of the furnace into air before quenching. Although exposure in air is relatively brief, it results in the formation of an adherent black scale on the steel that for many applications must be removed by dilute mineral acids or by grit blasting. Thus, parts that must remain bright and scale free after furnace treatment, such as parts with internal threads, are processed in horizontal batch furnaces and quenched under a cover of protective atmosphere.

Continuous Furnaces

Continuous furnaces consist of the same basic components as batch furnaces: an insulated chamber, heating system, and access doors. In continuous furnaces, however, the furnaces operate in uninterrupted cycles as the workpieces move through them. Consequently, continuous furnaces are readily adaptable to automation and thus are generally (though not always) used for high-volume work. For example, continuous carburizing furnaces are generally preferred for production loads exceeding 180 kg/h (400 lb/h) and requiring the same case depth, or for loads of sufficient size that require 24-h continuous operation. Some types are equipped to provide cooling under a protective atmosphere.

Another advantage of continuous furnaces is the precise repetition of time-temperature cycles, which are a function of the rate of travel through the various furnace zones. In terms of atmosphere control, however, the frequent door openings can upset internal atmospheres during the charge and discharge cycles. Also, it is sometimes difficult to keep the atmospheres segregated by zone in single-chamber continuous furnaces, and often the zone controllers "fight" each other because of the interaction between adjacent zones. Therefore, in some applications (such as carburizing), high accuracy, temperature control, and atmosphere control may be easier to achieve in a multichamber pusher-type system where the heating, carburizing, and diffusion portions of the cycle are separated. A batch furnace could also be used.

In a general sense, continuous-type furnaces can be classified as either rotary-hearth furnaces or straight-chamber furnaces. In a rotary-hearth furnace (Fig. 3), the floor of the heating chamber rotates inside a stationary roof and inner and outer walls, with a sand or liquid seal between the floor and walls. Rotary-hearth furnaces have been in use for many years, mainly as single-chamber units for low-production manual operations with a variable-product mix. Rotary-hearth furnaces are useful in shops or operations where only one operator is employed, because the charging and discharging can be located next to one another. Rotary furnaces are also used in combination with straight-chamber furnaces (see the section "Other Continuous Furnace Systems" in this article).

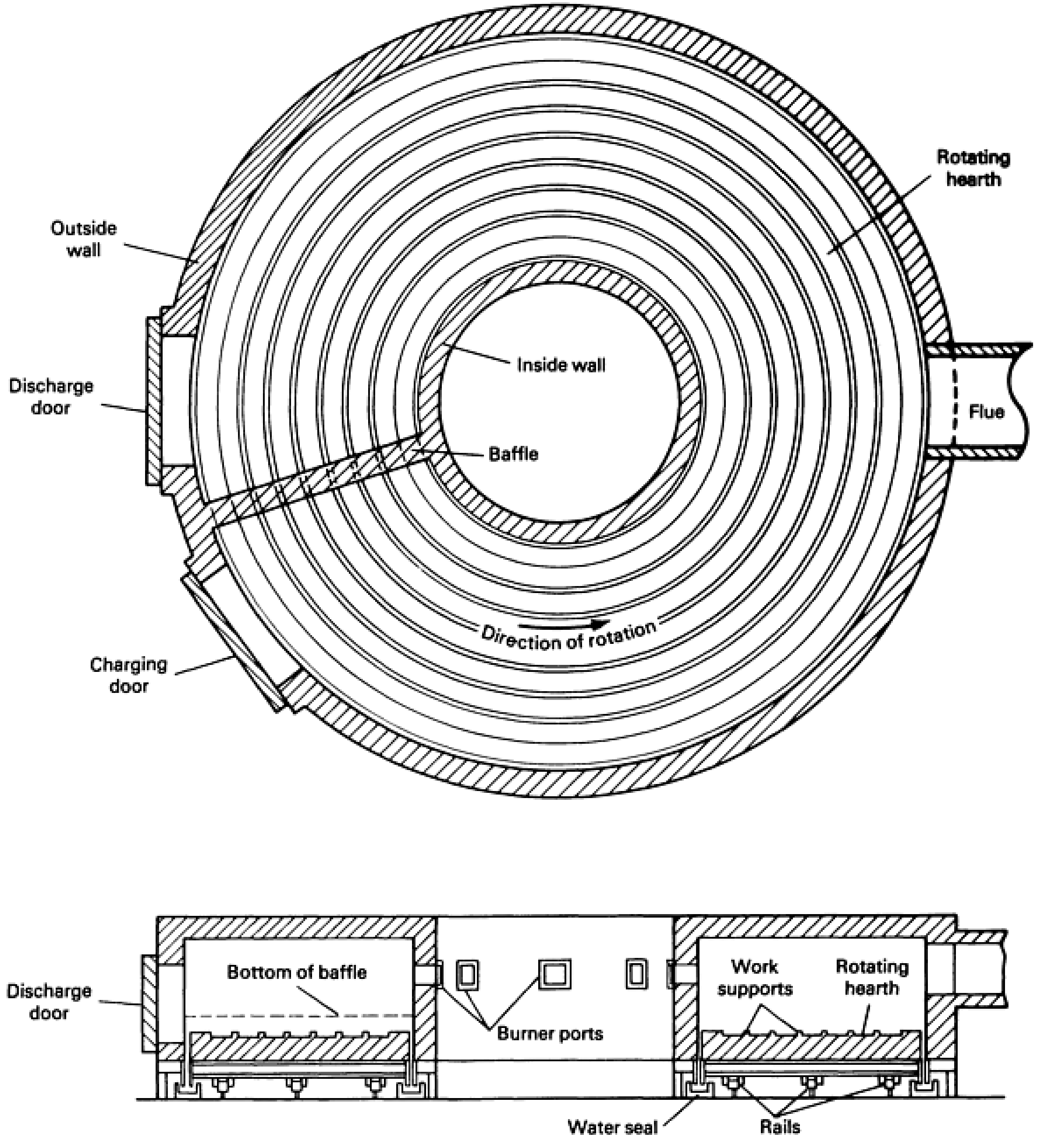


Fig. 3 Schematic arrangement of a relatively small continuous rotary-hearth heating furnace. Larger furnaces

of this type have burners firing through both inside and outside walls above the hearth, while very large furnaces (up to 30 m, or 100 ft, in diameter) use multiple heating zones that can be fired either with roof-type burners or burners located in the vertical portion of saw-tooth roof construction. Source: Ref 1

Straight-chamber continuous furnaces include various types, which can be classified as:

- Pusher-type furnaces
- Walking-beam furnaces
- Conveyor-type furnaces that use rollers or belts
- Continuous furnaces with tumbling or inertia action of the parts for movement

These four types of straight-chamber continuous furnaces are discussed in the following sections. Other types such as overhead monorail systems are also briefly mentioned. The common types of continuous furnaces are the pusher, rotary-hearth, roller-hearth, and continuous-belt furnaces. Walking-beam furnaces and the furnaces that impart tumbling or inertia of the parts (that is, the shaker-hearth and rotary-retort furnaces) are less common.

Pusher Furnaces

A pusher furnace uses the "tray-on-tray" concept to move work through the furnace, as shown schematically in Fig. 4. A pusher mechanism pushes a solid row of trays from the charge end until a tray is properly located and proven in position at the discharge end for removal. On a timed basis, the trays are successively moved through the furnace. Cycle time through the furnace is varied only by changing the push intervals.

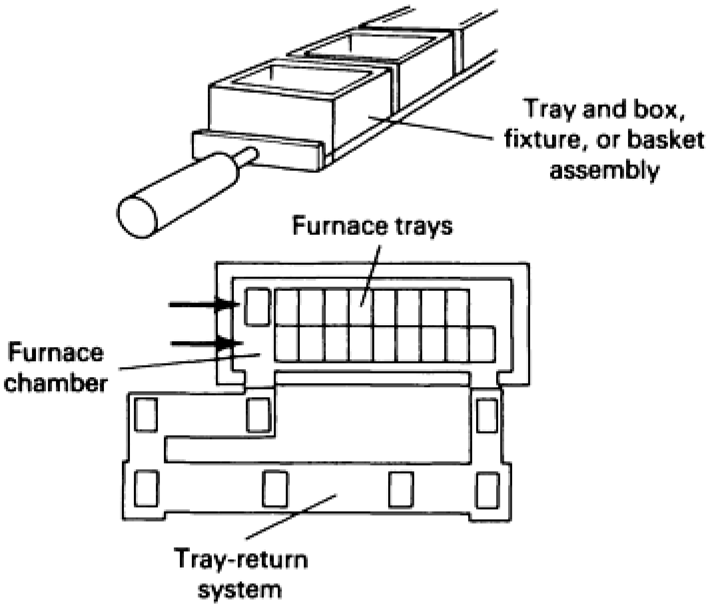


Fig. 4 Schematic of tray movement in a pusher furnace

Pusher-type furnaces are quite versatile and, depending on the size and shape of parts and on permissible distortion, parts may be loaded randomly and free quenched in an elevator-type quench tank. Alternatively, parts may be removed individually from the furnace trays for plug or press quenching. Furnaces can be designed to provide a variety of special equipment and process requirements, such as number of trays, tray size, atmosphere control, atmosphere recirculation, temperature-control zones, and quenching facilities. They may also have more than one row of work in process at the same time.

Pusher-type furnaces are by far the most widely used continuous furnace for gaseous carburization. Construction usually consists of a gastight welded shell with radiant tubes for heating. The work is pushed through on trays with or without fixtures and after completion of the carburizing cycle may be quenched or cooled slowly. Circulating fans are almost always used for more uniform temperature and carburization. Most pusher-type furnaces are built with purging vestibules at the charge and discharge ends to reduce contamination of the atmosphere by air. In many instances, washing and tempering equipment is incorporated to provide a fully automated heat-treating line.

Skid-Rail Furnaces. In a skid-rail pusher furnace, the work is placed on flat, normally reversible cast-alloy grid trays. The trays, in turn, are supported through the furnace on skid rails. The total gross load on the tray determines the number of rails necessary to minimize wear by maintaining the bearing pressure between the tray and the rail within acceptable limits. In certain applications, particularly when an endothermic or an enriched endothermic atmosphere is used, the skid rails are lubricated by the atmosphere and the coefficient of friction is reduced, decreasing wear and increasing tray and skid-rail life. Skid rails are used normally for light-to-moderate tray loadings.

Skid rails that are cast or fabricated from nickel-chrome heat-resisting alloy have been commonly used in pusher furnaces. These alloy skid rails normally are supported by and anchored to a series of cast or fabricated alloy pier caps and supporting pedestals.

Because of the ever-increasing cost of nickel-chrome alloys, alloy skid rails are being replaced where possible by less expensive silicon carbide refractory rails. Silicon carbide skid rails are molded and prefired into various rectangular shapes and are then bricked in and supported on the lower piers or are supported directly on the furnace floor. With the rails resting on edge, the alloy grid tray is thus supported on two or more rail faces, each normally 64 mm ($2\frac{1}{2}$ in.) wide. Because silicon carbide in contact with an alloy has a lower coefficient of friction than alloy on alloy, it makes excellent skid rails. However, in designing silicon carbide rails, precautions should be taken to eliminate severe temperature gradients or thermal shock in the rails, both of which could cause the rails to fracture.

Roller rails are used to both support and guide the trays as they are moved through the furnace. The rails are supported and anchored in a manner similar to that of alloy skid rails, but the mechanical advantage of the wheel and axle reduces the pushing force required to move the load when compared to skid-type support rails.

In certain instances, rails, wheels, and axles are all made of an alloy material. The use of a dissimilar material for the axle, however, can reduce the coefficient of friction between the wheel and axle, and the axle to rail, which can eliminate the natural "galling" effect of alloy on alloy.

The alloy roller rail tray usually has one or more runners and guides on its underside to keep the tray centered on the roller rails. Because the tray underside is normally not flat, it cannot be moved readily (skidded) at 90° to its normal travel, and a transfer carriage would be used. Also, the tray normally is not reversible. There are, however, designs of alloy trays employing recessed runner tracks, so that the tray will sit flat on a surface and is capable of being moved at 90° to its normal travel.

Because required pushing force is reduced, roller rails are used mostly for heavy tray loads and lengthy pushes. To keep wear in the wheel or axle to an acceptable minimum, the total load per wheel (line pressure), in pounds per inch (or kilograms per centimeter) must be kept within acceptable limits.

Buggy trays make use of the mechanical advantage of the wheel and axle in a manner similar to that of the roller rail. Wheels and axles attached to the underside of the tray are guided through the furnace in refractory or alloy troughs, supported on furnace piers or directly on the furnace floor.

This tray cannot be skidded at 90° to its normal travel, and a carriage would be required for such movement. Although buggy trays can be used for extremely heavy loads, the maximum recommended load per wheel should not be exceeded, to keep wear within acceptable limits.

A buggy tray with the wheels and axles attached normally results in a heavier tray weight per square foot. This could have an adverse effect in fuel economy as the weight of the tray to be heated and cooled is increased over other types of trays.

Walking-Beam Furnaces

A walking-beam furnace has movable rails that lift and advance parts along stationary rails inside the hearth. With this system, the moving rails lift the work from the stationary rails, move it forward, and then lower it back onto the stationary rails. The moving rails then return to the starting position and repeat the process to advance the parts again. Figure 5 shows a typical walking-beam furnace of this design used for moving steel slabs. In this type of system, the moving rail can be designed to move in an elliptical path or rectangular pattern. The frequency of lift and length of stroke determine the total processing time.

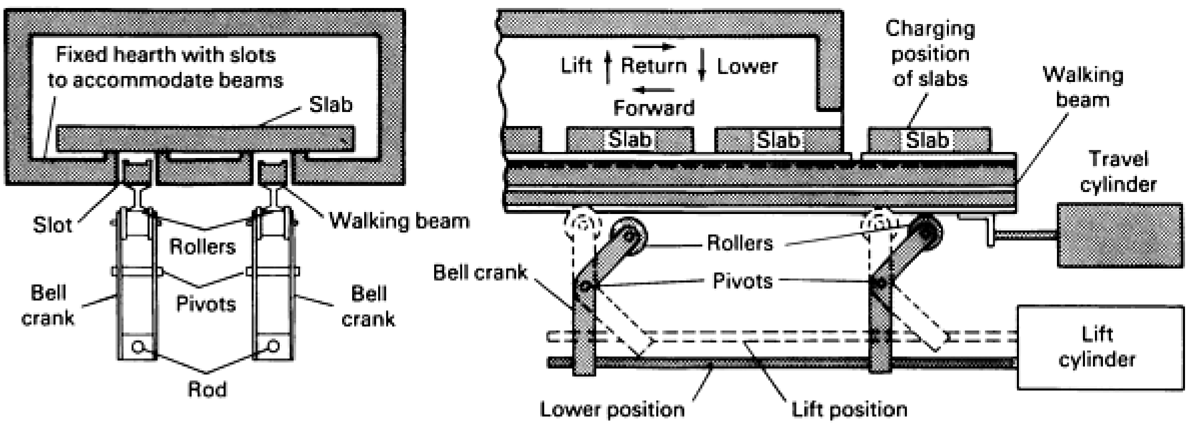


Fig. 5 Schematic of a walking-beam mechanism for advancing slabs through a furnace. In actual furnaces, water seals beneath the hearth prevent escape of furnace gases or air infiltration. Source: Ref 1

In another type of walking-beam furnace, both sets of rails move. One set of rails moves up and down, and the second set moves forward and backward. This system is known as a true rectilinear motion walking beam. The sequence normally is as follows: The lifting beam moves up and the traveling beam moves in reverse, then the lifting beam moves down and the traveling beam moves forward. The work is thus sequenced through the furnace.

Uses of Walking-Beam Furnace. Walking beams traditionally have been used in steel mills in reheat furnace hearth systems for slabs and billets. Walking-beam systems can be built ruggedly to move extremely heavy loads. In heat-treating operations, walking beams have been used successfully with flat-top beams to carry such work as flat plates or trays, or with pocketed-top beams to carry unstable parts such as rollers or shafts.

Advantages of Walking-Beam Furnaces. The typical advantages of walking-beam furnaces are:

- Only the work being processed has to be heated because normally trays or fixtures are not needed
- Friction is reduced for heavy loads because the work is never skidded
- The system can be loaded or unloaded automatically
- A part can be picked from a specific spot and placed in a specific spot by using the walking-beam mechanism
- Equipment is self-emptying on shutdown

Disadvantages of Walking-Beam Furnaces. The typical disadvantages of walking-beam furnaces are:

- Mechanisms are usually more expensive than for pusher-type systems
- On large high-temperature slab or billet reheat furnaces, there is a dramatic increase in thermal holding losses and related fuel consumption due to the water-cooled insulated walking-beam rail system
- Walking-beam mechanisms are not commonly used where protective atmospheres are required in the furnace chamber due to the inherent problems in adequately "sealing" the moving walking beams and mechanisms

Conveyor-Type Furnaces

Roller-hearth furnaces move the work-piece through a heating zone with powered, shaft-mounted rollers that contact the work-pieces or trays. This type of furnace might be used to advantage in heating much longer slabs than would be practical in a pusher-type or walking-beam furnace. These furnaces are available as single units (Fig. 6) for zone heating or cooling in a line of furnaces.

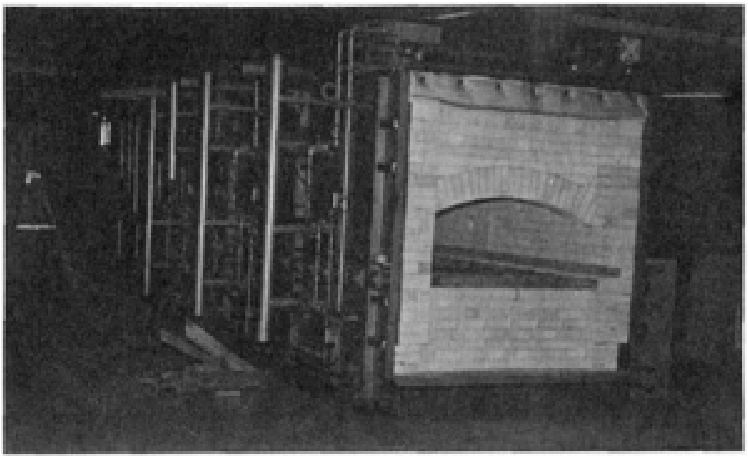


Fig. 6 Section of a roller-hearth furnace. Courtesy of Seco/Warwick Corporation

Continuous-belt furnaces are similar to roller-hearth furnaces except that mesh or cast-link belts are used to move the parts. Such furnaces are preferred for small parts that cannot be moved satisfactorily directly on rollers. Conveyors used include woven belts of suitable material, and chains with projecting lugs, pans or trays connected to roller chains.

The parts are fed automatically onto a mesh belt at the front of the furnace, which can have a liquid or gas atmosphere seal to maintain atmosphere integrity in the furnace chamber. Cast belts return inside the furnace. Belt-type furnaces generally are furnished with fans for recirculating the atmosphere.

Reciprocating and Rotary Agitation Furnaces

Shaker-hearth furnaces (Fig. 7(a) and 7(b)) use a reciprocating shaker motion to impart inertia to the work; this motion may be regulated to control the time cycle. Heating is efficient and confined mainly to the work load. Parts may be fed into the furnace by hand or by means of automatic metering and are typically drop quenched individually. Use of this type of furnace is generally limited to lightweight parts that are to be carburized to case depths of 0.3 mm (0.012 in.) or less. The furnace hearth must be kept smooth, clean, and at the proper level. Either the time cycle of work going through the furnace or uniformity of case depth should be checked at frequent intervals to detect any unwanted change in the forward force exerted by the shaker mechanism. When these precautions are adequately observed and the necessary atmosphere and temperature controls are provided, the shaker-hearth furnace can produce satisfactorily uniform case depth.

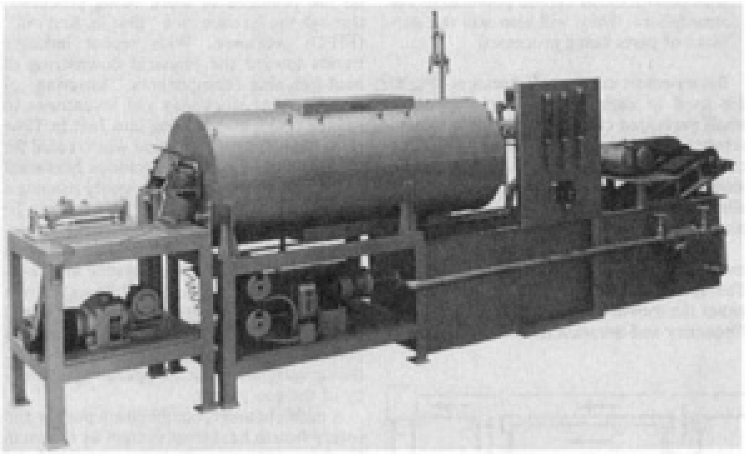


Fig. 7(a) Shaker-hearth furnace with conveyor removal of quenched parts. Courtesy of Lindberg Heat Treating Company

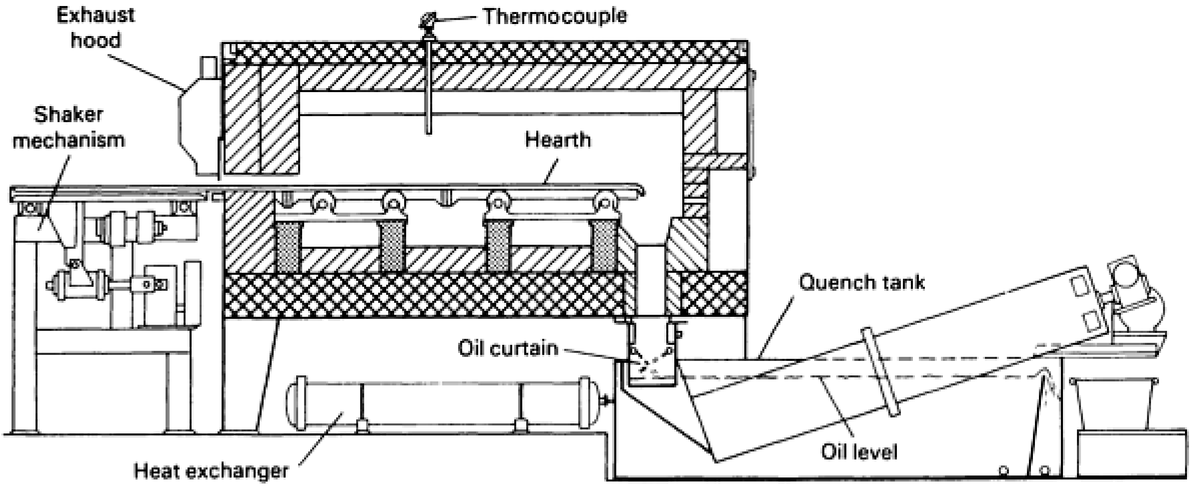


Fig. 7(b) Schematic of shaker-hearth furnace for continuous carburizing

Unless a specially designed hearth, such as a corrugated hearth, is provided, heavy, flat parts are not suited to processing in shaker-hearth furnaces, because of the difficulty of obtaining adequate and uniform case on the part surface making contact with the hearth. Delicate parts and parts with fine threads may be mutilated by the action of the conventional shaker hearth. Without a special hearth, balls and cylinders will not move and progress uniformly in this type of furnace.

Two aspects of the design of shaker-hearth furnaces require special attention:

- Hearth plates should be of suitable weight to respond to the reciprocating motion of the shaker mechanism. This action slides the parts forward randomly and ensures exposure and equal treatment to that portion of the part that rests on the hearth
- Adequate exhaust facilities should be provided to handle quenching-oil fumes. These fumes are highly carburizing and, unless properly disposed of, will interfere with control of the carbon potential of the atmosphere. They will also soil the surfaces of parts being processed

Rotary-retort continuous furnaces (Fig. 8) are used to carburize the same types of small parts that can be handled in a rotary-retort batch furnace. The advantage of the continuous rotary furnace is that it can be loaded and unloaded automatically, thus eliminating the need for removing and replacing the head.

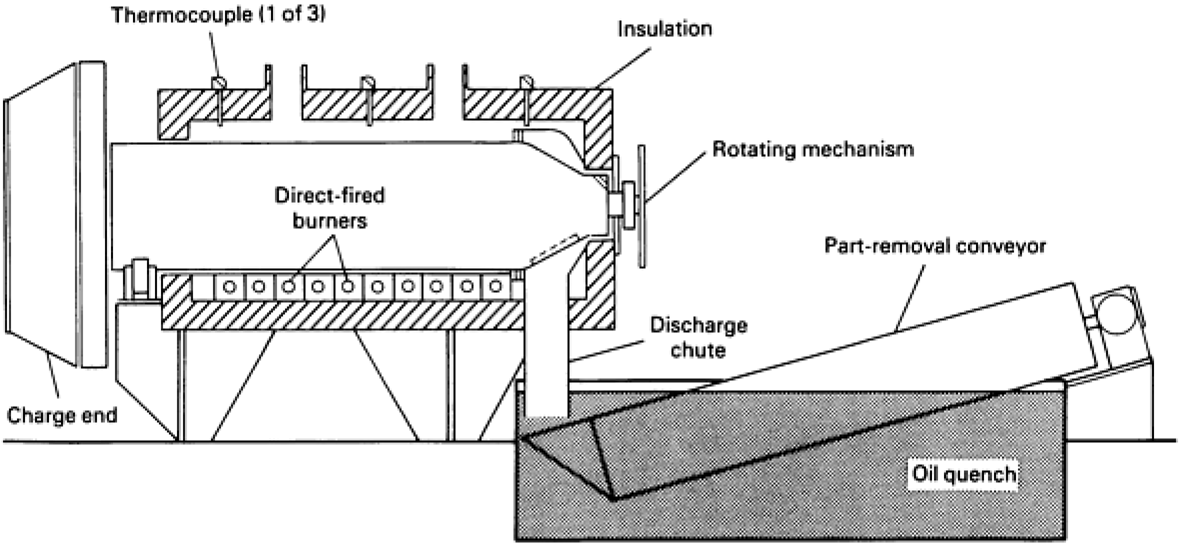


Fig. 8 Rotary-retort furnace for continuous carburizing

The inside of the retort is provided with a mechanized spiral rib throughout its length. The spiral rib can move the work load in either the forward or reverse direction. The frequency and duration of cycles of forward and reverse motion can be varied over any desired range. By this means, furnace length can be minimized, and a reasonable agitation or tumbling action of the parts is obtained. The tumbling action provides for a better uniformity of case depth. However, it can also serve to damage certain parts by nicking.

Continuous retorts cannot be tilted at will. Parts are fed at the front end and automatically issue from slots in the rear of the retort directly into the quenching medium. Because the front end of the furnace must be open to allow continuous charging, sufficient carburizing gas must be fed into the furnace to prevent the admission of outside air. These furnaces are suitable for carburizing to case depths of 0.4 to 2.5 mm (0.015 to 0.100 in.).

Other Continuous Furnace Systems

Combination Pusher-Type and Rotary-Hearth Furnace Heat-Treat System. The material above basically describes the traditional continuous-type furnace that operates on the principle of work being processed through the furnace on a "first in, first out" (FIFO) sequence. With recent industry trends toward the physical downsizing of heat-treatable components, lowering of manufacturer stockpiles and inventories to reduce costs, and moving into Just In Time (JIT) manufacturing, a need was created for a completely flexible continuous heat-treat system capable of simultaneously running a wide variety of parts to variable cycles. To accomplish this type of heat-treat processing using conventional FIFO furnaces would be extremely cumbersome and time-consuming. When changing the product mix or cycle in the FIFO-type furnaces, it would be necessary to either empty the chambers partially or completely, using empty trays, thus greatly affecting the operating efficiency of the equipment.

A multichamber, combination pusher and rotary-hearth heat-treat system as shown in Fig. 9 has only recently been conceived and built to address many of the shortcomings encountered when adapting existing continuous FIFO furnace systems to the new JIT manufacturing demands of industry. With pusher-type, continuous-type furnaces, it is not possible to simultaneously process side by side, a random mix of work parts, each requiring a different cycle time. When changing the process variable of "time" in a pusher-type continuous FIFO furnace, it is necessary to run a number of empty trays between the different types of tray loads in the furnace chamber. This has a negative effect on furnace efficiency, particularly if process cycle time changes are frequent.

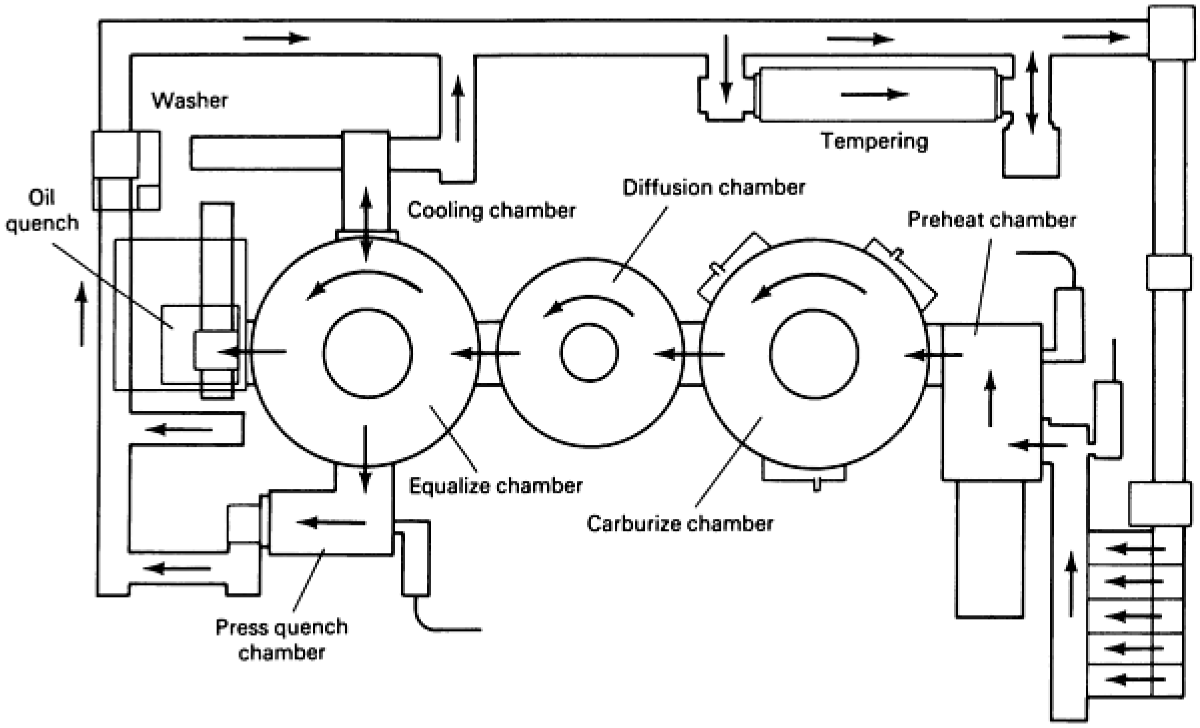


Fig. 9 Pusher-type and rotary-hearth heat-treat system

When shutting down a continuous pusher-type furnace, it is necessary to run empty trays into the charge end of the system to allow the work parts in the system to empty. The reverse is true on start-up, in that the system must first push out all the empty trays in the system before the product emerges. This arrangement wastes fuel and manpower in the heating and handling of empty trays.

The unique rotary hearth and pusher chamber concept allows tray loads with variable cycle times to be run simultaneously, side by side, in the same furnace chamber. This system also is built to be completely self-emptying without the use of empty trays. A complex system of this type is shown in Fig. 9, comprising three donut-shaped rotary furnaces: a carburize chamber, a diffusion chamber, and an equalize chamber, each having a circular rotatable hearth for supporting and moving trays of parts within an annular furnace chamber. Each rotary furnace is connected to the adjacent rotary furnace or pusher chamber through a tunnel with a special sealing door. The rotary hearths permit movement of any tray in any position within a furnace, at any time, by rotation of the selected position on the hearth to the charge or discharge door of that furnace, thus providing a high degree of flexibility in operation of the system. One or more pusher mechanisms are included within the circular space or "hole" of each donut-shaped furnace for moving the trays of parts between chambers.

The third rotary furnace of the system (equalize chamber) serves as a cooling chamber to 840 °C (1550 °F), a mechanism for transporting trays of parts to a selected quench system or to an atmosphere cooling chamber, and as a reheat chamber for trays of parts returned from the atmosphere cooling chamber. Trays that have been pushed into the atmosphere cooling chamber from the equalizing chamber can, after cooling, be reintroduced into the equalizing chamber for reheating and quenching or can be removed directly from the atmosphere cooling chamber to a tray-return transfer line.

Strand-Type Furnaces. Continuous strand-type furnaces for heat treating uncoiled strip reduce the handling and cycle times required with batch-type furnaces for sheet in coil form. Furnaces of this type also permit combining other operations, such as cleaning and/or coating. These furnaces usually have high production rates.

Overhead-Monorail Furnaces. In these furnaces, workpieces to be heat treated are suspended from rods attached to carriers on a monorail. Most continuous enameling is performed in overhead monorail furnaces.

Reference cited in this section

1. H.E. McGannon, Ed., *The Making, Shaping and Treating of Steel,* 9th ed., United States Steel Corporation, 1971

Direct-Fired Furnace Equipment

With direct-fired furnace equipment, work being processed is directly exposed to the products of combustion, normally referred to as flue products. To minimize the scaling (oxide) effect on the work, the flue products can be controlled or varied by adjusting the fuel-air ratio of the combustion system. Although fuel-air adjustments can be made manually, more precise control can be achieved automatically by a wide variety of fuel-air ratio control systems on the market today. When direct-fired burner equipment is used in a heat-treating furnace, the parts being processed often are in some primary or intermediate stage of manufacture. The oxide formed is not detrimental to the part because it will be removed later in the manufacturing process. For example, forged parts are sometimes hardened in the as-forged condition, and rough castings are annealed prior to machining.

Gas-Fired Equipment. Gaseous fuel used in heat-treating furnaces can be natural gas, straight propane, a propane-air mix, or a relatively low-energy manufactured gas.

With the proper selection of burners, controls, orifices, and pipe sizes, a combustion system can be designed to operate on 2500 Btu (2635 kJ) propane gas, 1000 Btu (1055 kJ) natural gas, or 160 Btu (170 kJ) producer gas. The number refers to the energy contained in a cubic foot (0.028 m^3) of the gas. Manual adjustments are required for conversion from one gas to another.

Oil-Fired Equipment. Almost any grade of oil that can be satisfactorily atomized can be burned in direct-fired equipment. Lower-viscosity oils such as diesel fuel and No. 2 fuel oil can be easily atomized with pressurized (room-temperature) air. These are probably the fuel oils most commonly used for heat treating. Even with easily atomized oils, caution should be employed in using them on flame-supervised furnaces operating below 760 °C (1400 °F) with interrupted pilots. At low oil flows and excess air conditions, nuisance shutdowns can occur from the flame supervision devices. In certain instances, as dictated by the National Fire Prevention Association, "constant pilots" may be used to eliminate the shutdowns. Insurance carriers must approve the use of constant pilots for the particular application, however. Heavier grades of oil must be atomized by a method other than low-pressure air. Normally, high-pressure air and steam are used.

Burners that can be fired by either gas or oil are available. In most instances, oil is used as the standby fuel to be used in peak periods when natural gas supplies are curtailed. Oil is considered desirable by some in the forging industry because it creates a "softer" scale on the billet, which is more easily removed in forging. High vanadium, potassium, and sulfur contents in fuel oil burned in the direct-fired process can reduce the useful life of various furnace components, especially the nickel-chrome heat-resisting alloys.

Advantages of Fuel-Fired Furnaces. The following advantages are common to fuel-fired furnaces:

- Lower energy cost
- Easy to adjust or alter connected input
- Recuperator heat-saving devices can be added easily, and controlled cooling can be initiated easily with proper design of combustion systems
- Faster heat-up times because inexpensive control factors can be added to accommodate the difference in fuel burned during heat-up

Disadvantages of Fuel-Fired Systems. The following disadvantages are common to fuel-fired furnaces:

- Requires extensive ventilation systems
- Potential explosion or fire hazard
- Requires more manpower for start-up and shutdown
- Adjustment more difficult to maintain, resulting in excessive fuel use
- Only certain materials or types of products can be run in direct-fired furnaces due to the effect of high

dew point and oxidizing flue gases on the part surface

Electrically Heated Furnace Equipment

Electrically heated furnaces are commonly found in all temperature ranges: from low-temperature tempering furnaces, through the heat-treating range, and up to forging temperatures. The basic consideration in selecting the type of heating element is to determine whether the elements are to be the open type, which are exposed to the furnace environment, or the indirect type, which are protected from the furnace environment by some means such as a radiant tube, muffle, or retort. Factors affecting this decision are furnace atmosphere, need to protect the element from mechanical damage, and space required for placement of the element.

Material Selection. Almost all furnace atmospheres other than air will in some way affect the overall performance and subsequent life of each type of heating-element material. Manufacturers of heating-element materials provide charts that allow designers to predict the material performance with any of the given atmospheres. Each heating-element material can be exposed to the different furnace atmospheres with varying degrees of success.

The notable exception is with a carburizing-type atmosphere. The conventional nickel-chrome strip heating element does not perform well in a carburizing atmosphere because the element itself carburizes, affecting element performance. Generally, in a carburizing atmosphere, heating elements are placed inside radiant tubes or outside work-protecting muffles or retorts. However, some alternative elements are designed specifically to operate when exposed in a carburizing atmosphere.

The selection of open or indirect elements is a choice also determined by the need to protect the element against mechanical damage from parts being heated, from accumulations of metallic scale, or from broken refractories. In furnaces where bottom heat is mandatory and scale can be formed readily on the parts, or where parts may fall from a tray or conveyor, electric elements should be protected in radiant tubes below the hearth. Open elements could still, however, be used throughout the upper portion of the furnace.

In some furnace designs, the physical space available determines the design of the element.

A further consideration is whether to use an element material other than nickel-chrome strip or rod. Silicon carbide elements (globar) or molybdenum disilicide rod elements have been used with success when directly exposed to various atmospheres, although the former normally is not recommended for use in a carburizing atmosphere. Silicon carbide elements have been used on occasion inside radiant tubes for protection against carburizing atmospheres.

Metallic Resistance Heating Elements. The following are general types of furnaces, with a description of the kinds of heating elements used in each. More detailed information on resistance heating elements is given in Volume 2 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.*

Low-Temperature Furnaces with Open Elements. The temperature range of this type of furnace varies from approximately 150 to 675 °C (300 to 1250 °F), and the furnace is normally a recirculated-wind convection heating type. The simplest type of heating element is a commercially available duct heater, usually full-voltage, 440 V or 220 V heaters. These are quite useful when the designer can stay within the manufacturer limitations. Maximum use temperature of the commercial duct heater element is normally limited to 400 °C (750 °F).

The heater should be large enough to cover the entire recirculated wind-duct cross section, but designs are limited to the heater sizes available. The design watt density for this type of duct heater is normally 34 000 W/m^2 (22 W/in.^{2}). Watt density is the expression commonly used for connected power of each element in watts divided by its total surface area. Watts per unit area is an important design consideration, and the allowances vary greatly with temperature, type of element, and furnace.

As an alternative to the commercial unit, a custom-built duct heater can be used. A steel or alloy frame can then be designed to completely fill the air-duct cross section, and such a unit can be removed easily through a sidewall bulkhead.

The nickel-chrome ribbon material is supported in ceramic insulators mounted in tiers. A common element material is 35Ni-18Cr-44Fe, and it is normally selected in the lighter gage thicknesses and narrower widths. A typical cross section for the ribbon material would be 13 by 0.8 mm (0.50 by 0.030 in.).

Variable with temperature and wind flow, the design watt density would be in the 23 250 to 46 500 W/m^2 (15 to 30 W/in.^{2}) range. This heater is also normally designed to operate at full-line voltage of 440 or 220 V.

High-Temperature Furnaces with Open Elements. The temperature range of this type of furnace varies from approximately 675 to 955 °C (1250 to 1750 °F), and the furnace is normally a radiant-heating type.

Where large wall areas are available inside a furnace, a common method of mounting the nickel-chrome strip element is to attach it in a serpentine pattern from insulated alloy or ceramic anchors normally on the vertical walls only. With this design, especially at the higher temperatures, the structural strength of the element material and configuration for expansion must be considered. The element must support itself at operating temperatures without excessive droop or warping. Sufficient warping to cause the element to touch at various points could shorten the effective length of the element, decrease the resistance, and cause premature failure due to excessive currents and watt densities.

On larger furnaces with accessible wall areas, maintenance on this design element, although done from inside the "cold" furnace, is relatively easy. On smaller furnaces, accessibility for replacement of wall elements becomes a problem.

Other types of modular or drawer-type elements are available, which makes element removal and maintenance much easier.

The element strip material used with open elements is generally one of the following types: 80Ni-20Cr, 68Ni-20Cr, or 35Ni-18Cr-44Fe. The nickel-chrome element is generally selected in the heavier gage thicknesses and wider widths. A typical cross-section range would be from 1.3 to 2.3 mm (0.050 to 0.090 in.) thick and 19 to 38 mm ($\frac{3}{4}$ to $1\frac{1}{2}$ in.) wide. Variable with temperature and location of elements, the design watt density would be 12 400 to 23 250 W/m^2 (8 to 15 W/in.^{2}).

An alternative to the nickel-chrome strip element is the cast nickel-chrome heating element. This element has good structural strength, stability, and resistance to atmospheric attack. The quality control necessary in the manufacture of this element has made it slightly less flexible and popular than nickel-chrome strip. The casting must have uniform density and cross section to ensure a guaranteed resistance without danger of hot spots. Castings made with the investment casting (or lost-wax) process generally meet the quality requirements. Low voltages at the element and high currents tend to make the control hardware and wiring quite expensive. A common cast element material would be 35Ni-15Cr, and the watt-density range again would be 12 400 to 15 500 W/m^2 (8 to 10 W/in.^{2}).

Nonmetallic Resistance Heating Elements. In general, the nonmetallic heating elements are used in furnaces operating above 1010 °C (1850 °F). Silicon carbide elements are generally used in temperature ranges of 1010 °C (1850 °F) and above. They tend to be very fragile, so care should be taken in the design to allow for proper support and freedom for the element to expand and contract as the furnace is heated and cooled.

Silicon carbide elements undergo resistance increase with age; thus, to maintain constant power over the life of the elements, it is necessary to have a voltage adjustment available, usually with a step transformer. The useful life of a silicon carbide element is usually established at the point when its resistance has increased four times. To maintain constant power would mean that a total voltage demand of twice the initial voltage would be required because power, P, is equal to E^2/R.

Silicon carbide elements are provided in various diameters and lengths, with published "hot" resistances. Design watt densities vary with such factors as temperature and atmosphere, but with silicon carbide elements, conservatively designed watt densities result in better element life.

In a sintering furnace operating at 1150 °C (2100 °F) with an endothermic atmosphere, a design watt density of 31 000 to 46 500 W/m^2 (20 to 30 W/in.^{2}) would be considered appropriate. Molybdenum disilicide elements are commonly formed in U-shaped rod configurations and normally are mounted vertically. The published maximum temperature-use range in air is above 1650 °C (3000 °F), which covers all furnace temperatures up through the forging range.

Element location for molybdenum disilicide elements is an important consideration because these elements are designed to operate at very high watt densities and related high thermal heads. These elements undergo a high resistance change from cold to hot, with resistance increasing with temperature. The control hardware and wiring must be properly designed to handle the high initial currents. A typical selection for a 955 °C (1750 °F)furnace with an endothermic atmosphere

would be a 9 mm (0.35 in.) rod element, rated at 244 900 W/m^2 (158 W/in.^{2}), with an element temperature of 1430 °C (2610 °F).

Advantages of Electrically Heated Furnaces. The following are advantages associated with electrically heated furnaces:

- Systems are clean and free of the pollution normally found with fuel-fired systems
- Cooler plant environment without exhaust stacks and hoods for some furnaces (atmosphere furnaces may still require stacks and hoods)
- Quieter because of the absence of blowers and combustion noise
- More uniform heat pattern from grid elements or from side-to-side of chamber temperature uniformity on electric radiant tubes
- No exhaust system required to affect building air pressures; no make-up air system required
- Does not generally (though not always) require purge or flame safety systems
- Electrical power available almost everywhere

Disadvantages of Electrically Heated Furnaces. The following are disadvantages of electrically heated furnaces:

- Inflexible system makes changing connected heating capacities or varying individual element capacities in the same zone difficult
- High initial equipment costs
- With numerous electric furnaces in a plant and no form of peak-demand control, the user pays at a high demand rate for all power
- Higher operating costs
- Cool-down times are longer because no combustion air is available
- Nonmetallic elements tend to become brittle as they age and are subject to breakage from handling, vibration, or shock

Radiant-Tube-Heated Furnace Equipment

With fuel-fired, radiant-tube-heated furnaces, the work chamber is protected from the products of combustion. With a radiant-tube furnace, the work chamber normally contains a controlled atmosphere as dictated by the process. There are, however, cases where the chamber remains filled with air, and the only purpose of the radiant tubes is to protect the work from the high dew point flue gas products. Electrically heated radiant tubes normally are used to protect the heating-element material from attack by the furnace atmosphere.

Gas-fired radiant tubes, as shown in Fig. 10, are by far the most common type of fuel-fired indirect method of heating. This is mainly due to the wide availability of natural gas. The proper selection of combustion system components such as burners, controls, orifices, and piping, will allow the same radiant tube to be fired with a wide variety of gases: natural gas, propane-air mix, straight propane, and certain low-Btu manufactured gases.

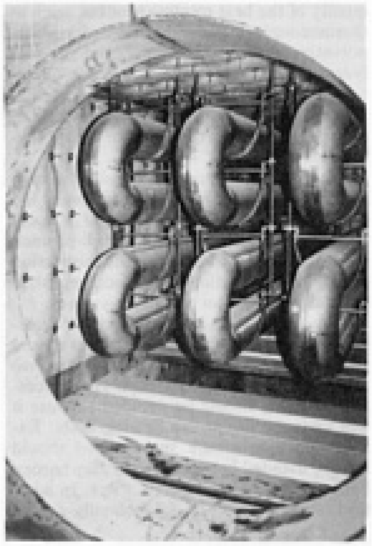


Fig. 10 Radiant tubes for indirect gas-fired furnace heating. Courtesy of Despatch Industries Inc.

Radiant-tube burners are of two basic types, sealed-head and open-type burners. A particular advantage of the sealed-head burner is that it is readily recuperable by using the products of combustion and an air-to-flue-gas heat exchanger to preheat the combustion air prior to its entering the burner. This advantage can result in considerable fuel savings (see the article "Energy-Efficient Furnace Design and Operation" in this Volume).

Open-type radiant-tube burners use room air for combustion, which is entrained into the radiant tube by an eductor on the exit end of the radiant tube. Open-type radiant-tube burners cannot be recuperated, although in most cases, they can be replaced with a sealed-head burner. Radiant tubes are normally constructed from centrifugally cast tubing of various diameters, with wall thicknesses of 3 to 8 mm ($\frac{1}{8}$ to $\frac{5}{16}$ in.). In many cases, tubes fabricated from 3 and 5 mm ($\frac{1}{8}$ and $\frac{3}{16}$ in.) wrought alloy are used.

With the high metal temperatures attained in radiant tubes in most heat-treating furnaces, the alloys commonly used are the higher-grade cast alloys HT, HK, and NA22H, or the wrought alloys 330, 601, and Incoloy 800. Additional information on the materials for radiant tubes is given in the article "Heat-Resistant Materials for Furnace Parts, Trays, and Fixtures" in this Volume.

Oil-Fired Radiant Tubes. Straight oil-fired radiant tubes are somewhat uncommon in heat-treating furnaces and are used mainly where an adequate supply of gaseous fuel is not available. Radiant tubes equipped to burn both oil and gas are more common, with the oil, usually No. 2 fuel oil, used as the standby fuel.

High vanadium, potassium, and sulfur contents in oil have a great effect on the useful life of nickel-chrome heat-resisting alloys. With the high temperatures attained inside the radiant tubes acting as a catalyst, attack on the radiant-tube alloy is accentuated.

When oil-fired radiant tubes are used, the construction and types of materials used are similar to those described for the gas-fired radiant tubes. Recuperation is also possible with certain sealed-head oil burners. When recuperation is employed, the burner manufacturer should be consulted regarding possible damage to or problems with the atomizing system in the burner, from the preheated combustion air, normally supplied at 370 to 540 °C (700 to 1000 °F).

Electrically Heated Radiant Tubes. With this design, the radiant tube protects the resistance heating element from the furnace atmosphere. A common design uses nickel-chrome alloy rod inside the radiant tube. These rods are formed into continuous hairpin shapes supported and contained by ceramic spacer discs.

With the heating element contained in a tube, it is very important to conservatively select the heating element watt density. The design watt density of the internal element is a direct function of furnace temperature and varies from 18 600 to 46 500 W/m^2 (12 to 30 W/in.^{2}). Some designs use nickel-chrome strip material rather than rod, formed into similar hairpin patterns.

If a gas-fired "U"-tube furnace is to be converted to electrically heated radiant tubes, it is desirable to directly replace the "U" tube with two straight tubes, rather than a single straight tube, for improved uniformity and reduced watt density. Thus, the conversion from natural gas to electricity can be accomplished without loss in production capacity.

Other types of electric radiant tubes are available, where the radiant tube itself becomes the resistive heating element. As with cast elements, however, the quality and condition of the radiant tube will determine whether it functions properly as the resistance element. Silicon carbide elements have also been used inside radiant tubes to protect them from carburizing atmospheres.

General Furnace Maintenance

Maintenance on a furnace should be performed on a regular basis to prevent unscheduled shutdowns. In most plants, major maintenance is performed once each year, normally during the plant vacation period.

Because unscheduled maintenance is very disruptive to production, especially in plants without backup heat-treating capabilities, some plants prefer a number of smaller furnaces rather than a single large furnace capable of handling all production.

Many components of furnaces must be considered as consumable items, although lifespan normally can be predicted from accurate maintenance records. Many furnace owners regularly inspect and change internal furnace components such as radiant tubes, thermocouples and wells, retorts, and electric heating elements. Trying to get a few more months of life from a certain internal component could result in an unscheduled shutdown, and an extended loss of production can occur if a replacement part is not readily available. Most furnace equipment manufacturers provide a recommended list of spare parts that the furnace owner should maintain in stock to ensure reasonably uninterrupted production.

In addition to the consumable items that have to be regularly replaced, many furnace components must be adjusted and/or calibrated at regular intervals to maintain the efficiency and accuracy of the heat-treating operation--once each shift, daily, weekly, monthly, or annually. Components that require regular monitoring for adjustment and calibration are mainly those that control the quality of the heat-treating process, such as thermocouples, temperature- and carbon-potential-control instruments, and gas analyzers. For example, some furnace operators regularly change all thermocouples at specified intervals to avoid the gradual deterioration that occurs prior to indiscriminate failure.

In addition, maintenance required to minimize wear and thus prolong component life must also be considered. This form of maintenance usually consists of a well-planned and documented adjustment and lubrication schedule. Lubrication can be accomplished manually or with an automatic system.

Care should be taken in the proper selection of the various greases and oils to ensure compatibility with the various furnace components and furnace atmospheres. Excessive greasing should be avoided because it will limit the life of the bearing seals. Excessively long grease supply lines should also be avoided because grease may harden before it reaches the point of use. In addition, supply lines are not normally routed through high-temperature areas to the lubrication points.

On manual systems, lubrication points should be carefully coded. Many special greases are incompatible with each other, and lubricating components with the wrong grease can have disastrous results.

For major maintenance, such as complete refractory replacement or complete rebuilding of mechanisms and systems, it is normally best to consult the original equipment manufacturer. Because this type of maintenance usually occurs when the equipment is quite old, the manufacturer will normally make recommendations that will improve the equipment and upgrade the system to the present state of the art and to comply with current recognized industry safety standards.

Salt Bath Heat-Treating Equipment

W. James Laird, Jr., The Metal Works Industrial Furnaces, Inc.

Introduction

HEAT TREATERS can no longer use heat-treating methods that are only uniform, quick, efficient, and economical. They must also be environmentally responsible. Salt bath heat-treating methods are uniform, quick, efficient, economical, and environmentally responsible.

Salt baths are used in a wide variety of commercial heat-treating operations including neutral hardening, liquid carburizing, liquid nitriding, austempering, martempering, and tempering applications. Salt bath equipment is well adapted to heat treatment of ferrous and nonferrous alloys.

Parts that are heated in molten salt baths are heated by conduction; the molten salt bath provides a ready source of heat as required. Although materials being heated come in contact with heat through their surfaces, the core of a part rises in temperature at approximately the same rate as its surface. Heat is quickly drawn to the core from the surface, and salt baths provide heat at an equal rate over the total part.

Neither convection nor radiation heating methods are able to maintain the rate of heating required to reach equilibrium with the rate of heat absorption. The ability of a molten salt bath to supply heat at a rapid rate accounts for the uniform, high quality of parts heat treated in salt baths. Heat-treating times are also shortened; for example, a 25 mm (1 in.) diam bar can be heated to temperature equilibrium in 4 min in a salt bath, whereas 20 to 30 min would be required to obtain the same properties in either convection or radiation furnaces.

Salt baths are very efficient methods of heat treating; about 93 to 97% of the electric power consumed with a covered salt bath operation goes directly into heating of the parts. In atmosphere furnaces, 60% of the energy goes for heating, and the remaining 40% is released up the furnace stack as waste. Steels that are heat treated in molten salts typically are processed in ceramic-lined furnaces with submerged or immersed electrodes containing chloride-based salts.

Applications

Applications of the various furnace designs and auxiliary equipment to specific heat-treating processes, such as austempering and martempering, are described in this and other articles in this Volume. Basic advantages of salt bath treatment include surface protection and control of distortion.

Surface Protection. Parts immersed in a molten salt bath develop a thin cocoon of solidified salt, which can be easily washed from the surface after treatment. This surface protection afforded by salt baths can eliminate the formation of damaging oxide scales. Moreover, because salt baths do not contain the oxygen, carbon dioxide, and water vapor levels found in most non-vacuum (or atmosphere) furnaces, immersed parts are protected further from scale formation. Decarburization of steel parts from contact with oxygen and carbon dioxide are also eliminated by the use of molten salts. Vacuum furnaces provide similar advantages in surface protection.

Control of Distortion. Salt baths offer a way to minimize the bad effects of nonuniform heating, lack of support, and poor quenching that may cause size and shape distortion. Unlike parts in an atmosphere or vacuum furnace, parts immersed in molten salts are supported by the density of the medium. Due to its buoyancy, sagging or bending of the parts is minimized in a molten salt bath.

Heating in molten salts is also very uniform. The temperature uniformity in a molten salt bath averages ±3 °C (±5 °F) throughout the bath, depending on furnace design. The layer of solidified salt around a part can also protect the part from rapid initial heating and the resulting thermal shock. As the cocoon of salt melts, the part is gradually and uniformly heated, minimizing distortion and preventing cracking.

Selecting a Salt for a Given Application. Information concerning the various salts suitable for heat-treating furnaces is available from many sources, such as the many competent salt companies. Also, military specification MIL-10699 describes the salts in detail. When selecting a salt for a given application, the following must be considered:

- The salt must have the proper working range to meet the operating temperature requirements
- The salt must have the proper melting point to avoid prolonged heat-up times for heavy loads
- The salt must be compatible with other salts and oil used in the same heat-treating line
- The versatility of the salts application
- The ease with which the salt is washed from the work after heat treatment and affinity of the salt for moisture

By balancing these factors, a salt best suited for a particular application can be chosen. Naturally, if a single salt must perform several functions, it will be necessary to make compromises and sacrifice some advantages to obtain the required versatility. Salts used in heat treating tool steels are described in the following example.

Example 1: Molten Salt Bath Treatment for Hardening High-Speed Tool Steel.

The use of molten salt baths for high-speed steel hardening has progressed during recent years. The greater degree of control and versatility, coupled with a simplicity of process, has been the chief reason for this progress. In addition to these factors, salt bath hardening ensures greater uniformity and rapid heating as well as freedom from scaling of the tools being heated.

The greater rate of heat transfer obtained through the use of molten salts permits the use of hardening temperatures approximately 15 °C (25 °F) below those in muffle-type furnaces, thereby reducing the possibility of sweating (melting of the surface) as well as undesirable grain growth. For best results, high-speed steel should be hardened in four steps. One procedure is described below.

1. Preheating. To safeguard against cracking and distortion, preheating tool steels before austenitizing is recommended. Small pieces of simple shape, which are not as susceptible to the damaging effect of thermal shock as are larger, more complex pieces, may not require preheating. Other more intricate shapes may require one or more preheating steps. Preheating is usually done in a ternary eutectic chloride mixture, which melts at approximately 541 °C (1006 °F) and is usable from 600 to 1010 °C (1100 to 1850 °F). These salts are formulated to preheat or harden steel without decarburization and with a minimum amount of sludge formation. Usually, the replenishment offered by mechanical dragout is sufficient to control bath chemistry. After a period of idling, however, it is usually necessary to rectify the bath as well as remove any sludge to be certain that the bath is neutral. The heating rate in this type of salt is rapid. It thoroughly heats most tools in 10 min or less. Prolonged heating times are not detrimental to steel and will help achieve thermal equilibrium negating the need for long austenitizing cycles.

2. Austenitizing. The most critical treatment in tool steel hardening is that of austenitizing. Austenitizing of high-speed tool steel is done at temperatures close to its melting point. Long heating times, or excessively high temperatures, will cause increased grain growth, distortion, loss of strength, and loss of ductility. Low hardnesses and low wear resistance will result from inadequate heating of the steel. Achievement of thermal equilibrium is a must before quenching to eliminate damaging the workpieces, Heating for 1 min for each 6 mm ($\frac{1}{4}$ in.) of total steel section thickness being heated is a good rule of thumb.

Austenitizing baths generally consist of anhydrous barium chloride, which begins to melt at approximately 960 °C (1760 °F) and has a working range of 980 to 1315 °C (1800 to 2400 °F). Neutrality of barium chloride operating above 1090 °C (2000 °F) is maintained by using a 50 mm (2 in.) diam carbon rod with a length of 300 or 600 mm (12 or 24 in.). The carbon rod reacts chemically to reduce metal oxides that are then deposited in droplets on the carbon rod. Frequency of immersion is usually 1 h, divided into 15 to 20 min intervals, for every 5 h of heat-treating operation. Too long an immersion will allow droplets of metal to flow together and run off the rod. The user should take caution not to allow this to happen, as it will recontaminate the bath.

Methyl chloride rectification is highly recommended in neutral salt baths operating between 1040 and 1315 °C (1900 and 2400 °F). The bath temperature should be kept below 1040 °C (1900 °F) while methyl chloride is being introduced. Methyl chloride is introduced under the surface of the bath to avoid a chemical breakdown above the surface of the bath, which would result in gas loss. The broken down methyl chloride supplies chloride ions, which combine with the harmful metallic oxide to form neutral metallic chlorides. Self-rectifying neutral salts are also available from most salt suppliers. It

is recommended that the users thoroughly familiarize themselves with the disadvantages and detrimental effects rectifying salts can have on equipment before deciding to use self-rectified salts.

3. Quenching. For the quenching bath, the use of water is recommended for most cold heading tools, while the use of triple eutectic chloride salts is suggested for high-speed steels. For quenching air hardening steels, it is recommended that a 540 °C (1000 °F) triple eutectic chloride salt be used to reduce the temperature of the steel to a point where the heat color has been taken out of the workpiece so that it will not rapidly oxidize when air cooled. These are typical salts mentioned previously for use as a preheating medium.

As a majority of high-speed steels are quenched to temperature between 540 and 700 °C (1000 and 1300 °F), the triple eutectic chloride salts will have sufficient fluidity at these temperatures to allow effective quenching without the serious corrosion resulting from the use of salts containing highly hygroscopic constituents. Lower melting point salts usually contain calcium chloride and, if allowed to remain on the workpiece until it is cooled to room temperature, may severely corrode the surface.

The exact quenching temperature to use is dependent chiefly upon the composition of the steel. In some instances, use of low quenching temperatures cause the salt to freeze on the surface. This condition is caused by contamination of quench salt by barium chloride carried from the high heat bath, which gradually raises the freezing point of the quench bath. Proper salt handling techniques will eliminate this problem.

4. Drawing or tempering is done to obtain the desired strength, hardness, and toughness by modifying the microstructure of the quench hardened tool steel. More than one tempering cycle may be required to alter the ausquenched and heterogeneous mixture of retained austenite, untempered martensite, and carbides. All retained austenite and untempered martensite will be transformed when tempered, using a few short cycles rather than one long one. Some steels may require three or four cycles before the optimum structure is obtained. Each cycle will require not less than one hour at tempering temperature. Tempering is accomplished in nitrate/nitrite mixtures, which melt at approximately 140 to 600 °C (290 to 1100 °F). Neutral chloride salts can be used to temper small parts and light loads, but they are not recommended for production unless the temper temperatures are above 600 °C (1100 °F).

Externally Heated Furnaces

Externally heated salt bath furnaces may be fired by gas or oil, or heated by means of electrical resistance elements. Figure 1 shows typical externally fired furnaces used in liquid carburizing applications. Pots may be press formed from a single piece of low-carbon steel or iron-nickel-chromium alloy; a composition of Fe-35Ni-15Cr is usually preferred for the latter. Less expensive welded pots may be fabricated from either of these materials.

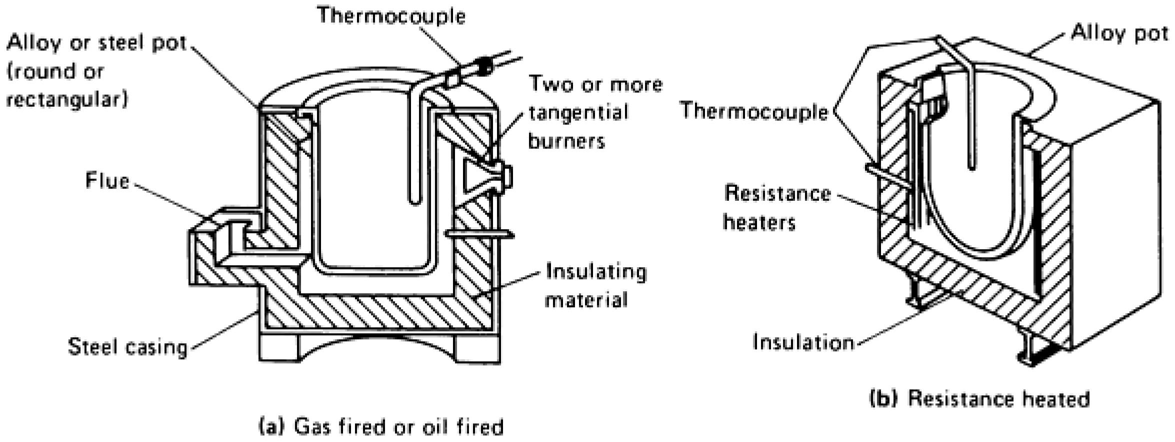


Fig. 1 Externally heated salt bath furnaces for liquid carburizing

A flange usually supports salt pots; consequently, pot size is limited by the strength of the flange material. Round pots for gas- and oil-fired furnaces range from 250 to 900 mm (10 to 35 in.) in diameter and from 200 to 750 mm (8 to 30 in.) in depth; they are about 10 mm (0.4 in.) thick. Larger sizes have been built for special applications and have operated

successfully. Pots larger than about 350 mm (14 in.) in diameter and 450 mm (18 in.) deep are rarely used for electrical resistance furnaces. Although it is physically possible to support the bottom of a large pot on a refractory pier, excessive temperature gradients may result.

Gas- or oil-fired salt bath furnaces (Fig. 1 a) are generally lower in initial cost than electrode- or resistance-heated furnaces and are simple to install and operate. As described above, gas- and oil-fired salt bath furnaces also have larger salt pots than resistance-heated furnaces.

To contain the molten salt, fuel-fired furnaces employ a round or rectangular pot made of either steel or alloy. Heat is applied by two or more self-cooling burners that fire tangentially between the outer wall of the pot and the inner surface of the furnace lining. The hot gases are vented through a flue located near the top for atmosphere-type type burners, or near the bottom for pressure-type burners and atmosphere-type burners for which the flue is connected to a stack about 1 to 2 m (3.3 to 6.6 ft) high. The height and placement of the flue allows a negative pressure to be maintained within the firing chamber. Firebrick and additional required insulation lines the combustion chamber. A steel casing completely surrounds all sides of the furnace housing and provides adequate safety in the event of pot failure.

Electrical resistance furnaces (Fig. 1b) for neutral heating of liquid baths are less widely used than furnaces fired by gas or oil. A series of resistance heaters surrounding the salt pot heat these furnaces. For this reason, pot failure may result in the total destruction of the electrical heating elements. Operating temperatures below 900 °C (1650 °F) are used to reduce pot failure.

Pot Service Life. In a well-designed furnace, the life of a round alloy pot will vary with the maximum operating temperature approximately as follows:

Temperature		Service life, mo
°C	°F	
840	1550	9-12
870	1600	6-9
900	1650	3-6

In one installation, the placement of an additional control thermocouple in the combustion chamber to prevent the temperature of the chamber from exceeding 1095 °C (2000 °F) served to extend the life of high-temperature (HT) alloy pots to 2 years (previous life had been 6 months). Pot temperature was maintained at 900 °C (1650 °F) during a work week of 120 h (24 h/day, 5 days/week). Other factors affecting pot life are considered in the section "Design and Operating Factors."

Temperature of the salt is measured by a thermocouple and suitable pyrometer. Operating within the range from 790 to 920 °C (1455 to 1690 °F), the externally fired furnaces may vary as much as 10 °C (18 °F) above and below the set temperature when using on-off or high-low control systems. This is considered acceptable for many applications. Where closer control of the temperature is required, a proportional control system, which will hold temperature variations to less than ±5 °C (±9 °F), should be used.

Design and Operating Factors. In the design of fuel-fired furnaces, ample space must be provided for combustion so that the flame will not impinge on the pot. If flame impingement is unavoidable, the pot should be rotated slightly at least once a week. Rotating the pot and/or using a sleeve reduces local deterioration in the region of flame impingement and prolongs the service life of the pot. The combustion-chamber atmosphere also has important effects on pot life. A system with a control range from high-fire to low-fire is preferable to an on-off system because the latter allows air to enter the combustion chamber during the "off" portion of the cycle, thereby increasing the rate of sealing of the outer surfaces of the pot.

Electrical-resistance-heated furnaces should be equipped with a second pyrometer controller whose thermocouple is located within the heating chamber. This will prevent overheating of the resistance elements, particularly during meltdown, when the thermocouple that controls the temperature of the main bath is insulated by unmelted salt. Because heating elements and refractories are severely attacked by salt, all salt must be kept out of the combustion chamber. For this purpose, a high-temperature refractory fiber rope may be used to seal joints where the pot flange rests on the retaining ring at the top of the furnace.

Externally heated pots should be started on low fire (low heat input) regardless of the method of heating. Once the salt appears to melt around the top, heat can be gradually increased to high fire to complete meltdown. *Caution: Excessive heating of the sidewalls or pot bottom during startup may create pressures sufficient to expel salt violently from the pot.* For added safety, the pot should be covered during meltdown with either a cover or an unfastened steel plate.

The waste heat of flue gases may be fed to an adjacent chamber and used to preheat work. Flue gases should always be visible to the operator. The appearance of bluish-white or white fumes at the vent indicates the presence of salts within the combustion chamber; prompt action is required.

Advantages and Disadvantages. Because of the ease with which they can be restarted, externally heated furnaces are well suited to intermittent operations. Another advantage of furnaces of this type is that a single furnace can be used for a variety of applications by simply changing the pot for one containing the proper salt composition.

Externally heated furnaces do have several characteristics, however, that limit their usefulness in certain operations. They are less adaptable to close and uniform temperature control because the furnace dissipates heat by convection, creating temperature gradients in the bath. Also, the temperature lag of the thermocouple and the recovery time of the furnace may result in overshooting or undershooting the desired temperature by 15 °C (25 °F). In addition to requiring an exhaust system for generated flue gases, externally heated furnaces may overheat at the bottom and sidewalls in restarting, which creates a pressure buildup in the thermally expanding molten salt and may cause an eruption. Finally, externally heated furnaces are seldom practical for continuous high-volume production because of the limitations of pots with respect to size and maximum operating temperature. High maintenance cost is also a factor.

Immersed-Electrode Furnaces

Ceramic-lined furnaces with immersed (over-the-side) electrodes (Fig. 2), when compared to externally heated pot furnaces, have greatly extended the useful range and capacity of molten salt equipment. The most important of these technical advances are:

- The electrodes can be replaced without bailing out the furnace
- Immersed electrodes allow more power capacity to be put into the furnace, thus increasing production
- Immersed electrodes permit easy startup when the bath is solid. A simple gas torch is used to melt a liquid path between the two electrodes, thus allowing the electrodes to pass current through the salt to obtain operating temperatures

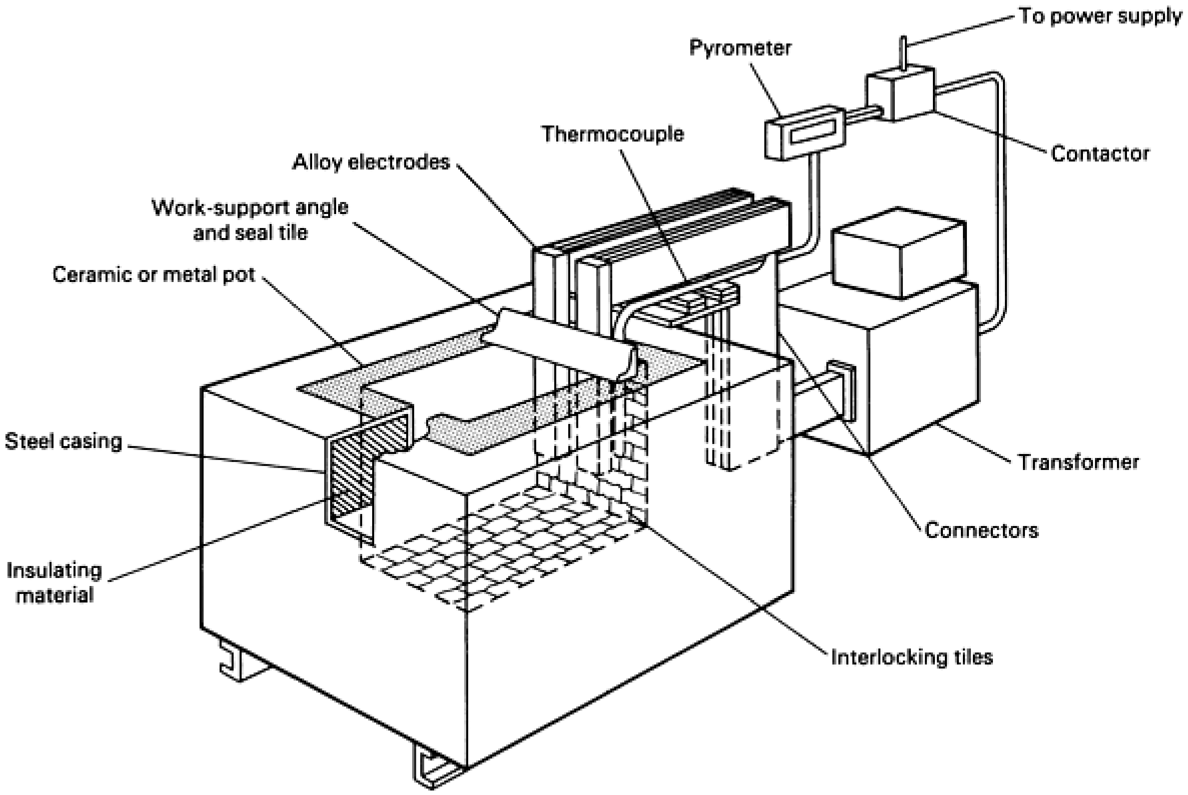


Fig. 2 Internally heated salt bath furnace with immersed electrodes and ceramic tiles

Immersed-electrode furnaces, however, are not as energy efficient as submerged electrode furnaces. The area in which the immersed electrodes enter the salt bath allows additional heat loss through increased surface area. As exhibited in Table 1, the surface area of the salt bath (A) in the submerged-electrode furnace is smaller than the surface area plus the immersed electrodes (A + B) in the immersed-electrode furnace. However, a good cast ceramic and fiber-insulated cover placed over the bath and electrodes will reduce surface radiation losses up to 60%.

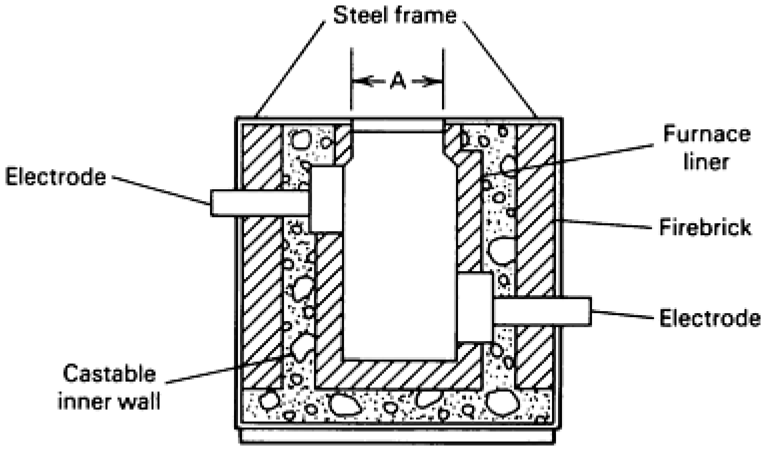
Table 1 Service life of electrodes and refractories

Operating temperature		Service life, years	
°C	°F	Electrodes	Refractories
Submerged-electrode furnaces			
Furnace A			
535-735	1000-1350	15-25	15-25
735-955	1350-1750	6-12	6-12
955-1175	1750-2150	5-7	5-7

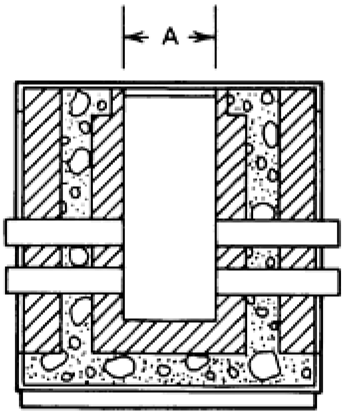
1010-1285	1850-2350	2-4	2-4
Furnace B			
535-735	1000-1350	10-20	10-20
735-955	1350-1750	4-8	4-8
955-1175	1750-2150	3-4	3-4
1010-1285	1850-2350	1-3	1-3
Immersed-electrode furnaces			
Furnace C			
535-735	1000-1350	2-4[(a)]	4-5
735-955	1350-1750	1-2[(a)]	2-3
955-1175	1750-2150	$\frac{1}{2}$-1[(a)]	1-2
1010-1285	1850-2350	$\frac{1}{4}$-$\frac{1}{2}$[(a)]	$1\frac{1}{2}$
Furnace D			
535-735	1000-1350	2-4[(a)]	4-5
735-955	1350-1750	1-2[(a)]	2-3
955-1175	1750-2150	$\frac{1}{2}$-1[(a)]	1-2
1010-1285	1850-2350	$\frac{1}{4}$-$\frac{1}{2}$[(a)]	$1\frac{1}{2}$
Furnace E			
535-735	1000-1350	2-4[(a)]	4-5

735-955	1350-1750	1-2[(a)]	2-3
955-1175	1750-2150	$\frac{1}{2}$-1[(a)]	1-2
1010-1285	1850-2350	$\frac{1}{4}$-$\frac{1}{2}$ [(a)]	$1\frac{1}{2}$

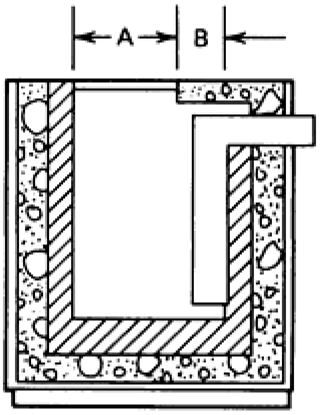
Note: Service life estimates are based on the assumption that proper rectification of chloride salts is being done, as well as routine unit maintenance and care.



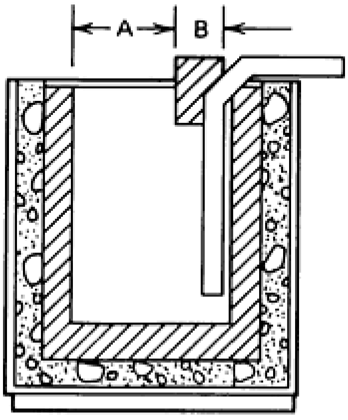
Furnace A



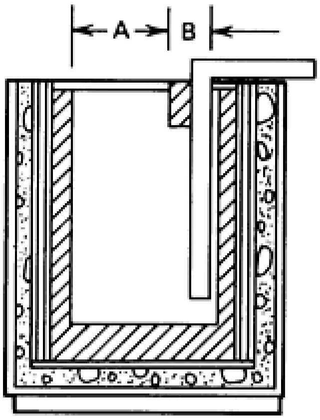
Furnace B



Furnace C



Furnace D



Furnace E

(a) Hot leg only

Super-duty fireclay brick lines the immersed-electrode furnace. Approximately 130 mm (5 in.) of castable and insulating brick then surrounds the fireclay brick on five sides. Figure 2 is a schematic drawing of an immersed-electrode furnace with interlocking tiles and removable electrodes. The removable electrodes enter the furnace from the top, and a seal tile is located in the front of the electrodes to protect them from exposure to air at the air-bath interface. This protection helps prolong electrode life. Table 1 compares service life of electrodes and refractories for some basic furnace designs.

Over-the-top (or over-the-side) electrodes are usually built with laminated cold legs, and water cooling is always required. A typical life expectancy for electrodes operating in such a furnace at 840 °C (1550 °F) is approximately 6 mo to 2 y for over-the-top electrodes, compared to 4 to 8 y for submerged electrodes.

The salt is heated by passing alternating current through it with immersed electrodes. As a result of the resistance built up to passage of current through salt, heat is generated within the salt itself. This heat is quickly dissipated by a downward stirring action created by the electrodes. The electrodes are attached by copper connectors to a transformer that converts the line voltage of the plant to a much lower secondary voltage (approximately 4 to 30 V) across the electrodes. Temperature is measured and automatically controlled by a system containing a thermocouple, pyrometer, relay, and magnetic contactor.

The energy required by an immersed-electrode furnace is a function of:

- Furnace size necessary to hold the load and electrode well
- The energy (Q_w) needed to heat the load to the desired temperature. (The value of Q_w is a function of load mass, the specific heat of the load, and bath temperature)
- Energy losses and safety factors

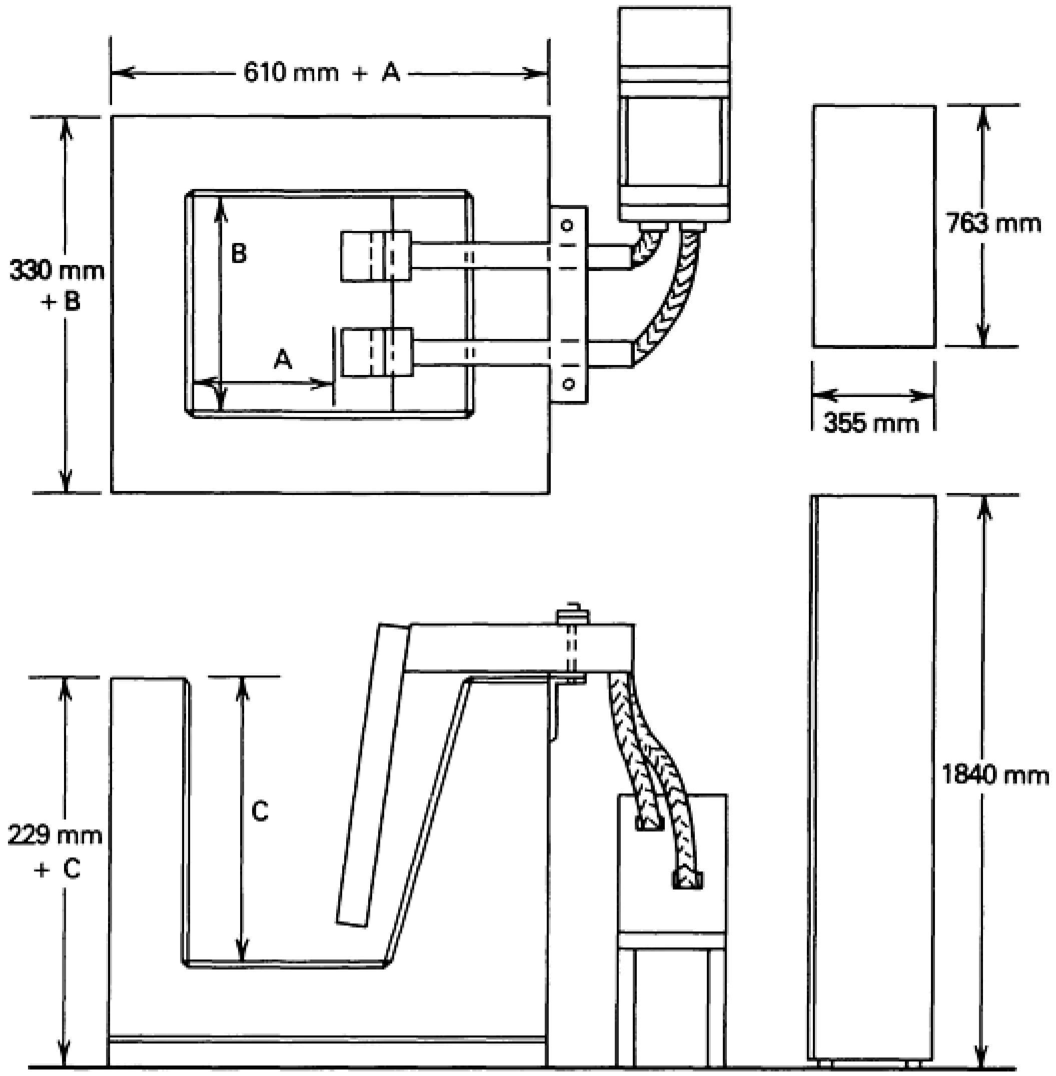
Once energy requirements are determined, then electrode number, size, and spacing can be determined.

Microcomputers are used to calculate the rate of heat generation per unit length of the electrode to ensure that the current is uniform from the top and bottom of the electrodes, taking into account the complexity of the current paths between the electrodes, the electromagnetic forces, and the circulation (influenced by the viscosity of the salt).

The electrode spacing is usually selected between 25 and 100 mm (1 and 4 in.); the height of the electrode should be smaller than the depth of the pot, the difference depending on electrode spacing. The electrode width is usually 50 to 75 mm (2 to 3 in.) and rarely exceeds 125 mm (5 in.). Transformer voltages usually range from 4 to 30 V, with the ratio of maximum to minimum voltage of a given transformer approximately 4.5 (Ref 1).

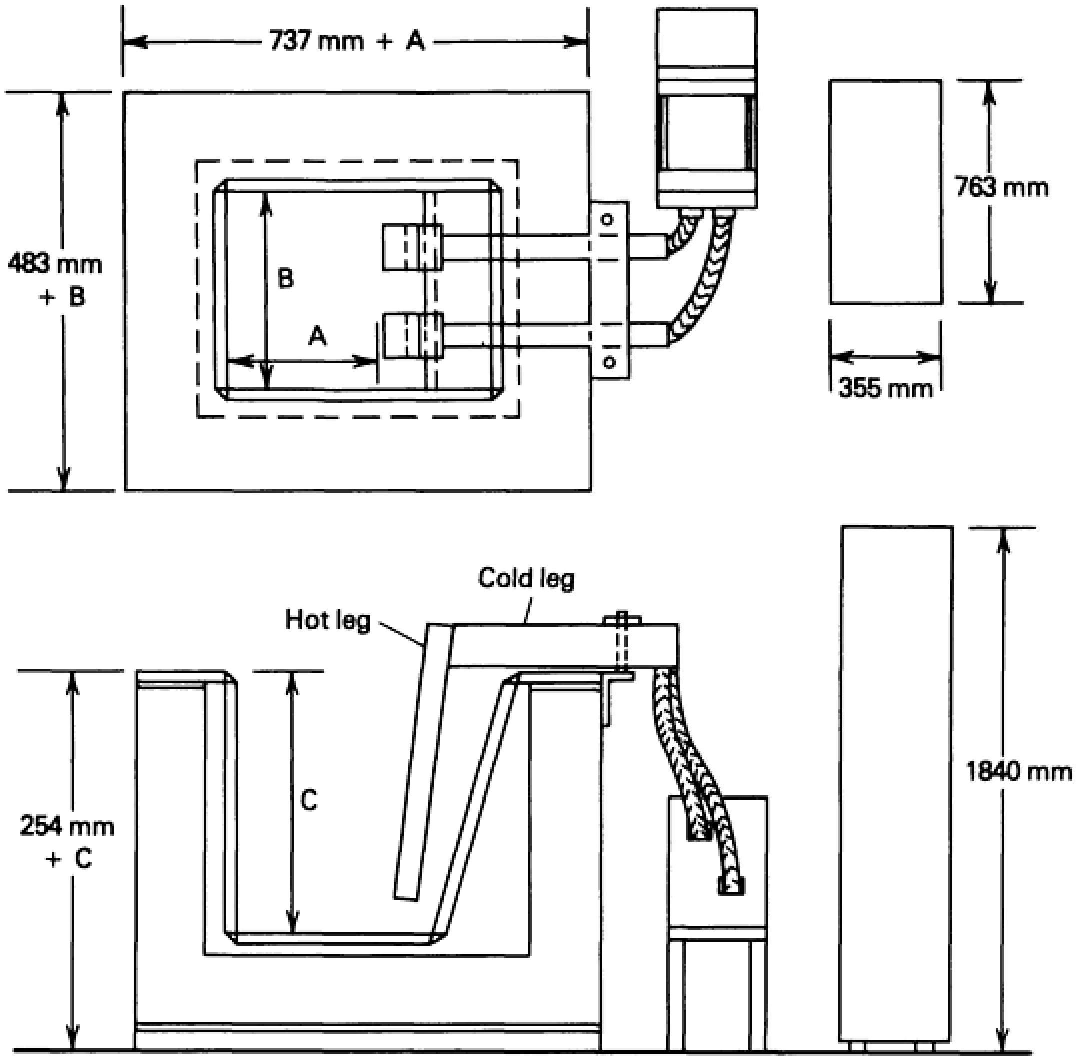
Steel-Pot Furnaces. Some metal-treating processes are performed in salt compounds that cannot be contained in a ceramic liner. For these applications, furnace manufacturers make use of a welded steel pot with immersed electrodes. This type of furnace is suitable for special applications such as case hardening in straight cyanide baths, tempering, and marquenching.

The steel pot often has a sloped back wall, which produces a bottom heating effect resulting in better circulation and uniform temperature. This is accomplished by sloping the electrodes shown in Fig. 3 and 4. As the current passes through the salt between the electrodes, the salt is heated, decreasing its density and causing it to rise toward the bath surface. Control of the rate of rise of the salt is effectively gained by decreasing the distance from the electrodes to the steel pot. At the lower extremity of the electrode, the current enters the metal pot upon leaving the electrode to follow a shorter path to the other electrode. This arrangement ensures current flow through the salt along the entire electrode length. Due to the close proximity of the lower portion of the electrode to the pot, most of the heating is done in the lower part of the bath. This is the desired method of heating any liquid.



Typical standard sizes										
Temperature range		Working dimensions						Input, kW	Heating capacity	
		(A) Length		(B) Width		(C) Depth				
°C	°F	mm	in.	mm	in.	mm	in.		kg/h	lb/h
540-150	1000-300	457	18	457	18	610	24	25	45	100
540-150	1000-300	457	18	686	27	610	24	25	68	150

Fig. 3 Metal pot, immersed-electrode salt bath furnace for ferrous tempering and isothermal annealing



Typical standard sizes										
Temperature range		Working dimensions						Input, kW	Heating capacity	
		(A) Length		(B) Width		(C) Depth				
°C	°F	mm	in.	mm	in.	mm	in.		kg/h	lb/h
955-650	1750-1200	305	12	305	12	455	18	25	34	75
955-650	1750-1200	305	12	455	18	610	24	40	68	150

955-650	1750-1200	455	18	610	24	610	24	75	159	350

Fig. 4 Metal pot, immersed-electrode salt bath furnace for liquid carburizing, cyaniding, and carbonate baths

The metal pots are made of either plain steel or hot-dipped aluminized steel, depending on the application. Thicknesses range from 12 to 38 mm ($\frac{1}{2}$ to $1\frac{1}{2}$ in.). Reinforcing members for light plate, usually angular in shape, are welded from the top. Where depth of the pot so requires, additional members are used at the midsection.

The pot is housed in an insulated 230 mm (9 in.) thick wall furnace either with a brick outside wall contained in a rigid welded steel frame or in a steel-clad frame, depending on personal preference. In either type of construction, the frame is self-supporting on a lattice formed by welding channels or beams to the underside of a steel base plate. The pot is supported on an insulated refractory pedestal.

Electrode Arrangement. Immersed electrodes are made of either mild steel or an alloy "hot" leg welded to a mild steel "cold" leg. As previously mentioned, these are shaped to follow approximately the slope of the pot wall. The portion of the electrode that crosses over the top of the salt bath and is connected to the plant power source is referred to as the cold leg. This is welded to the hot leg, the portion of the electrode that is immersed in the bath, with sufficient weld cross section to provide necessary current conductor capacity. The shanks are drilled and tapped at the tinned terminal connection end for water cooling when necessary. If the latter is not required, the electrical connection is water cooled. Suitable clamping devices are used to facilitate electrode replacement.

Electrode arrangements can vary as follows:

- *Single-phase operation with metal or ceramic pots:* Several electrode arrangements can be used, depending on the size of the bath. If only two electrodes are required, they are normally positioned on the sloped-wall side and at least 125 mm (5 in.) apart. Three electrodes are usually placed so that the center electrode, equal in size to two of the other electrodes, is used as a common conductor with equal current paths to each of the outer electrodes. More than three electrodes would be arranged in multiple groups
- *Three-phase operation with metal pots:* Three electrodes are used and spaced in a manner similar to the spacing described above. They are connected to three single-phase transformers that have Y-connected secondaries and delta-connected primaries. The current flows from the electrodes to the metal pot, which is the neutral point. Several variations of the three-phase connections are used, depending on the type of furnace and load requirements

All accessories, such as starting units, sludging tools, and secondary connectors, are the same for steel-pot immersed-electrode furnaces as for ceramic furnaces.

Advantages and Disadvantages. Immersed-electrode furnaces do not require the use of iron-chromium-nickel alloy pots.

These furnaces require minimum floor space and maintenance and can be used for all types of neutral salts. Electrodes made of alloy steel should have an average service life equivalent to that indicated for steel pots in the section "Pot Service Life." Worn electrodes can be replaced while the furnace is in operation.

Depending on the positioning of electrodes, control to within ±3 °C (±5 °F) is easily obtained with immersed-electrode furnaces. Heat is generated within the bath, and overshooting is readily avoided. These furnaces lend themselves to mechanization and are suitable for high-volume production in the range of 815 to 1300 °C (1500 to 2370 °F).

The depth of salt pots for immersed-electrode furnaces is not restricted for ceramic or ceramic-lined pots. Metal pots may be restricted to depths of about 0.6 m (2 ft). Pots may vary in length and width to suit requirements, and multiple pairs of electrodes can be installed to furnish the necessary heating capacity.

The immersed-electrode furnace is not recommended for intermittent operation. Depending on furnace size, reheating the salt charge may require a day or more. Pots are not intended to be interchangeable. Removal of the pot usually involves replacement of the surrounding insulation.

Reference cited in this section

1. V. Paschkis and J. Persson, *Industrial Electric Furnaces and Appliances,* Interscience, 1960

Submerged-Electrode Furnaces

Submerged-electrode furnaces (Fig. 5 and furnaces A and B in the figure to Table 1) have the electrodes placed beneath the working depth for bottom heating. Many submerged-electrode furnaces are designed for specific production requirements and are equipped with patented features, which offer certain economical and technical advantages. General characteristics of submerged-electrode furnaces include:

- *Maximum work space with minimum bath area:* The electrodes do not occupy any portion of the bath surface, so that they only come in contact with the salt. Bath size is consequently smaller, and electrode life increases many times over by incorporating unidirectional wear and eliminating excessive deterioration at the air-bath interface
- *Circulation-convection currents:* Bottom heating provides more uniform bath temperatures and bath movement through the use of natural convection currents
- *Triple-layer ceramic wall construction:* The temperature gradients through the wall cause any salt penetrating the wall to solidify before it can penetrate the cast refractory material that forms the center portion of the wall construction. The design requires from 5 to 8% of the initial salt charge to fill the ceramic pot. By comparison, in some designs 140 to 150% of the initial charge is needed to seal the ceramic walls of furnaces built with two layers of ceramic brick, backed up and supported by a steel plate. Salt penetrates the ceramic walls of any furnace and distorts the geometry of the walls. Reducing the amount of salt allowed to penetrate the ceramic walls aids in maintaining dimensions and in promoting a longer furnace life
- *Electrode placement:* Enclosing the electrode in a clear rectangular box, free of any protruding obstructions, eliminates any potential hazards to operating personnel during cleaning. Any sludge formed in the furnace is removed easily by operating personnel

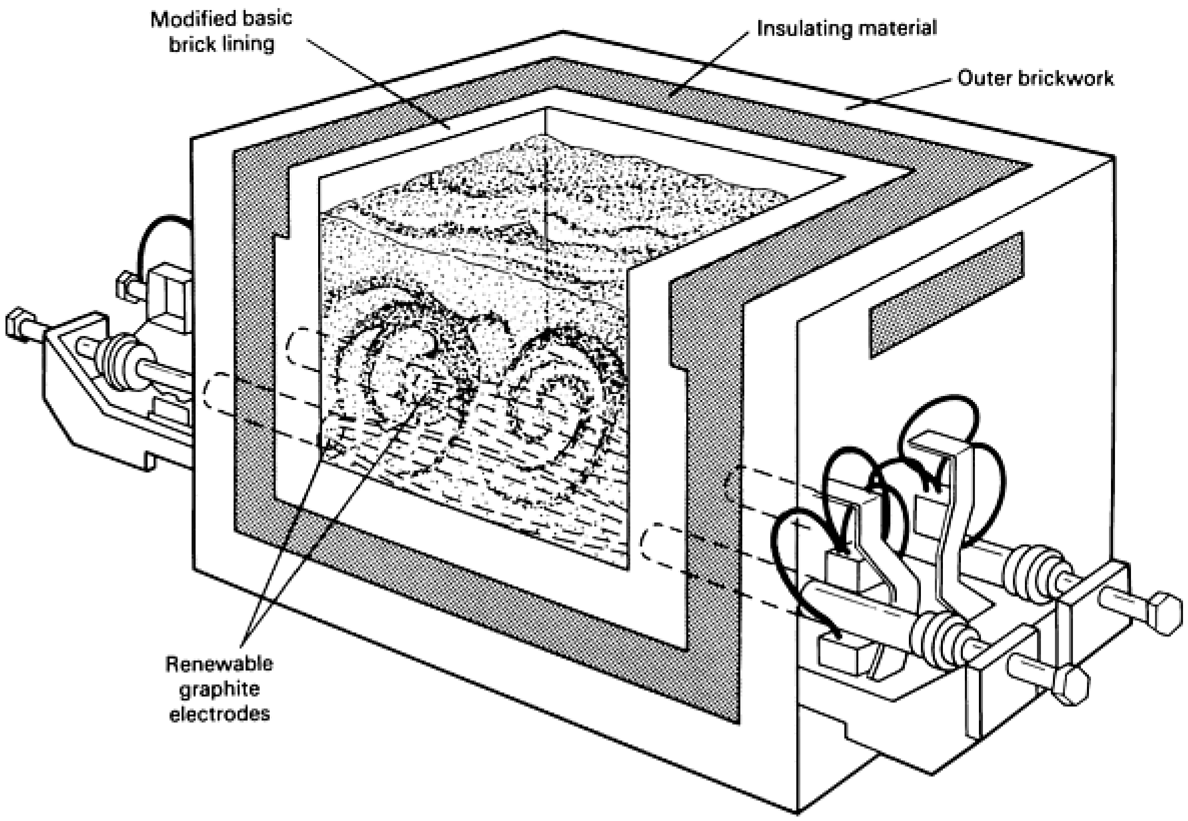


Fig. 5 Internally heated salt bath furnace with submerged electrodes. This furnace has a modified brick lining for use with carburizing salts.

Frame Construction. A typical submerged-electrode furnace is made of brick and ceramic material reassembled, regardless of size, in a rigid, self-supporting welded steel frame (see, for example, Table 1). This frame consists of supporting channels or beams welded to the underside of a heavy steel plate that forms the frame base. To this base are welded lengths of heavy angle iron around the outside and on top of the plate. These pieces are notched to permit welding of the heavy angle-iron posts to the plate and vertical sides of the base-plate angle iron. Lengths of heavy angle iron are welded similarly to the top of the posts. When required, additional vertical reinforcing members are welded between the bottom and top pieces of angle iron, and prestressed horizontal members also are used to ensure that the refractory material cannot move after the furnace has been brought to operating temperature.

Brick Construction. Three types of refractory materials are commonly used in submerged-electrode furnaces. A typical design is shown by furnace A in Table 1.

Submerged-electrode furnace liners are constructed with 230 mm (9 in.) thick high-temperature burned bricks. Consisting of approximately 42% alumina and 52% silica, the brick material is used in standard brick sizes such as 60 by 115 by 230 mm ($2\frac{1}{2}$ by $4\frac{1}{2}$ by 9 in.) and in various brick shapes, such as straights, flat backs, and splits. The bricks are laid with a high-quality air-setting mortar that resists abrasion, erosion, and chemical attack by chloride, fluoride, and nitrate-nitrite salts. The mortar offers sufficient wear and corrosion resistance to be economically used with some salts containing cyanide. For straight cyanide or carbonate salts, a welded steel pot or a furnace with a modified brick lining (Fig. 5) is used.

The outer wall of the salt bath furnaces is made of a second-quality firebrick with the same dimensions as brick used for the liner. The important qualities of this brick are the strength of the material and uniformity in size and shape.

The inner castable wall is constructed with a maximum of refractory cement and aggregate that is poured between the liner and outer wall to form a 240 mm (9.5 in.) thick monolithic wall structure. This dimension provides a temperature

gradient sufficient to cause the salt to freeze in the wall, thus making the wall self-sealing. With this design, salt penetration into the wall amounts to less than 8% of the bath volume. The maximum temperature of the outside wall during furnace operation is 60 °C (140 °F).

Electrode Construction. The electrodes used in submerged-electrode salt bath furnaces vary widely in size and shape, depending on the geometry of the furnace and the power requirements. All of the electrodes are located near the bottom of the bath and are built into the wall (furnace A in Table 1) so only one face of the electrode is in contact with the salt. This placement leaves the bath area free of obstruction for ease of cleaning and eliminates the possibility of touching the electrodes to the work.

Alloy electrodes are made by welding a 1610 mm^2 (2.50 $in.^2$) alloy material to a mild steel backing, or by welding a 125 by 125 mm (5 by 5 in.) alloy material directly to the mild steel tank. The spacing between electrode pairs is usually 65 mm (2.5 in.), or 190 mm (7.5 in.). The spacing is fixed and nonadjustable. For this reason, computation of the secondary tap voltages is critical to the successful operation of the furnace throughout its lifetime.

The durability of typical electrode and ceramic components of submerged-electrode furnaces is described in Table 1. Alloy electrodes can be replaced with graphite electrodes, which are renewed as they become consumed without disconnecting them (Fig. 5) or shutting off the power.

Startup and Shutdown. The submerged-electrode furnace can be started by adding molten salt from another furnace or by using a gas-fired torch or electric starting coil to melt a pool of salt that will wet both electrodes and provide molten salt for the current path. After the current path has been established in the molten salt between the electrodes, salt may be added to bring the bath up to working level. Additional salt will be required to maintain this level because a small amount, approximately 5%, will seep into the brickwork and freeze.

If the furnace must be shut down, the molten salt should be bailed from the furnace before it freezes. However, if the salt is allowed to remain in the furnace, a resistance-heated starting coil should be submerged in the bottom of the furnace while the salt is still molten. This coil remains in the frozen salt and it is connected to the transformer leads to start up the furnace.

Newer designs have one pair of electrodes close to the surface of the bath. When the furnace cools, the surfaced electrode pair is exposed, thus simplifying startup.

Advantages and Disadvantages. In common with the immersed-electrode furnaces, submerged-electrode furnaces require minimum floor space and maintenance and are highly adaptable to mechanization.

Because the submerged-electrode furnace employs water to cool the electrodes and transformer, it may be operated at 50% overload without overheating the transformer, whereas the immersed-electrode furnace, being air-cooled, should not be operated at an overload above 10%.

Because a ceramic pot is used, unexpected pot failure is rare with submerged-electrode furnaces, and the furnaces can be rebuilt on a planned schedule during annual shutdowns. In common with other electrical equipment, submerged-electrode furnaces are at a disadvantage where electric power rates are high, but this can be overcome to some extent by working the furnace in nonpeak periods when lower power rates are applicable.

Because of the erosive effects on ceramic pots of water-soluble salts with high sodium carbonate or high sodium cyanide contents, submerged-electrode furnaces can be used with only low-cyanide, low-carbonate salts. Baths with high cyanide or carbonate salt require a modified basic brick. The furnace with modified brick and submerged alloy electrodes provides many years of service in noncyanide and cyanide operations. To increase furnace life, the furnace shown in Fig. 5 is recommended. This furnace has a modified basic brick lining for use with basic carburizing salts. The alloy electrodes are replaced with continuing graphite electrodes. The electrodes are renewed as they become consumed without disconnecting them or even shutting off the power.

Air-Quality Assurance

Salt bath furnaces that operate at temperatures above 650 °C (1200 °F) will fume. An open furnace containing a 50-50% NaCl/KCl mix, operating at 870 °C (1600 °F) at sea level, will fume at a rate of 0.2 kg/m^2 per h (0.04 lb/ft^2 per h).

Sodium chloride and potassium chloride are both edible; however, in large quantities they can be a nuisance. The best way to overcome this nuisance is to capture it at the source.

Figure 6 illustrates two ways of capturing fumes from a salt bath furnace. The 380 mm (15 in.) location of a capture hood (Fig. 6a) requires treatment of 200 m^3/min (7120 ft^3/min) of air and fumes, whereas a canopy hood (Fig. 6b) at 305 mm (120 in.) requires treatment of over 900 m^3/min (32 000 ft^3/min) of fumes and air. When the basket and parts are lifted from the salt bath, fumes are greatly increased, probably in proportion to the total surface area of the basket and parts exposed to air (plus the bath surface fumes). It is important to remember that the fumes coming off a salt bath are hotter and have more energy than fumes at standard temperature and pressure. To calculate the type and amount of ventilation required, consult Ref 2.

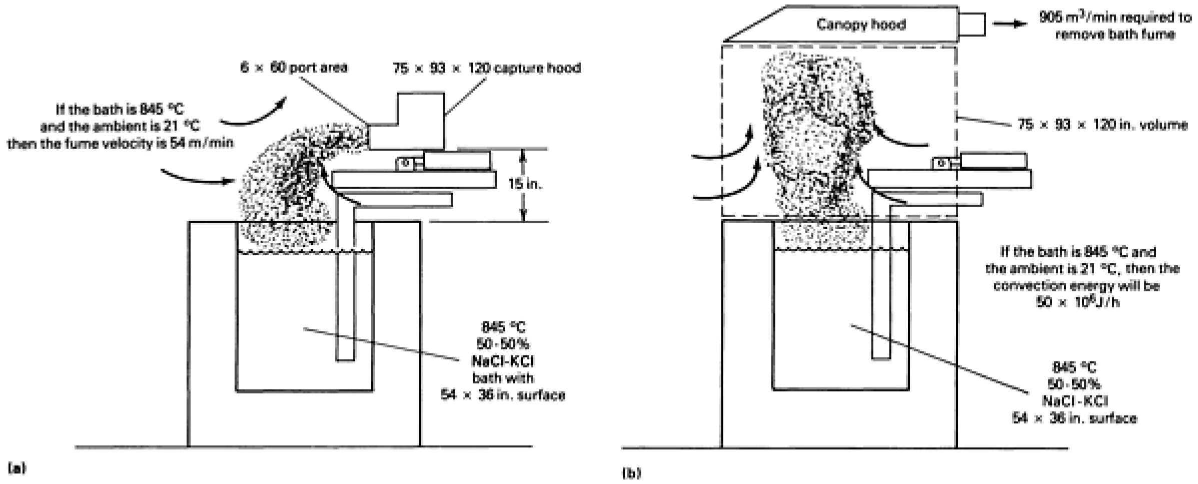


Fig. 6 Ventilation of a salt bath furnace with (a) a capture hood and (b) a canopy hood. The capture hood in (a) requires a ventilation rate of 200 m^3/min (7120 ft^3/min), whereas the canopy hood in (b) requires a larger ventilation rate of 905 m^3/min (32 000 ft^3/min). All dimensions given in inches

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2. *Industrial Ventilation,* 20th ed., American Conference of Governmental Industrial Hygienists, 1988

Isothermal Quenching Furnaces for Austempering or Martempering

Isothermal quenching furnaces are pot-type furnaces with salt agitation, cooling, and chloride-elimination features. As little as 10% chloride salt will cause the quench rate of a salt quench to be reduced by 50%. Isothermal quenching furnace systems were designed to eliminate the occurrence of chloride carryover from the austenitizing bath to the quench bath, through salt separation and uniform vertical lamellar flow agitation. The three most common approaches to alleviating the salt concentration are chemical, temperature, and gravity separation.

Chemical Precipitation. Chemical agents have been used to attempt to lower the solubility of the chloride salts so that they will precipitate in the quenching salt. When the salts settle to the bottom of the quench tank, they are removed as sludge. This method offers little success because the precipitate that forms is fine textured and buoyant and therefore tends to remain in suspension rather than to precipitate out.

Temperature Precipitation. The elimination of carryover salts has also been attempted by continuously pumping salt through a small auxiliary chamber whose temperature is maintained at a lower level than the main chamber. As the salt is processed through the auxiliary chamber, chlorides are continuously precipitated out.

Although this method appears practical, a fundamental error exists in its application. The salt is cooled by air blown through a space between the pot and the outer shell of the precipitation chamber. Air is blown through this space to maintain the temperature levels of the main chamber and precipitation chambers. The moving air cools the pot walls below the salt-precipitation point so that the salt freezes and cakes to the sides. Salt buildup continues until the bath is

unusable. Consequently, depending on the level of salt concentration, the bath would have to be shut down, possibly after only a few weeks of operation, to remove the remaining molten salt and chip away the caked salt.

Gravity Separation. This system of carryover salt removal also uses a two-chamber design. The caking problem is eliminated by heavily insulating the pot walls at all points and using an internal air-water heat exchanger. Because the pot walls and the salt are at the same temperature, there is no caking action. The chloride salts settle into an easily removable shallow pan at the bottom of the precipitation chamber, or, if they are fine textured and buoyant, the salts float to the top of the tanks and are easily skimmed off.

The main advantages of two-chamber gravity-separation equipment include:

- Easily removable variable-speed propeller-type agitator with suitable baffling to provide vertical lamellar flow within the quench area, therefore ensuring maximum quench power and minimum distortion
- Separate chloride precipitation chamber with adjustable weirs to maintain a low chloride level and subsequently high quenching power
- Easily removable internal heat exchanger to maintain quench temperature and precipitate chlorides
- Easily removable settling pan to ensure maximum efficiency in removal of chlorides
- Heavily insulated pot and precipitation chamber to eliminate salt caking on walls

Furnace Heating. Generally either gas or electricity may be used to heat isothermal quenching furnaces. When gas heating is desired, immersion tubes are recommended because they are usually made of mild steel and provide long service life.

Further, if the pot should develop a leak, the insulation and outer shell will contain the salt. *Caution: If a furnace with an externally heated pot were to develop a leak, the nitrate-nitrite salt would drip on the hot refractory and may cause a fire hazard.* One or more immersion tubes normally are used, depending on bath size. Generally, they will have nozzle-mix sealed-in burners and will be available to Factory Mutual or Factory Insurance Association specification.

Electric heating may be by one of the following methods, depending on the maximum operating temperature:

- *Sheathed resistance strip heaters* are mounted externally to the side walls near the bottom. Maximum operating temperature is 425 °C (800 °F). They are easily removable through the insulated plug-type door. Protection against overshooting is achieved by locating a sensing device close to the heaters. The sensors operate directly on line voltage
- *Sheathed resistance immersion heaters* have a maximum operating temperature of 425 °C (800 °F). They can operate without a transformer but are susceptible to premature burnout due to the sludge accumulation or operator tampering and abuse
- *Immersed-electrode heaters* operate in the same manner as electrode pot furnaces for carburizing and tempering

Furnace Construction. The pot is fabricated from firebox-quality steel plate, double welded inside and out and properly supported to maintain its shape. Steel plate offers adequate resistance to chemical attack by the standard alkaline nitrate-nitrite salts at normal austempering and martempering temperatures. The pot is insulated with 100 to 150 mm (4 to 6 in.) of slab-type mineral insulation to prevent the chloride-saturated nitrate salt from freezing to the side walls or the bottom. The insulation is externally contained by a continuously welded outer steel shell. The shell is reinforced to ensure retention of the original shape and dimensions throughout its designed operating temperature range.

Automatic and Semiautomatic Lines

The use of automated hoists makes possible the combination of austempering, martempering, and tempering or carburizing in one line. One or more hoists travel back and forth, automatically advancing the fixture carriers of work through the required stations.

The hoist movement is controlled by a solid-state programmable control with functions that would normally require hundreds of relays, counters, switches, and extensive wiring. Once programmed, the controller performs the desired commands and functions. Time cycles, sequences, drills, and skips are easily entered or changed to meet metallurgical requirements. For instance, parts can be programmed to be carburized, air cooled, washed, rinsed, and returned for unloading. A push-button command then returns the program to standard processing.

Parts suitable for fully automatic or semi-automatic installations are those that can be fixtured by wiring, racking, or placing in baskets and that do not present problems in either buoyancy or drainage.

Fluidized-Bed Heat-Treating Equipment

Revised by Robert F. Sagon-King, Can-Eng Ltd

Introduction

FLUIDIZED-BED TECHNIQUES are not new to the metalworking industry. A 19th century American patent describes the roasting of minerals under fluidized-bed conditions. Other established applications include potter's clay and miner's hydraulic slurries. Systems of fluidized solid particles, such as quicksand, occur in nature.

Early attempts to use fluidized beds in the heat treatment of metals were limited in the temperatures that could be employed. Electrically heated furnaces capable of maintaining fluidized beds at temperatures up to 500 °C (930 °F) could be produced commercially, but difficulties were encountered when attempts were made to attain higher temperatures. A principal problem was the high rate at which refractory distributors, which distribute the hot fluidizing gases, were consumed.

In early gas-fired fluidized-bed furnace design, gas entered the base of the container after being mixed with air to make it ignitable at the point of entry. With newer designs, the mixtures are introduced separately and thus cannot be ignited accidentally. This design eliminates the danger of explosion at the point of entry. The surface of the bed is heated first, and the heating of surface particles causes progressive ignition downward through the container until the entire contents of the bed achieves uniform heat-treating temperature. Newer furnace designs extend fluidized-bed technology into the higher temperature ranges (540 to 1040 °C, or 1000 to 1900 °F) required for most common heat treatments.

Principles of Fluidized-Bed Heat Treating

In fluidization, a bed of dry, finely divided particles, typically aluminum oxide in the heat-treating context, is made to behave like a liquid by a moving gas fed upward through a diffusor or distributor into the bed. A gas-fluidized bed is considered a dense-phase fluidized bed when it exhibits a clearly defined upper limit or surface. At a sufficiently high fluid-flow rate, however, the terminal velocity of the solids is exceeded, the bed goes into motion, and the upper surface of the bed disappears. This state constitutes a disperse, dilute, or lean-phase fluidized bed with pneumatic transport of solids. The general phases or stages of fluidization are shown in Fig. 1. Usually the aggregative or bubbling-type stage is used for heat-treatment processes.

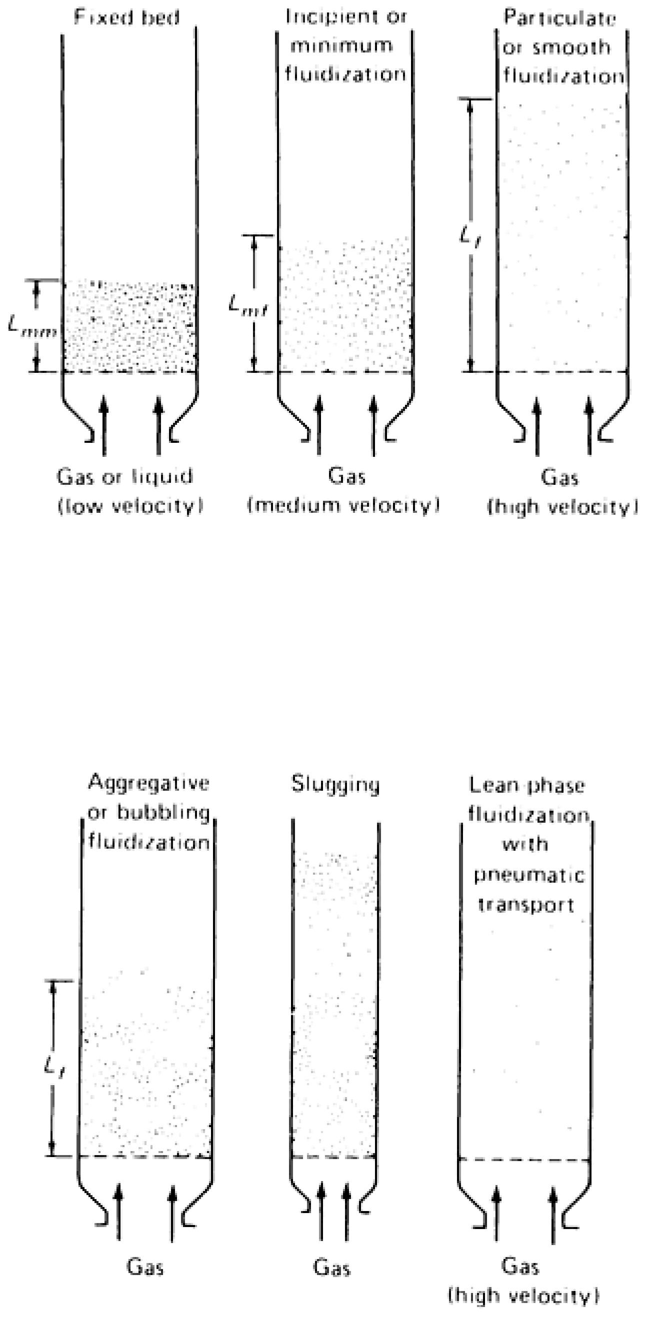

Fig. 1 Various types of contacting in fluidized beds

Although the properties of solid and fluid alone determine the quality of fluidization (that is, whether smooth or bubbling fluidization occurs), many factors influence the rate of solid mixing, the side of the bubbles, and the extent of heterogeneity in the bed. These factors include bed geometry, gas-flow rate, type of gas distributor, and internal-vessel features such as screens, baffles, and heat exchangers.

Determination of Fluidization Velocity. In determining the quality of fluidization, a diagram of pressure drop (Δp) versus velocity (μ_0) is useful as a rough indication when visual observation is not possible. A well-fluidized bed will behave as shown in the diagram in Fig. 2, which has two distinct zones. In the first, at relatively low flow rates in a packed bed, the pressure drop is approximately proportional to the gas velocity and usually reaches a maximum value (Δp_{max}) slightly higher than the static pressure of the bed. With an increase in gas velocity, the packed bed suddenly "unlocks" and becomes fluidlike.

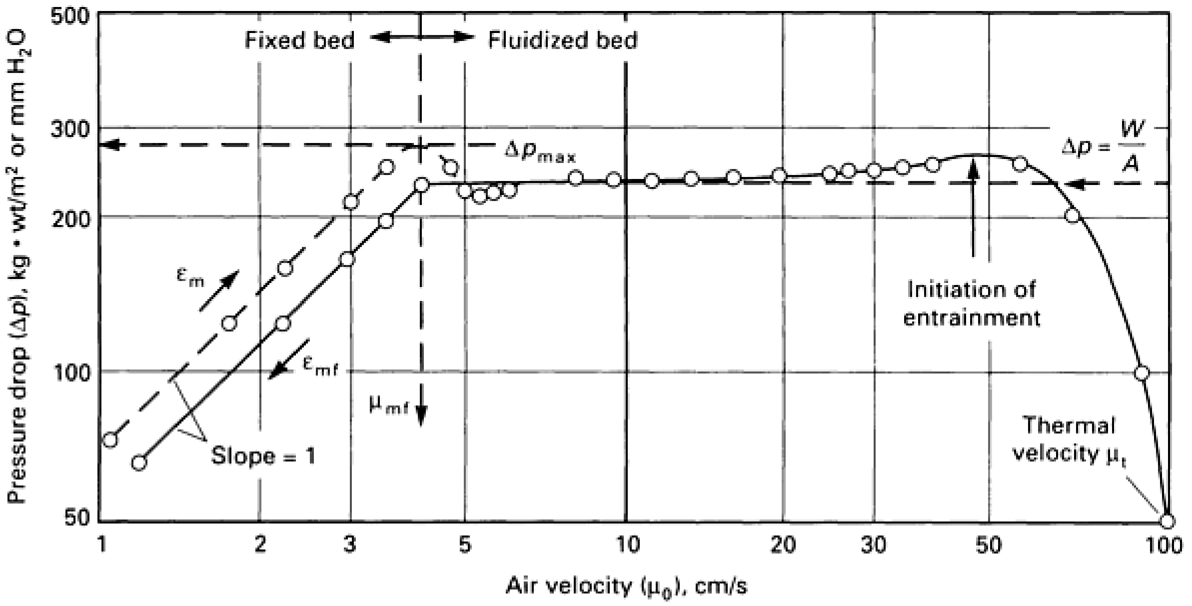

Fig. 2 Pressure drop versus gas velocity for a bed of uniform-sized particles. M_{mf}, minimum fluidization velocity. Source: Ref 1

When gas velocity increases beyond minimum fluidization (μ_{mf}), the bed expands and gas bubbles rise, resulting in a heterogeneous bed. This is the second zone, in which, despite a rise in gas flow, the pressure drop remains practically unchanged. The dense gas-solid phase is well aerated and can deform easily without appreciable resistance. In its hydrodynamic behavior, the dense phase can be likened to a liquid. If a gas is introduced into the bottom of a tank containing a liquid of low viscosity, the pressure required for injection is roughly the static pressure of the liquid and is independent of the flow rate of the gas. The constancy in pressure drop in both the bubbling liquid and the bubbling fluidized bed may be taken intuitively to be analogous.

The diagrams in Fig. 3 show poorly fluidized beds. The large pressure fluctuations in Fig. 3(a) suggest a slugging bed. In Fig. 3(b), the absence of the characteristic sharp change in slope at minimum fluidization and the abnormally low pressure drop suggest incomplete contacting, with particles only partly fluidized.

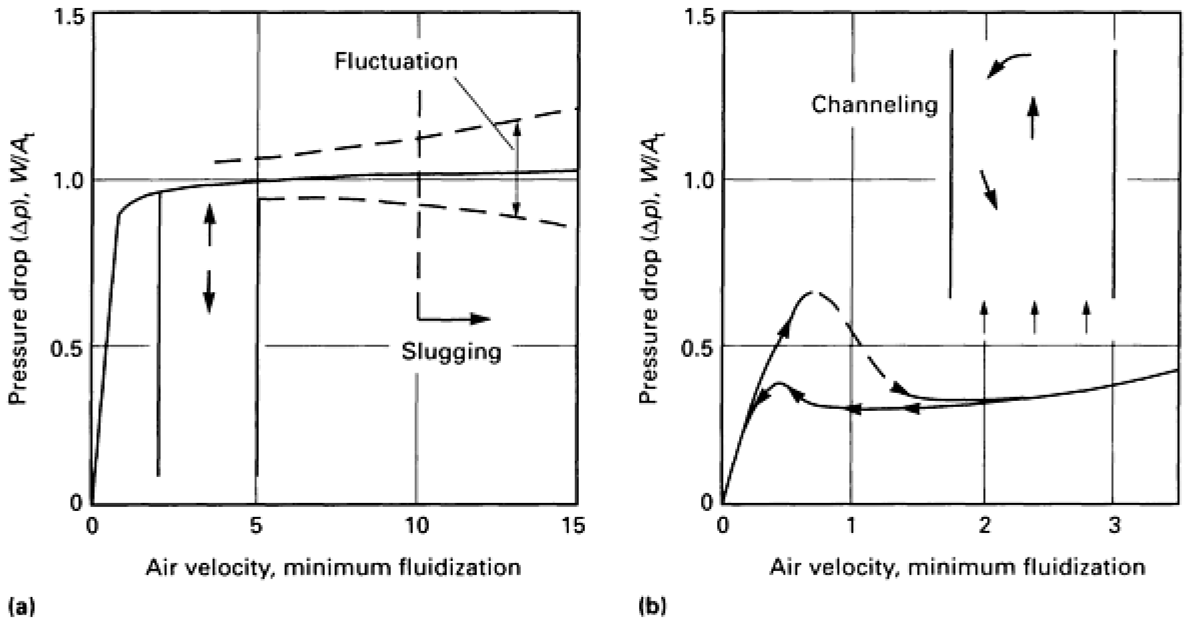

Fig. 3 Pressure drop diagrams for poorly fluidized beds. Source: Ref 1

One of the most important factors influencing the quality of fluidization is the uniformity of gas flow across a constant pressure drop. Figure 4 illustrates this schematically.

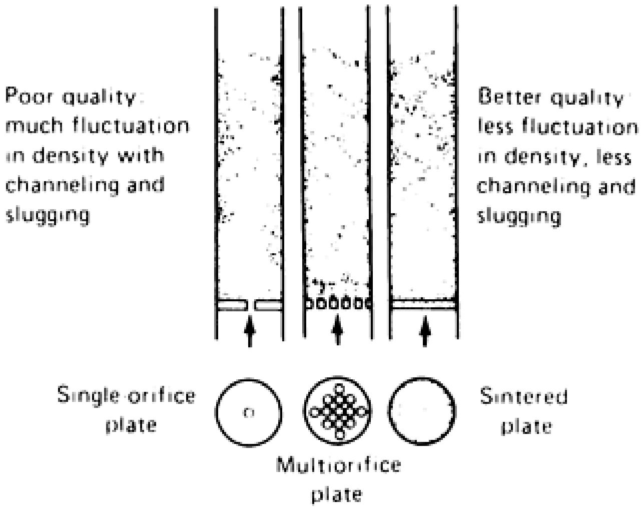

Fig. 4 Quality of fluidization as influenced by type of gas distributor. Source: Ref 1

Temperature Effect on Minimum Fluidization Velocity. One of the most important parameters of a fluidized bed is the minimum fluidization velocity. In simplified terms, minimum fluidization velocity (μ_{mf}) approximates to a function of the square of the particle diameter (*d*) and a linear function of particle mass (*p*) as:

$$\mu_{mf} \cong d^2 p \qquad \textbf{(Eq 1)}$$

In the design of heat-treating furnaces, the effect of temperature must be considered. Figure 5 shows that the flow of gas required for fluidization decreases rapidly with increases in temperature.

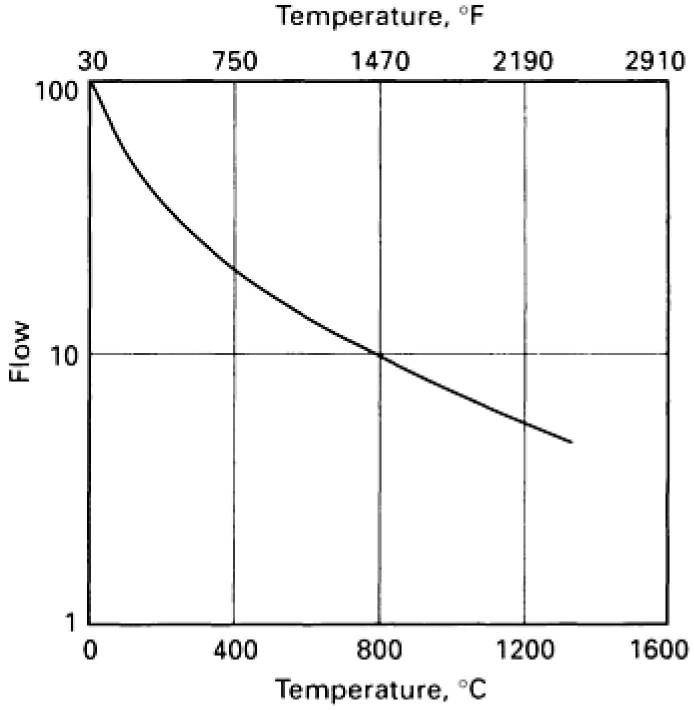

Fig. 5 Effect of temperature on the flow corresponding to minimum fluidization for particles 0.1 mm (0.004 in.) in diameter having an apparent density of 2

Defluidization. One of the common concerns about fluidized beds is that, because of their principle of operation, they are not well suited for large, solid parts with horizontal surfaces that remain stationary in the bed. This a result of the incorrect belief that fluidization occurs only in a vertical direction. With parts of this type, a cap of nonfluidized particles collects on the horizontal surfaces, forming a thermal screen. The higher the temperature of operation, however, the greater the energy and agitation of the bed and the smaller the likelihood that the bed will collapse. Moreover, various methods can be used to overcome this apparent disadvantage, and these are designed into most fluidized beds. These methods are:

- Movement of the part being treated
- Introduction of additional agitation in the zone of fluidization around the part, either by localized injection of fluidizing gas or by careful design of the outline of the basket that holds the parts
- Increased fluidizing velocity
- A more favorable orientation of the part

Selective Heat Treatment. Bed collapse can be turned to advantage for special heat treatments in which one area of the path must be hard and tough and the remainder must be soft and more ductile, as in the case of the engineered parts of the shape described above. In this case, after uniform heating, the part is removed from a hot fluidized bed and partially submerged in a fluidized quenching bed, with the part to be hardened facing down. The top horizontal surface becomes covered with a cap of particles that form a thermal screen, which retards the vigorous cooling caused by the fluidized bed.

Reference cited in this section

1. R.W. Reynoldson, Controlled Atmosphere Fluidized Beds for the Heat Treatment of Metals, *Heat Treatment of Metals,* University of Aston in Birmingham, 1976

Heat Transfer in Fluidized Beds

An important characteristic of fluidized beds is high-efficiency heat transfer. The turbulent motion and rapid circulation of the particles in the fluid furnace provide a heat-transfer efficiency comparable to that of conventional salt bath or lead bath equipment.

The heat transfer coefficient of a fluidized bed is typically between 120 and 1200 W/m^2 · °C (21 and 210 Btu/ft^2 · h · °F). The turbulent motion and rapid circulation rate of the particles and the extremely high solid-gas interfacial area account for this feature. The following factors are important in heat transfer.

Particle Diameter. Of all the parameters that affect the heat transfer coefficient in fluidized beds, particle diameter exerts the greatest influence. Particle diameter is generally a compromise between conserving fluidized gas flows and avoiding entrainment or carry-out. Normally a sieve size of 80 to 100 grit is used.

Bed Material. The governing physical property of any bed material is its density. There appears to be an optimum density for bed materials: about 1280 to 1600 kg/m^3 (80 to 100 lb/ft^3). High-density materials tend to produce lower heat transfer coefficients and in addition require more power for fluidization. Carry-out problems occur with low-density materials. Other properties, such as thermal conductivity and specific heat, are less important.

Fluidization Velocity of Gas. It is essential to use the optimum flow rate, that is, one that provides the maximum heat transfer rate for a particular particle density and diameter. Generally, this flow rate is considered to be between two and three times the minimum fluidization velocity. Too high a velocity leads to particle entrainment, high consumption of fluidizing gas, and poor heat transfer; too low a velocity leads to poor heat transfer and lack of uniformity in processing.

Heating Rates. Relative heating rates of a 16 mm (0.6 in.) steel bar in salt, in lead, in a fluidized bed, and in a conventional furnace are illustrated in Fig. 6(a); relative cooling rates for air, oil, water, and a fluidized bed are shown in Fig. 6(b). Figure 7 presents heating and recovery rates for a fluidized bed. Results of both hardening and isothermal quenching of type D3 tool steel with salt baths and with fluidized beds are given in Table 1. The difference between the two installations in total time for final heating and holding resulted from a difference in preheating conditions.

Table 1 Comparison of the effects of hardening and isothermal quenching of type D3 tool steel in salt baths and in fluidized beds

Heating or cooling medium	Diameter of test pieces		Preheating temperature		Total time for final heating and holding at 960 °C (1760 °F), min	Hardness, HRC	
	mm	in.	°C	°F		At surface	At center
Salt bath	80	3.2	500	930	44	65.5	65
Fluidized bed[(a)]	80	3.2	490	915	51	65	65
Salt bath	40	1.6	540	1000	36	64.5	64
Fluidized bed	40	1.6	500	930	41	64.5	64

(a) Small parts of the same steel but with a diameter of 8 mm (0.3 in.) were treated at the same time; hardness of these parts was 66 HRC.

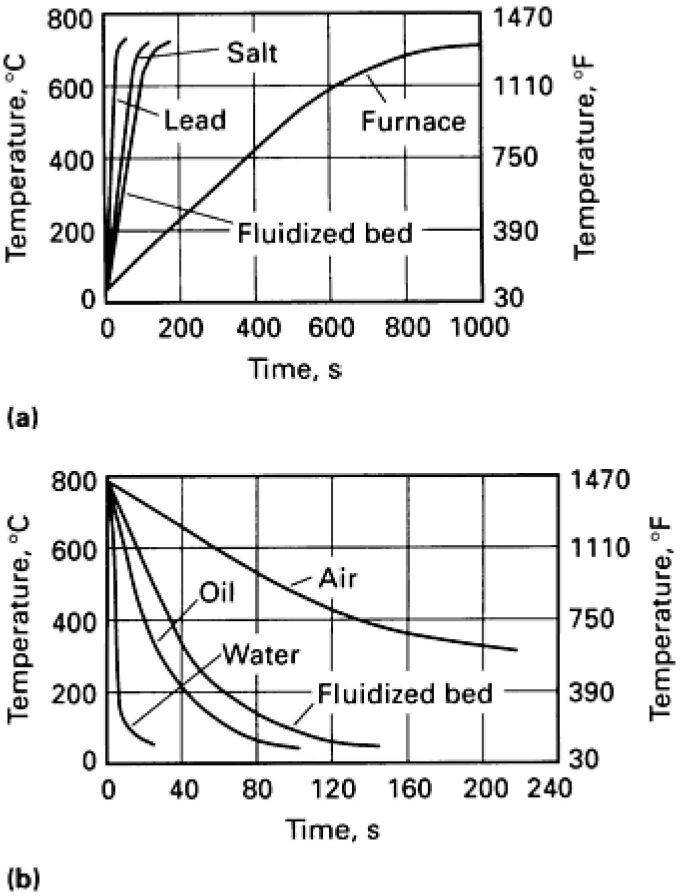

Fig. 6 Relative heat transfer rates. (a) Heating rates for 16 mm (0.6 in.) diam steel bars in lead, in salt, in a fluidized-bed furnace, and in a conventional furnace. (b) Quenching rates for 16 mm (0.6 in.) diam steel bars in air, in oil, in water, and in a fluidized-bed furnace. Source: Ref 1

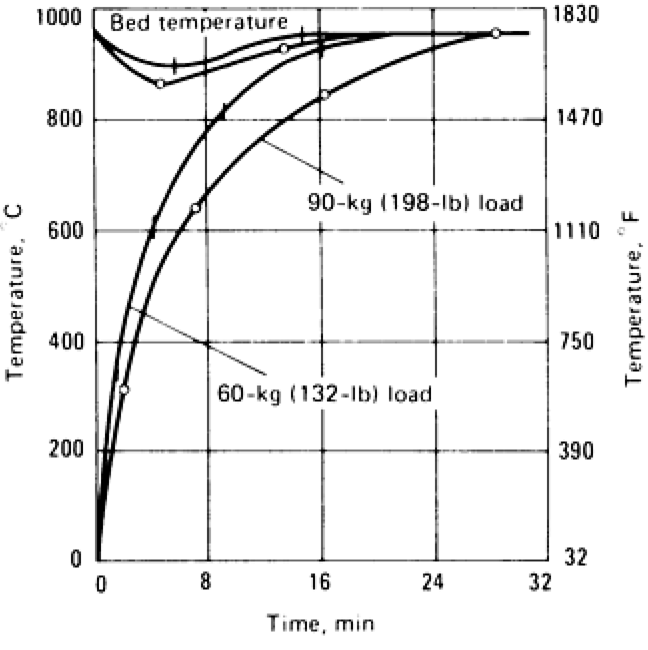

Fig. 7 Recovery rates for 25 mm (1 in.) diam steel parts in a 0.3 m^3 (10 ft^3) fluidized bed furnace

Reference cited in this section

1. R.W. Reynoldson, Controlled Atmosphere Fluidized Beds for the Heat Treatment of Metals, *Heat Treatment of Metals,* University of Aston in Birmingham, 1976

Control of Atmospheres

A full range of atmospheres can be used within the work zones of fluidized beds. The volume of gas used is clearly dictated by particle size, temperature of operation, and optimum fluidization velocity. However, it can be shown that, with careful design and the use of low-cost carrier gases such as nitrogen, even low-temperature surface treatments can be both effective and economical. In addition, one of the major advantages of a fluidized bed is that expensive gas need not be consumed while there is no work in the bed. Atmosphere conditioning is rapid: within about 30 to 60 s after an inert gas is introduced into the bed, the purity of the atmosphere is equivalent to that of the gas supply. In fluidized beds, various types of atmospheres can be obtained, as discussed below.

Reducing or Oxidizing Atmosphere. Adjustment of a gas-air mixture to the bed so that it is either gas-rich or oxidizing causes some decarburization or oxidation reactions in the materials being processed (the gas-rich mixture produces somewhat less severe reactions). However, these are time-dependent reactions, and, because of the rapid heating rates of parts being processed and the subsequent short immersion times needed to obtain the correct structure and through hardness, little surface effect other than discoloration and slight scaling is exhibited in section sizes up to 25 mm (1 in.). For larger sizes, the user must be aware of surface reactions that can occur, particularly as the processing temperature increases. Figure 8 shows the relative decarburization bands for steels held in a fluidized bed.

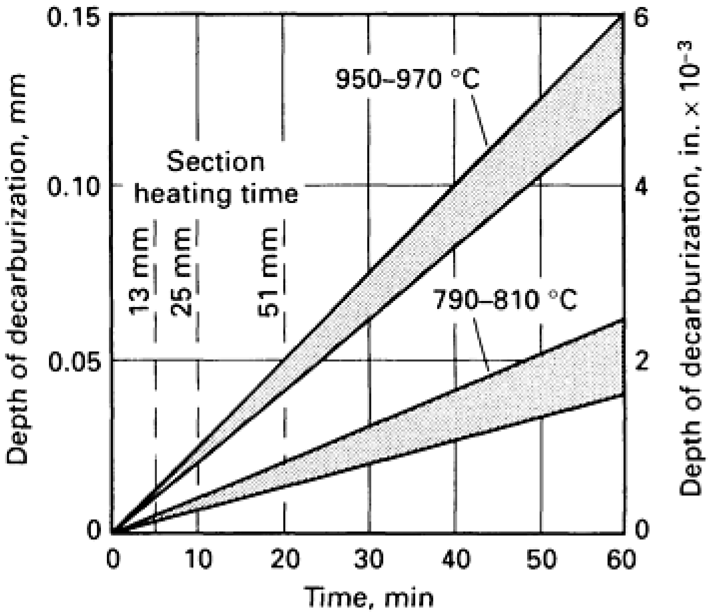

Fig. 8 Representative decarburization bands for steel held in a fluidized bed. Steels used: type O1 and type D3 tool steels and 0.75% C plain carbon steel. Source: Ref 1

Neutral Hardening and Carburizing. Atmospheres for the neutral hardening of tool steels or the carburizing of low-carbon steels can be used for bed flotation. This practice allows oxygen-free heating of tool steels. However, care must be taken during the transport of workpieces to the quench tank to prevent decarburization or oxidation.

Reference cited in this section

1. R.W. Reynoldson, Controlled Atmosphere Fluidized Beds for the Heat Treatment of Metals, *Heat Treatment of Metals,* University of Aston in Birmingham, 1976

Fluidized beds, using atmospheres composed of ammonia, natural gas, nitrogen, and air, or similar combinations, are capable of performing low-temperature nitrocarburizing treatments equivalent to conventional salt bath processes or other atmosphere processes. High-speed steel tools oxynitrided in a fluidized bed are comparable to similar tools treated by the more conventional gaseous process. Carburizing and carbonitriding in a fluidized bed can yield results similar to those achieved in conventional atmosphere furnaces.

Mixtures of propane and air produced the results shown in Fig. 9, which compares the case depths obtained on SAE 8620 steel bearing rings carburized in a fluidized bed and by the conventional atmosphere process. An effective case depth of 1 mm (0.04 in.) was achieved in 1.5 h using the fluidized-bed technique. Developmental work on this process is still being performed, but sufficient knowledge exists to compare the mechanisms of conventional gas carburizing and the fluidized-bed process.

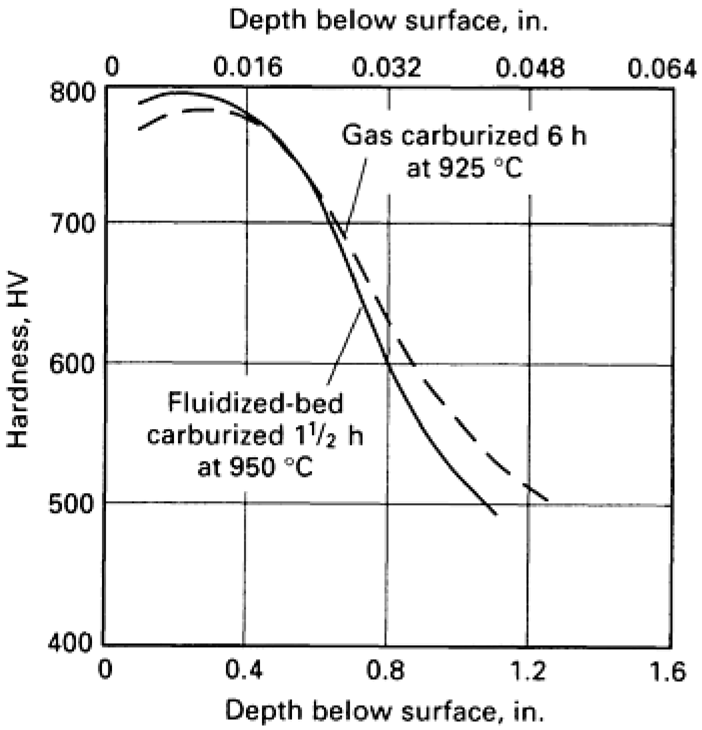

Fig. 9 Comparison of hardness profiles obtained by fluidized-bed and conventional gas carburizing. SAE 8620 steel, rehardened from 820 °C (1510 °F). Source: Ref 1

Conventional Gas Carburizing. Carburizing occurs through the catalytic decomposition of CO according to:

$$CO + H_2 \rightarrow C_{Fe} + H_2O \quad \textbf{(Eq 2)}$$

Propane enrichment aids this reaction according to:

$$C_3H_8 + 3CO_2 \rightarrow 6CO + 4H_2$$
and
$$C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2 \quad \textbf{(Eq 3)}$$

Fluidized-Bed Carburizing. The relatively large volumes of propane consumed during fluidized-bed carburizing, together with high gas velocities, favor carburization by the thermal decomposition of propane to precipitate carbon in accordance with:

$$C_3H_8 \rightarrow C \downarrow + 2CH_4 \qquad \textbf{(Eq 4)}$$

The amount of carbon precipitated is proportional to the number of carbon atoms in the hydrocarbon fuel gas; that is, propane forms more carbon than does methane. In addition, the purity of propane is important, especially with respect to unsaturated hydrocarbon content, which increases its carbon-forming capability.

The precipitated carbon reacts instantaneously with the oxidizing products of combustion:

$$C_3H_8 + 5O_2 \; f \; 3CO_2 + 4H_2O \qquad \textbf{(Eq 5)}$$

to form carbon monoxide and hydrogen:

$$\begin{array}{l} C + H_2O \rightarrow CO + H_2 \\ \text{and} \\ C + CO_2 \rightarrow 2CO \end{array} \qquad \textbf{(Eq 6)}$$

Carburization then proceeds by the catalytic decomposition of CO by H_2 as in conventional carburizing. It is possible that carburization is further complemented by thermal dissociation of the methane formed during carbon precipitation:

$$CH_4 \rightarrow C_{Fe} + 2H_2 \qquad \textbf{(Eq 7)}$$

The carbon potential of the atmosphere varies with the air-to-gas ratio. For each type of hydrocarbon gas (typically propane, methane, or vaporized methanol), a relationship can be established among air-to-gas ratio, temperature, and carbon potential. Control of the reaction and carbon potential of the atmosphere by conventional gas analysis is possible, and fluidized-bed furnaces are equipped with sample ports and probes so that suitable measurements can be taken.

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1. R.W. Reynoldson, Controlled Atmosphere Fluidized Beds for the Heat Treatment of Metals, *Heat Treatment of Metals,* University of Aston in Birmingham, 1976

Types of Furnaces for Heat Treating with Fluidized Beds

The type of fluidized bed most widely used for heat treatment is the dense-phase type, although units based on the dispersed-phase bed have been constructed, with particle circulation for the heat treatment of long, thin metal parts such as shafts and plates. In a typical dense-phase fluidized bed, the parts to be treated are submerged in a bed of fine, solid particles held in suspension, without any particle entrainment, by a flow of gas.

Liberation of adequate quantities of heat within fluidized beds is a prime consideration in adapting them for metal processing. Because transfer of heat from the bed to the workpiece is usually much more efficient than transfer of heat from the heat source to the fluidizing medium, the greatest difficulty is encountered in transferring suitable quantities of heat to the fluidizing medium. In addition, the major part of the heat loss from any practical fluidized system is the heat content of the spent fluidizing gas. In instances in which thermal efficiency is unduly influenced by this factor, recirculation of the fluidizing gas or installation of a recuperative system may be justified. Each has been used in practical applications. Heat input to a fluidized bed can be achieved by several different methods; the most accepted, however, are described in the paragraphs below.

External-Resistance-Heated Fluidized Beds. A fluidized bed contained in a heat-resisting pot can be heated by external resistance elements (Fig. 10). Waste heat recovery can be used to increase thermal efficiency, and the fluidizing gas can be maintained at any desired composition. Heat-up time from ambient to operating temperatures of 815 to 870 °C (1500 to 1600 °F) typically takes 3 to 4 h.

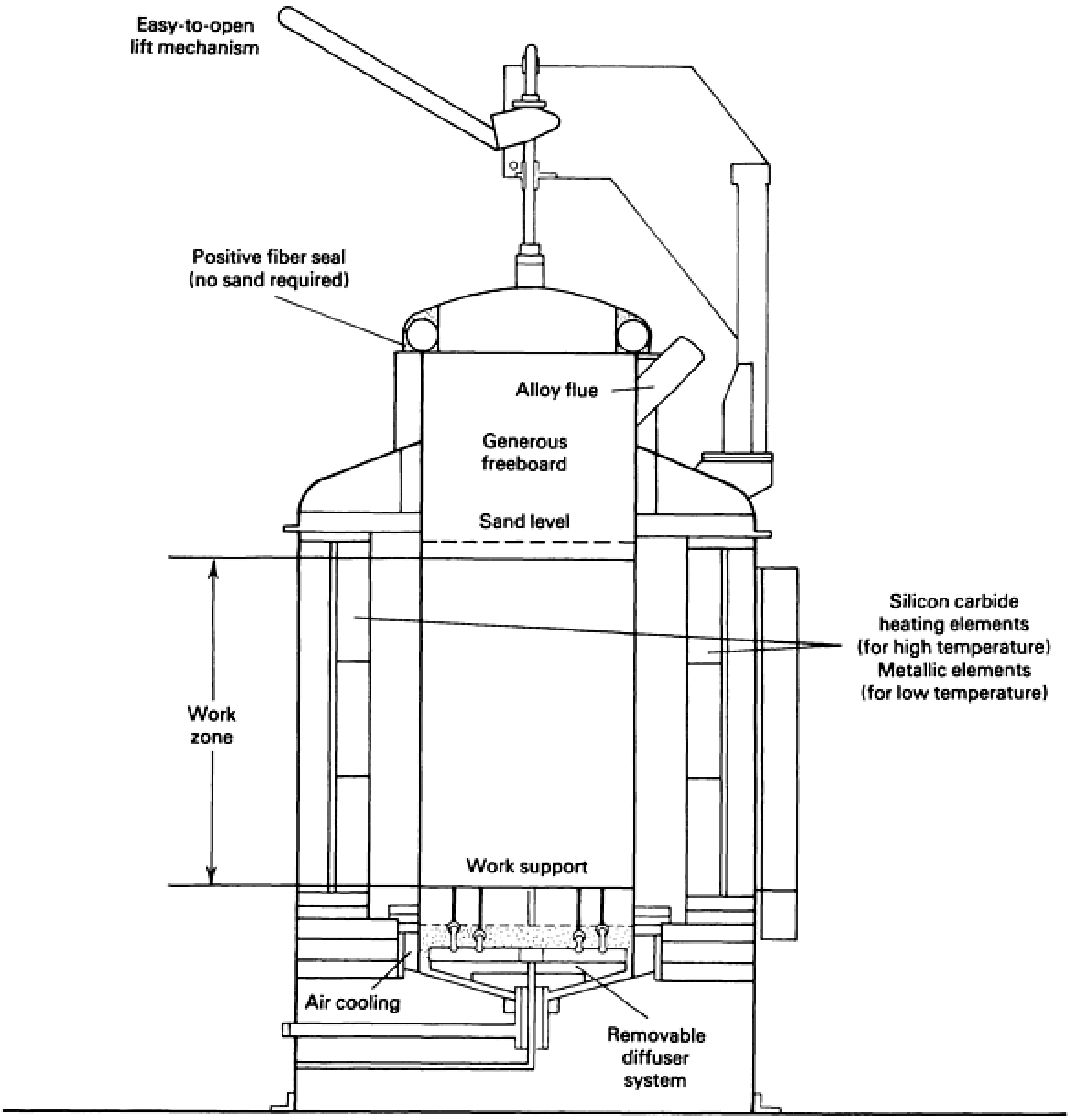

Fig. 10 Fluidized-bed furnace with external heating by electrical resistance elements

External-Combustion-Heated Fluidized Beds. A fluidized bed contained in a heat-resisting pot can be heated by external gas firing (Fig. 11). In this arrangement, a fuel-air mixture is introduced through a standard commercial burner. The burner can be controlled very accurately down to low temperatures for low-temperature tempering. The products of combustion are then removed by flue in the normal fashion.

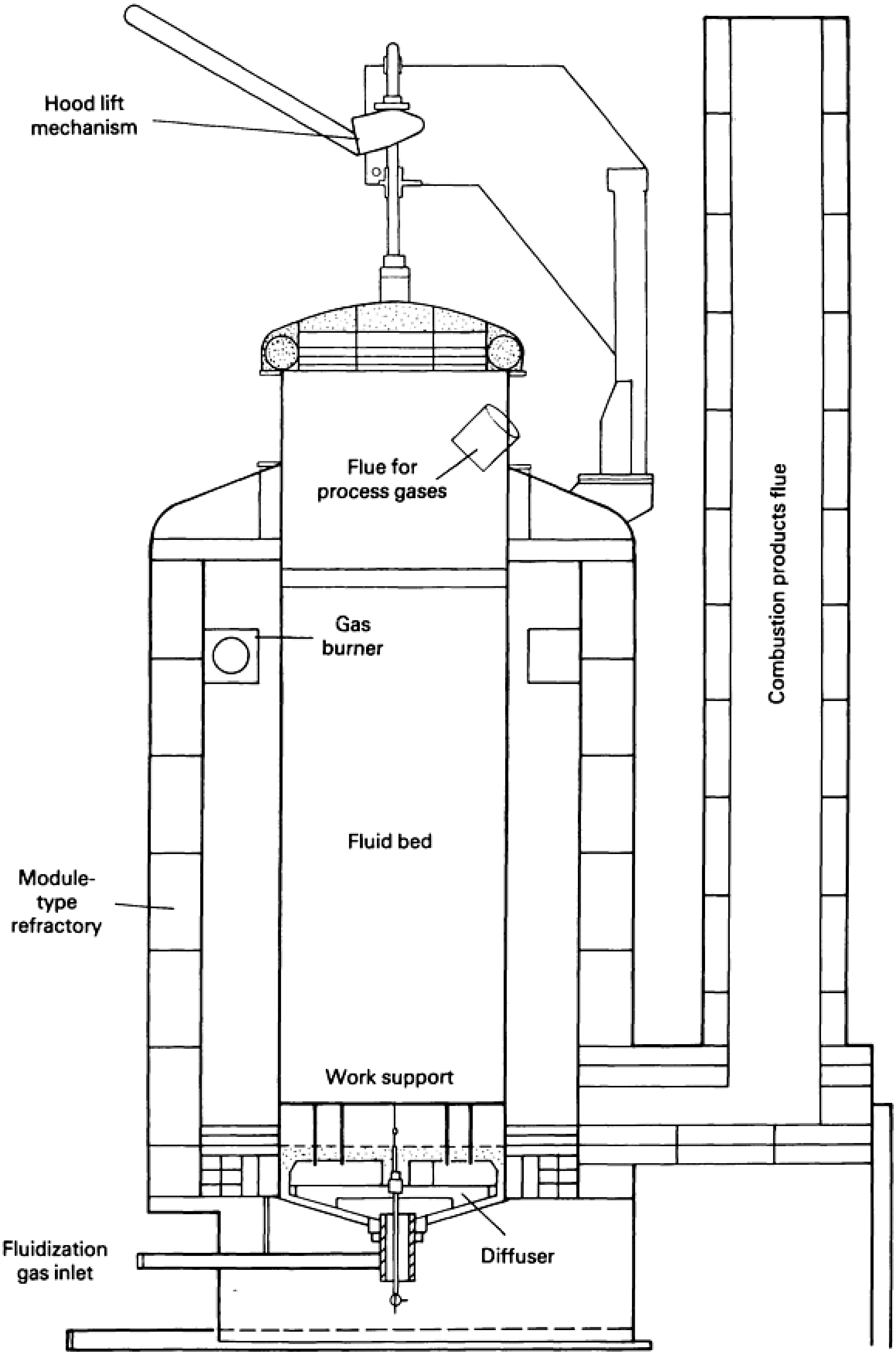

Fig. 11 Externally gas-fired fluidized-bed furnace

Submerged-Combustion Fluidized Beds. The technique of submerged combustion consists of passing the combustion products directly through the mass to be heated. This method provides an excellent rate of heat transfer and is now well established for a wide range of liquid-heating applications, from the heating of swimming pools to the concentration of acid solutions. The application of this method to the heating of a fluidized bed requires that the burner be used such that it provides strong agitation of the suspended particles, thereby achieving the desired properties of excellent heat transfer and uniformity of bed temperature.

Equipment developed for this purpose consists essentially of a burner, two concentric tubes, and a particle separator. A suitable gas mixture is fed through the burner into the central tube, where it is ignited. The flame develops in the tube, and the combustion products escape at its lower end, where they impart heat to the suspended particles before moving up through the annular space between the two tubes. As they rise, a quantity of particles is entrained. These are separated from the gas stream by the deflector plate and fall back into the bed by virtue of gravity. Figure 12 shows a system that incorporates submerged combustion with a controlled atmosphere for the low-temperature treatment of metals.

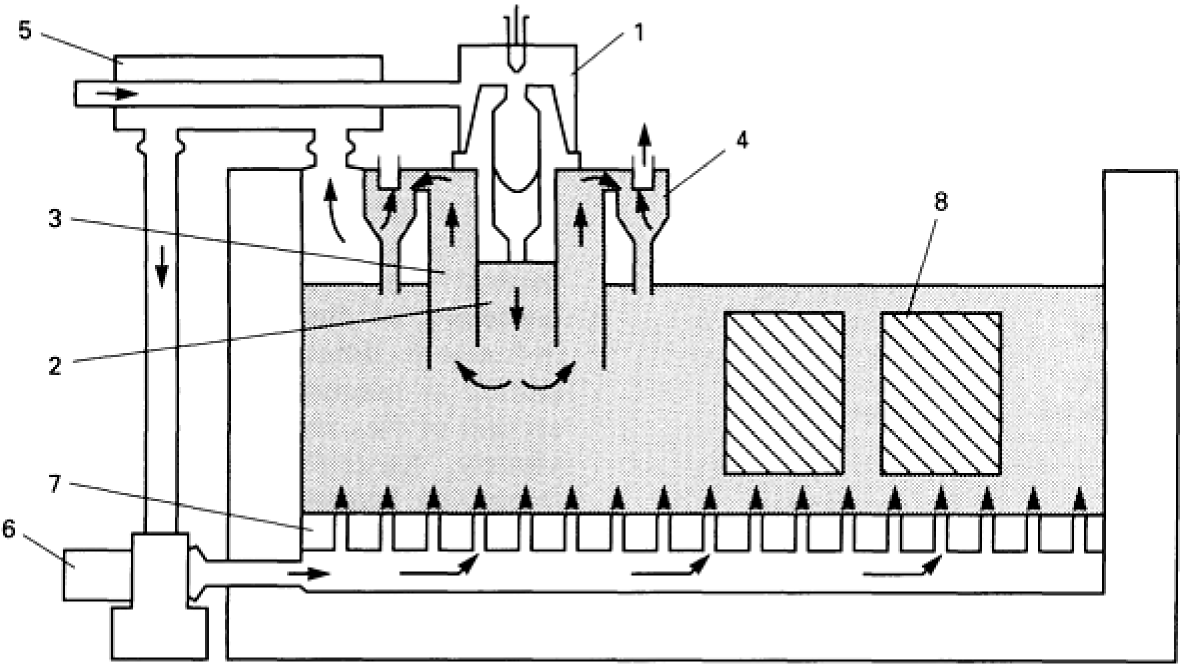

Fig. 12 Controlled-atmosphere fluidized-bed furnace heated by submerged combustion. 1, burner; 2, combustion tube; 3, tube through which combustion gases and particles rise; 4, particle separators; 5, heat exchanger; 6, gas recycle compressor for fluidization; 7, distributor plate; 8, parts to be treated

Internal-Combustion Gas-Fired Fluidized Beds. A major development in the heating of fluidized beds occurred when an air-gas mixture was used for fluidization and was ignited in the bed, generating heat by internal combustion. Prior to this breakthrough, many technical difficulties prevented the use of this mode of fluidized-bed heating. A typical furnace design incorporating this technique is shown in Fig. 13.

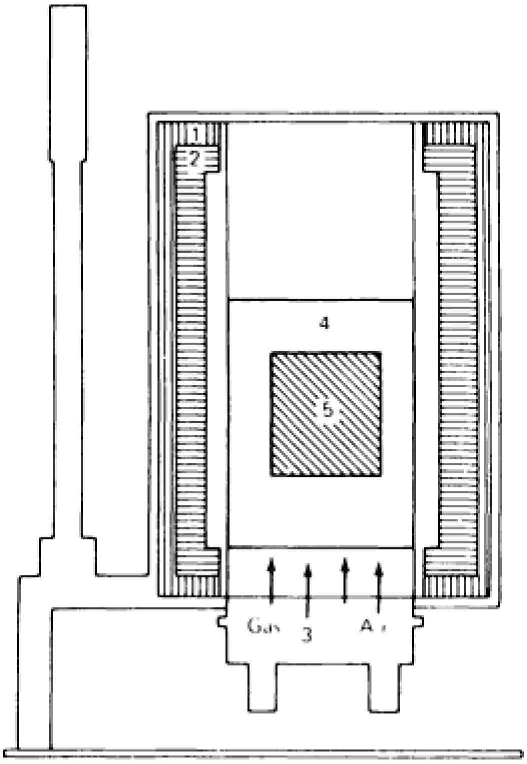

Fig. 13 Gas-fired fluidized-bed furnace with internal combustion. 1, insulating lagging; 2, refractory material; 3, air and gas distribution box; 4, fluidized bed; 5, parts to be treated

The advantage of this system is that the bed is fluidized by burning gases, and thus the heat is generated within the bed. In gas-fired fluidized beds, the supporting gas or fluidizing medium is a near-stoichiometric mixture of gas and air. This combustible mixture is ignited above the bed and quickly imparts its heat to the particles, which in turn heat the incoming gas further down the bed. After a period, combustion takes place spontaneously within the bed and is complete within the first 25 mm (1 in.) of the diffuser once the spontaneous combustion temperature for the gas being used is reached. This temperature commonly varies between 600 and 800 °C (1110 and 1470 °F). If the vessel is well insulated, the bed temperature can rise to a theoretical combustion temperature, and heat-up times from cold to 800 °C (1470 °F) are typically between 1 and $1\frac{1}{2}$ h. However, problems inherent to the basic technique are:

- The bed is fluidized by burning gases. To obtain good temperature control and optimum fluidizing conditions, however, it is desirable that the fuel input rate and fluidizing velocity be independently variable
- Combustion is somewhat unstable below the spontaneous combustion temperature
- Very high temperatures can occur in the immediate vicinity of the distributor/diffuser tile. When the bed is incorrectly fluidized so that this heat cannot be removed from the top of the distributor, theoretical flame temperatures are achieved with consequent deterioration of the distributor. The thermal stresses of expansion and contraction on the distributor tile at these high temperatures tend, even with the best fixing techniques available, to cause failure of joints, which enhances the problem

Two-Stage, Internal-Combustion, Gas-Fired Fluidized Beds. The basic problem of separating the control of heat input from the control of fluidizing velocity has been overcome in two alternative designs (Fig. 14). In both designs, the initial heat-up from cold to operating temperatures is carried out by two-stage internal combustion. A noncombustible mixture of gas and air is introduced beneath the distributor tile. Secondary air is added to make up a stoichiometric or slightly gas-rich mixture immediately above the tile by means of jet holes drilled into heat-resisting tubes. This is done to reduce the possibility of explosion and to avoid high flame temperatures at the surface of the tile. The technique has an

adverse effect on good fluidization, but this is unimportant during initial heat-up, in which the prime objective is to raise the temperature of the bed to operating temperature as quickly as possible. Once this has been accomplished, the remaining objective is to isolate the heat-up control from the control of the fluidizing velocity. This is achieved in two ways:

- *Three-chamber design:* In this design (Fig. 14a), the heat control outer chambers are separated from the treatment zone by a muffle. The fluidizing velocity and atmosphere are independently controlled in the inner chamber, while the outer two zones are still supplying heat by internal combustion. To achieve adequate heat input, fluidization levels in these outer chambers are above the optimum for heat transfer and surface reactions, but this is relatively unimportant
- *Back-radiation design:* When fuel-rich gases are permitted to burn by the injection of secondary air immediately above the control chamber of the fluidized bed, a back-radiation effect causes a rise in bed temperature. This design (shown operating in the heating/controlling and cooling modes in Fig. 14b and c) makes use of this effect and at the same time utilizes heat that is normally dissipated when gases are burned outside the furnace. It therefore uses fuel more economically. In principle, the gas-rich mixture is supplied to the central chamber, and extra air is added to produce stoichiometric conditions during initial heating of the bed. When cold work is loaded for treatment, the extra air is injected above the bed to produce a radiating flame and recover bed temperature. If bed temperature exceeds set temperature, the extra air is switched to the outside of the furnace wall to provide cooling and finally is mixed with the rich gas/air to produce combustion at the top of the specially constructed hood

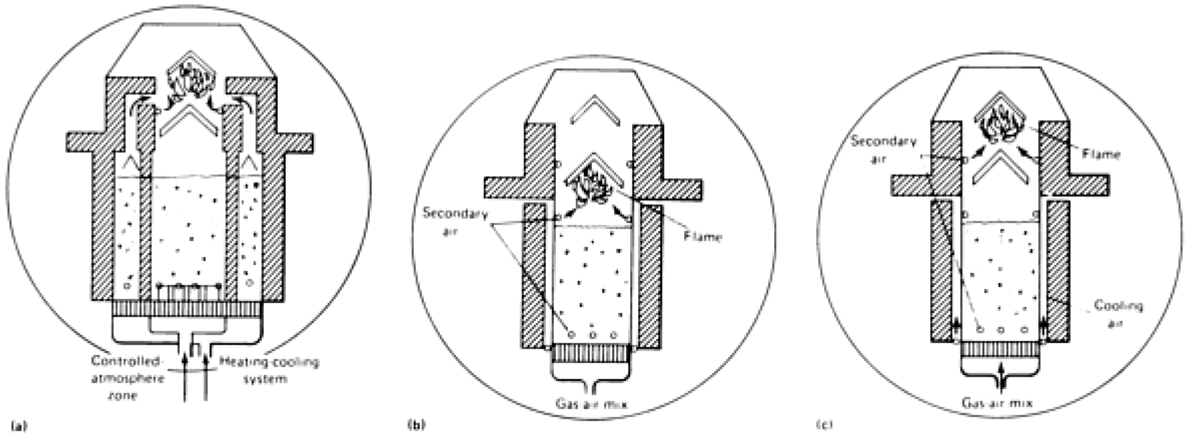

Fig. 14 Two-stage, gas-fired, internal-combustion fluidized beds. (a) Three-chamber design. (b) Back-radiation design in heating mode. (c) Back-radiation design in cooling mode

Internal-resistance-heated fluidized beds are not accepted by users. The elements and work load will make contact if insufficient care is taken.

Applications of Fluidized-Bed Furnaces

The potential applications of fluidized-bed technology to heat treating are many. Figure 15 specifies those applications in which fluidized beds can compete with conventional furnaces.

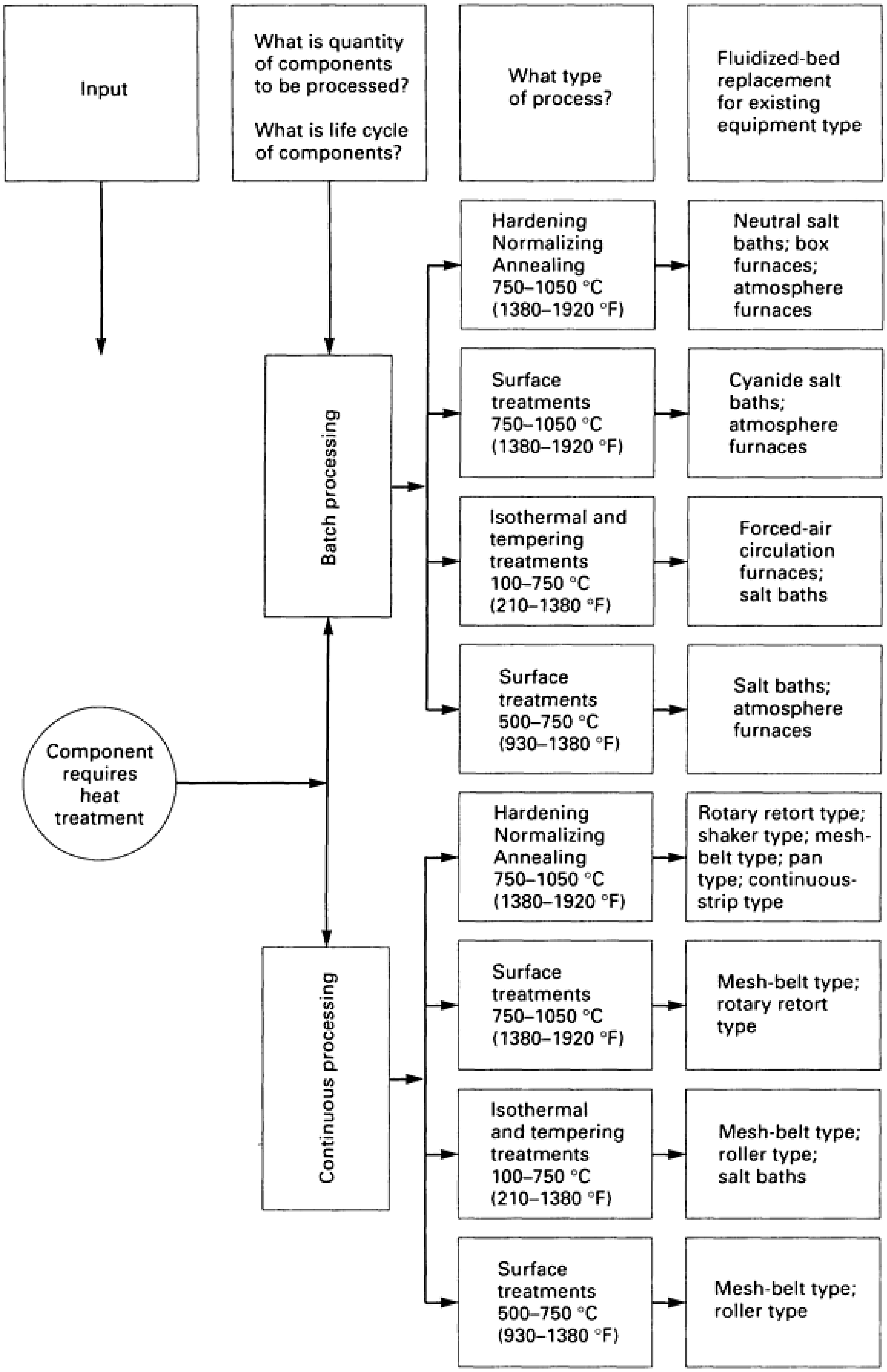

Fig. 15 Fluidized-bed applications; decision model. Source: Ref 1

Applications of fluidized-bed furnaces to the heat treatment of metals include continuous units for all types of wire and strip processing (patenting, austenitizing, annealing, tempering, quenching, and so on) and all configurations of batch-type units for general heat-treating applications. A typical batch-type unit with an output of approximately 150 kg/h (330 lb/h) is available as a standard furnace. Using mechanical handling equipment, it can be automated into a continuous heat-treatment line. The following example describes one firm's decision to install fluidized-bed furnaces for heat treatment.

Example 1: Improved Turnaround Time with Fluidized-Bed Treatment.

A company specializing in the design and production of aluminum extrusion dies had relied on sub-contract heat-treatment facilities for the hardening of dies. The decision to install in-house facilities came as a result of difficulties in meeting the 7- to 14-day turnaround of dies required by customers. Previously, hardening, case hardening, and tempering had been done by salt bath immersion. After studying alternatives, the firm decided to employ the latest fluidized-bed technology. Approximately one year later, the firm installed a second fluidized-bed furnace and made available its surplus capacity to other firms on a subcontract basis.

Carburizing, Nitriding, and Carbonitriding. In recent years, design innovation has led to the use of fluidized-bed furnaces as a practical tool for carburizing, carbonitriding, nitriding, and nitrocarburizing processes. In this technique, 80 mesh or 180 μm aluminum oxide particles produce a fluidizing effect so that the bed behaves like a liquid. When gas or electricity is used as the heat source, the bed provides a faster heat transfer medium. This is provided with quench and tempering furnaces.

Previously, gas-fired internal-combustion units or submerged combustion units were used successfully to provide both heat source and fluidizing/carburizing medium. Recently, more attention has been directed toward the use of externally heated fluidized beds, which is claimed to allow greater control over the carburizing process as a result of separate heating and fluidizing functions (Ref 2, 3). *The advantages* of the fluidized-bed process include:

- High rates of heating and flow cause the utilization of higher treatment temperatures, which, in turn, provide rapid carburizing
- Temperature uniformity with low capital cost and flexibility is ensured
- A fluid bed furnace is very tight; the upward pressure of the gases minimizes air leakage
- The process produces parts with very uniform finish

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3. K. Boiko, *Heat Treat.,* Vol 18 (No. 4), 1986, p 65, 66

Operational Safety

As with all forms of gas heating, normally accepted safety devices are incorporated on the majority of beds presently manufactured. The "flexible-tile" concept ensures that any failure of joints does not influence the performance of the bed.

Parts carrying surface oil or moisture do not create an explosion risk because the contaminants simply vaporize and are removed with the waste gas, as in conventional furnaces. The heat transfer medium (aluminum oxide) is nonhazardous and as such is not subject to disposal restrictions.

Cleaning Operations

Fluidized solids are nonabrasive and non-corrosive and do not wet immersed objects. There is some drag-out loss of the aluminum oxide, however, because some particles accumulate on flat surfaces as work loads are removed from the fluidized bed. These particles can be removed in part by agitation, bouncing, or blowing with an air pipe. Particles can be reused by being dried, sieved, and returned to the bed. When parts already scaled or preoxidized are placed in a fluidized

bed, particles tend to adhere to the scale to a greater degree than if the workpieces were clean. These particles can be removed by water spraying.

Heat Treating in Vacuum Furnaces and Auxiliary Equipment

Revised by the ASM Committee on Vacuum Heat Treating*

Introduction

VACUUM HEAT TREATING consists of thermally treating metals in heated enclosures that are evacuated to partial pressures compatible with the specific metals and processes. Vacuum is substituted for the more commonly used protective gas atmospheres during part or all of the heat treatment. Furnace equipment used in vacuum heat treatment differs widely in size, shape, construction, and method of loading.

Although originally developed for the processing of electron tube materials and refractory metals for aerospace applications, vacuum furnaces are now employed in brazing, sintering, heat treating, and the diffusion bonding of metals. Vacuum furnaces also are used for annealing, nitriding, carburizing, ion carburizing, heating and quenching, tempering, and stress relieving. Furnaces for vacuum heat treating are equipped for workloads ranging from several pounds to 90 Mg (100 tons), and heated working chambers range in size from 0.03 m^3 (1 ft^3) to hundreds of cubic feet. Although most vacuum furnaces are batch-type installations, continuous vacuum furnaces with multiple zones for purging, preheating, high-temperature processing, and cooling by gas or liquid quenching also are used. Vacuum heat-treating furnaces also:

- Prevent surface reactions, such as oxidation or decarburization, on workpieces, thus retaining a clean surface intact
- Remove surface contaminants such as oxide films and residual traces of lubricants resulting from fabricating operations
- Add a substance to the surface layers of the work (through carburization, for example)
- Remove dissolved contaminating substances from metals by means of the degassing effect of a vacuum (removal of H_2 from titanium, for example)
- Remove O_2 diffused on metal surfaces by means of vacuum erosion techniques
- Join metals by brazing or diffusion bonding

Note

* Roger C. Anderson, Abar Ipsen Industries; David Scarrott, Scarrott Metallurgical; Roger Keeran, Metal-Lab Inc.; Walter Prest, Seco-Warwick Corporation; and Roger F. Carlson, Lindberg, A Unit of General Signal

Vacuum Measurements

A theoretical or ideal vacuum is an empty space that does not contain either vapors, particles, gases, or other matter and consequently has no absolute pressure. Because this condition does not exist, even in outerspace, an ideal vacuum cannot be achieved. Normally, when the term vacuum is used, it refers to an absolute pressure below that of the normal atmosphere.

The standard absolute pressure of the atmosphere at sea level, 45° latitude, and 0 °C (32 °F) can be expressed in various values and units:

$$
\begin{aligned}
1 \text{ atm} &= 760 \text{ torr} \\
&= 760 \text{ mm Hg} \\
&= 760{,}000\ \mu\text{m Hg} \\
&= 29.921 \text{ in. Hg} \\
&= 14.696 \text{ psia}
\end{aligned}
$$

The standard absolute pressure of the atmosphere is the reference or 0 gage pressure for a normal pressure gage. Hence, gage pressure is negative for a vacuum condition. For some technologies other than vacuum furnaces, a degree of vacuum is measured by pressure below gage pressure. It is important to know how degrees of vacuum are expressed in the various technologies.

Most vacuum furnace pressure levels are expressed in terms of absolute pressure rather than gage pressure. Normally the units of measure used are torr, mm Hg, or μm Hg. When vacuum furnaces are pressurized above atmospheric pressure, such as for gas quenching, the pressure is expressed in terms of bars. One bar is slightly less than one standard atmosphere of absolute pressure. A bar is equal to 14.50 psia, 29.53 in. Hg, 750 torr or mm Hg, or 750,000 μm Hg.

The vacuum or pressure value of Hg refers to the height of a mercury column sustained by the differential between standard atmospheric pressure and an attained level of vacuum (or, more accurately, partial pressure) or pressure level (above standard atmospheric pressure) being measured.

Table 1 compares vacuum and pressure to standard atmospheric pressure. The normal pressure range of vacuum heat treating should be noted.

Table 1 Pressure ranges required for selected vacuum furnace operations relative to standard atmospheric (0 gage) pressure

Gage pressure classification	**Furnace application**	**Vacuum classification**	**Equivalent pressures**								
			Pa	**torr**	**mm Hg[(a)]**	**μm Hg**	**in. Hg**	**psia[(b)]**	**psig**	**atm**	**bar**
Pressure	Pressure quenching										
	High gas	. . .	. . .	. . .	. . .	. . .	177.17	87.02	72.32	5.92	6
			. . .	. . .	. . .	. . .	147.65	72.52	57.82	4.93	5
			. . .	. . .	. . .	. . .	118.12	58.02	43.32	3.95	4
			. . .	. . .	. . .	. . .	88.59	43.51	28.81	2.96	3
	Gas		. . .	. . .	. . .	. . .	59.06	29.01	14.31	1.97	2
Zero	. . .	. . .	1.01×10^5	760	760	7.6×10^5	29.92	14.696	0	1	1.01
Negative	Vacuum treatment	. . .									
	Normal backfill	Rough	1.00×10^5	750	750	7.5×10^5	29.53	14.50	. . .	0.99	1
			1.3×10^4	100	100	10^5	. . .	. . .	. . .	. . .	. . .
			1.3×10^3	10	10	10^4	. . .	. . .	. . .	. . .	. . .

			130	1	1	10^3	. . .	. . .	. . .	. . .	. . .
	Normal range	Soft	13	0.1	0.1	100	. . .	. . .	. . .	. . .	. . .
			1.3	0.01	0.01	10	. . .	. . .	. . .	. . .	. . .
			0.13	10^{-3}	10^{-3}	1	. . .	. . .	. . .	. . .	. . .
	Maximum	Hard	0.013	10^{-4}	10^{-4}	0.1	. . .	. . .	. . .	. . .	. . .
			1.3×10^{-3}	10^{-5}	10^{-5}	0.01	. . .	. . .	. . .	. . .	. . .
			1.3×10^{-4}	10^{-6}	10^{-6}	10^{-3}	. . .	. . .	. . .	. . .	. . .
			1.3×10^{-5}	10^{-7}	10^{-7}	10^{-4}	. . .	. . .	. . .	. . .	. . .
			1.3×10^{-6}	10^{-8}	10^{-8}	10^{-5}	. . .	. . .	. . .	. . .	. . .

(a) Equal to 133.322387415 Pa, it differs from torr by one part in 7×10^6.

(b) psia = psig + 14.7 psi.

Comparison of Vacuum and Atmosphere Furnace Processing

In most heat-treating processes, when materials are heated, they react with normal atmospheric gases, which consist of approximately (by volume) 21% O_2, 77% N_2, 1% H_2O vapor, and 1% other gases. If this reaction is undesirable, the work must be heated in the presence of some gas or gas mixture other than normal air. This is done in normal atmosphere furnace processing.

The gas or gas mixture may be varied to cause desirable reactions with the material being processed or it may be adjusted so that no reactions occur. At different temperatures, different reactions may occur with the work and furnace atmosphere. In most atmosphere furnaces it is not possible to change the atmosphere composition rapidly enough for optimum reactions or to control the atmosphere composition with the degree of precision required for some heat-treating processes. Vacuum furnaces allow gas changes to be made quite rapidly because they contain gases of low weight.

Vacuum furnace technology removes most of the components associated with normal atmospheric air before and during the heating of the work. An analysis of the residual atmosphere in a leakproof vacuum furnace at a vacuum of about 0.1 Pa (10^{-3} torr) indicates that less than 0.1% of the original air remains. The residual gases primarily consist of water vapor, with the remainder largely comprised of organic vapors from the seals, vacuum greases, and vacuum oils. The oxygen content at 0.1 Pa (10^{-3} torr) is less than 1 ppm. If all of the residual gas in the vacuum furnace were converted to water vapor, the water vapor content would be approximately 1.5 ppm, or equal to that of a gas with a dew point of about -80 °C (-110 °F). At a vacuum level of 10 Pa (10^{-4} torr), the equivalent dew point of gas is estimated to be approximately -90 °C (-130 °F) or less.

These low dew point equivalents compare favorably with the driest inert gases available from highly efficient gas dehydration equipment. With suitable vacuum pumping systems, the concentration of oxygen and water vapor can be reduced to lower levels than those achieved in inert or reducing-gas atmospheres.

After a vacuum heat-treating furnace has been evacuated, gaseous reactions such as those encountered with atmosphere heat treatment are virtually eliminated. Moreover, the vacuum extracts many gases, surface contaminants, and processing lubricants that would be difficult and costly to remove by any other method. Gases drawn from the metal surface into the vacuum surrounding the charge are trapped by the vacuum pumps and exhausted from the system as the work is being processed. This advantage of a vacuum system is of greater significance when parts with complex shapes, blind holes, or deep recesses are heat treated. A complete purging of such parts in a protective atmosphere requires an extended purging period. Even long-time purging, however, may not ensure the complete removal of entrapped air, other contaminants, or contaminants generated by reactions with the atmosphere.

When more thorough purging is required, the furnace can be evacuated with a simple vacuum system, and the enclosure or retort can be backfilled with the desired protective or reactive atmosphere (see the article "Furnace Atmospheres" in this Volume). This method markedly reduces the amount of protective atmosphere and time required to produce satisfactory results.

Volatilization and Dissociation

In a vacuum furnace, materials can be pressed at temperatures and pressures at which the vapor pressure of the materials becomes an important consideration. Vapor pressure, which is the gas pressure exerted when a substance is in equilibrium with its own vapor, increases rapidly with temperature because the amplitude of molecular vibration increases with temperature. Some molecules in the outer surface of the solid material have higher energies than others, and they escape as free molecules or vapor. If a solid substance is contained in an enclosure devoid of any other material, molecules will continue to escape from the solid surface until their rate of escape is exactly balanced by the rate of condensation or recapture of the gaseous molecules. The equilibrium pressure developed is the vapor pressure of the substance at that temperature. The vapor pressure of a metal is dependent on temperature and pressure only but the effect is time dependent.

It is normally desirable to use a vacuum-temperature combination that accelerates the desorption of gases without producing the vaporization of more volatile alloy constituents. Alloys with high concentrations of volatile elements, such as brass, are not heat treated in vacuum furnaces.

If brass is heated in a vacuum at a temperature of 540 °C (1000 °F) and a vacuum level on the order of 13 mPa (0.1 μm Hg), the zinc component will vaporize (volatilize) and the brass will eventually be converted to copper sponge. The zinc will deposit in the cold section of the furnace and can revolatilize on subsequent runs at higher temperatures, causing unwanted pitting or other surface reactions on the work load.

Metals such as lead, zinc, and magnesium have relatively high vapor pressures; if heated above a temperature at which the vapor pressure of the element exceeds the pressure in the furnace, they will evaporate or sublime rapidly. Thus, high-vacuum heat treatment is not applicable to some metals and alloys. To handle certain metals and alloys properly, either the pressure must be limited to the soft (fine) vacuum range (Table 1) or a backfill to a higher vacuum pressure level must be employed.

Alloys with lower concentrations of volatile elements can be processed in vacuum by using the backfill pressure of an inert gas such as nitrogen or argon that exceeds the sublimation pressure of the element at the temperature involved. A backfill pressure of a few hundred μm Hg at temperatures of about 980 °C (1800 °F) precludes the vaporization of elements such as chromium, copper, or manganese from steels processed at these temperatures.

For example, if pure manganese were heated to approximately 790 °C (1455 °F) at a pressure of 13 mPa (10^{-4} torr), it would vaporize. If the material were held at a higher temperature or lower pressure for an adequate period of time, the metal would become depleted and would eventually disappear, and the vapors would condense on the colder areas of the furnace and/or pumping system. Backfill or higher pressures greatly slow the rate of evaporation or volatilization. The vapor pressures of carbon and selected pure metals, as related to temperature, are shown in Fig. 1 and Table 2.

Table 2 Vapor pressures of various elements

Element	Vapor pressure at				
	0.013 Pa	0.13 Pa	1.3 Pa	13 Pa	1.0×10^5 Pa

	10^{-4} mm Hg 0.1 µm		10^{-3} mm Hg 1.0 µm		10^{-2} mm Hg 10 µm		10^{-1} mm Hg 100 µm		760 mm Hg 760,000 µm	
	°C	**°F**	**°C**	**°F**	**°C**	**°F**	**°C**	**°F**	**°C**	**°F**
Aluminum	808	1486	889	1632	996	1825	1123	2053	2056	3733
Antimony	525	977	595	1103	677	1251	779	1434	1440	2624
Arsenic	. . .	. . .	220	428	. . .	. . .	310	590	610	1130
Barium	544	1011	625	1157	716	1321	829	1524	1403	2557
Beryllium	1029	1884	1130	2066	1246	2275	1395	2543	. . .	. . .
Bismuth	536	997	609	1128	699	1290	720	1328	1420	2588
Boron	1140	2084	1239	2262	1355	2471	1489	2712	. . .	. . .
Cadmium	180	356	220	428	264	507	321	610	765	1409
Calcium	463	865	528	982	605	1121	700	1292	1487	2709
Carbon	2290	4150	2471	4480	2681	4858	2926	5299	4827	8721
Cerium	1091	1996	1190	2174	1305	2381	1439	2622	. . .	. . .
Caesium	74	165	110	230	153	307	207	405	690	1274
Chromium	992	1818	1090	1994	1205	2201	1342	2448	2482	4500
Cobalt	1362	2484	1494	2721	1650	3000	1833	3331	. . .	. . .
Copper	1035	1895	1141	2086	1273	2323	1432	2610	2762	5003
Gallium	859	1578	965	1769	1093	1999	1248	2278	. . .	. . .
Germanium	996	1825	1112	2034	1251	2284	1420	2590	. . .	. . .
Gold	1190	2174	1316	2401	1465	2669	1646	2995	2996	5425
Indium	746	1375	840	1544	952	1746	1090	1990	. . .	. . .

Iridium	2154	3909	2340	4244	2556	4633	2811	5092	. . .	. . .
Iron	1195	2183	1310	2390	1447	2637	1602	2916	2735	4955
Lanthanum	1125	2057	1242	2268	1381	2518	1549	2820	. . .	. . .
Lead	548	1018	620	1148	718	1324	820	1508	1744	3171
Lithium	377	711	439	822	514	957	607	1125	1372	2502
Magnesium	331	628	380	716	443	829	515	959	1107	2025
Manganese	791	1456	878	1612	980	1796	1020	1868	2151	3904
Molybdenum	2095	3803	2295	4163	2533	4591	3009	5448	5569	10056
Nickel	1257	2295	1371	2500	1510	2750	1679	3054	2732	4950
Niobium	2355	4271	2539	4602	. . .	. . .	. . .	. . .	. . .	. . .
Osmium	2264	4107	2451	4444	2667	4833	2920	5288	. . .	. . .
Palladium	1271	2320	1405	2561	1566	2851	1759	3198	. . .	. . .
Platinum	1744	3171	1904	3459	2090	3794	2293	4159	4407	7965
Potassium	123	253	161	322	207	405	265	509	643	1189
Rhodium	1815	3299	1971	3580	2150	3900	2357	4274	. . .	. . .
Rubidium	88	190	123	253	165	329	217	423	679	1254
Ruthenium	2058	3736	2230	4046	2431	4408	2666	4831	. . .	. . .
Scandium	1161	2122	1282	2340	1422	2593	1595	2903	. . .	. . .
Silicon	1116	2041	1223	2233	1343	2449	1485	2705	2287	4149
Silver	848	1558	920	1688	1047	1917	1160	2120	2212	4014
Sodium	195	383	238	460	291	556	356	673	892	1638

Strontium	413	775	475	887	549	1020	639	1182	1384	2523
Tantalum	2599	4710	2820	5108	. . .	. . .	. . .	. . .	. . .	. . .
Thallium	461	862	500	932	606	1123	660	1220	1457	2655
Thorium	1831	3328	2000	3630	2196	3985	2431	4408	. . .	. . .
Tin	922	1692	1010	1850	1189	2172	1270	2318	2270	4118
Titanium	1250	2280	1384	2523	1546	2815	1742	3168	. . .	. . .
Tungsten	2767	5013	3016	5461	3309	5988	. . .	. . .	5927	10701
Uranium	1585	2885	1730	3146	1898	3448	2098	3808	. . .	. . .
Vanadium	1586	2887	1725	3137	1888	3430	2079	3774	. . .	. . .
Yttrium	1362	2484	1494	2721	1650	3000	1833	3331	. . .	. . .
Zinc	248	478	290	554	343	649	405	761	907	1665
Zirconium	1660	3020	1816	3301	2001	3634	2212	4014	. . .	. . .

Note: The vapor pressure of metals is fixed with probable values at a given temperature, and the temperature at which the solid is in equilibrium with its own vapor descends as the pressure to which it is exposed descends. For example: iron must be heated to 2735 °C (4955 °F) at atmosphere before its vapor pressure is greater than atmosphere (760 mm Hg); this point is reached at 1311 °C (2390 °F) at a pressure of 130 mPa (10^{-3} mm Hg).

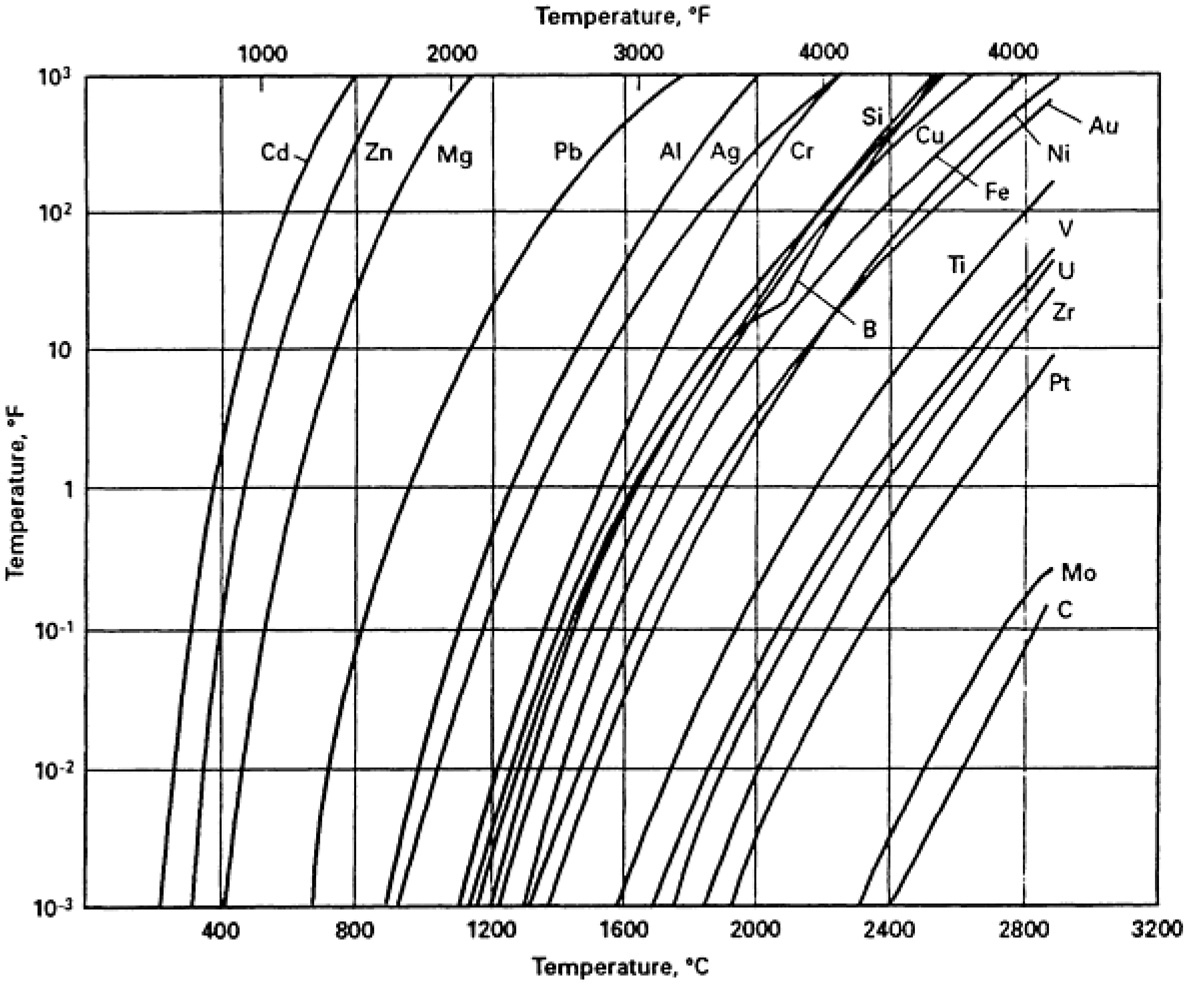

Fig. 1 Vapor pressure versus temperature for carbon and various pure metals

Alloy Vapor Pressures. The vapor pressures of pure metals are constant, well-established values. The vapor pressure of a given alloy varies according to conditions. The vapor pressure of an alloy is governed in part by a law analogous to Dalton's law of partial pressures: The total vapor pressure of an alloy, under ideal conditions, is equal to the sum of the partial vapor pressures of its constituents. However, the partial pressure of each element in the alloy is lower than its normal vapor pressure and is proportional to its concentration.

In processing at temperatures where the vapor pressures of more volatile minor constituents are still in the micron range, alloys behave in accordance with Dalton's law. For example, if pure manganese is heated to 790 °C (1455 °F), its vapor pressure will reach 13 mPa (0.1 μm Hg), making it impossible to evacuate to lower pressures without evaporating all of the manganese. However, when manganese is alloyed with other elements, as a solid solution in iron, for example, its effective vapor pressure is lowered. The total vapor pressure for the alloy is the sum of vapor pressures of the individual elements multiplied by their concentrations in the alloy. The vapor pressure of manganese in a 1% Mn alloy at 790 °C (1455 °F) is about 0.13 mPa (10^{-6} mm Hg). When alloys such as stainless steel are processed at high vacuum levels (theoretically exceeding the vapor pressures of some of its pure metal components), the volatilization is only a few molecules thick. This volatilization tends to draw the stable elements with it in a complex molecular destabilization that results in a surface chemistry similar to that of the core material. It is this molecular surface activity that can remove thin film oxides even though their theoretical combined vapor pressure has not been exceeded.

Many metals form compounds by reaction with oxygen, hydrogen, and nitrogen. These reactions are usually exothermic, and the possibility for dissociation of the resulting compound increases with higher temperatures. Some oxides, such as water, vaporize at temperatures so low that dissociation occurs only in the vapor phase. For an oxide, nitride, or hydride that remains a solid over a wide range of temperatures, a dissociation pressure exists at any temperature that represents an equilibrium between the compound, gas, and the metal.

All metallic compounds decompose into constituent elements when heated to sufficiently high temperatures. However, many of the metal oxides are quite stable, requiring low pressures at high temperatures to effect dissociation. It is impractical to dissociate many of these compounds because of the combination of vacuum level and temperature required. When a metal oxide dissociates, the metal remains and the oxygen is evacuated.

For example, chromium oxide will dissociate in a 1.3 mPa (10^{-5} torr) vacuum at 1300 °C (2370 °F). The dissociation of a metal oxide usually depends more on temperature than on pressure. Most oxides can be dissociated under normal operating vacuum levels at approximately their reduction temperature in a highly reducing hydrogen atmosphere.

The nitrides and hydrides often have higher dissociation pressures, making many of them unstable when heated in a vacuum. For this reason, vacuum heat treating can be used both to dissociate these compounds and to remove the evolved gas without disturbing the base metal.

It is believed that when oxidized surfaces brighten during vacuum heat treating, the mechanism involved is not simply thermal dissociation of the oxide. Bright surfaces do not discolor, or become brighter, when they are exposed to a vacuum atmosphere that is theoretically oxidizing. A metal surface can be maintained almost free of visible oxidation at a partial pressure several decades higher than that suggested by theoretical calculations. The following theories have been proposed to explain this apparent anomaly:

- The solution and diffusion rate for oxygen exceeds its surface absorption rate
- Oxide nucleation occurs at discrete sites rather than as a continuous film
- The effective concentration of oxygen is reduced by carbon and hydrogen in the solid metal and by the vacuum atmosphere

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Heat Treating in Vacuum Furnaces and Auxiliary Equipment

Revised by the ASM Committee on Vacuum Heat Treating*

Vacuum Furnace Design

Although conventional atmosphere furnaces can be adapted for vacuum heat treating by adding a vacuum-tight retort connected to a suitable pumping system, furnace equipment developed especially for vacuum heat treating is generally used. There are two distinctly different types of vacuum furnaces: hot wall (no water cooling of the exterior walls) and cold wall (water-cooled walls).

Vacuum furnaces can be grouped into one of three basic designs:

- Top-loading, or pit, furnaces
- Bottom-loading, or bell, furnaces
- Horizontal-loading, or box, furnaces

Furnace designs can be varied to fit a wide variety of processing requirements by changing the chamber length or by adding internal doors, circulating fans, recirculating gas systems, and/or internal quenching systems.

Every vacuum furnace, regardless of its end use and basic hot- or cold-wall design, requires:

- Heating elements controlled to generate proper processing temperatures and cooling rates
- Suitable vacuum enclosures with access openings
- Vacuum pumping system
- Instrumentation to monitor and display critical processing data

Production furnaces may be single-chamber units, batch-type units, or multichamber, semicontinuous units.

Hot-Wall Vacuum Furnaces

Vacuum furnaces are classified according to the location of the heating and insulating components. Hot-wall furnaces were the first type to be designed. Because of the demand of the heat-treating industry for higher temperatures, lower pressures, rapid heating and cooling capabilities, and higher production rates, hot-wall vacuum furnaces have become essentially obsolete--with the exception of low-pressure chemical vapor deposition (LPCVD) and ion-nitriding processes--and have largely been replaced by cold-wall vacuum furnaces.

The entire vacuum vessel is heated by external heating elements in the hot-wall construction. The heat is contained by insulation materials similar to the materials used in electrically heated heat-treating furnaces. Hot-wall furnaces have limited use because of slow heating and cooling capabilities. They are also limited in temperature because the strength of materials is reduced at elevated temperature. However, hot-wall equipment is readily adaptable to low-temperature operations not exceeding 980 °C (1800 °F), with moderate-sized chambers.

The double-pump modification of the hot-wall furnace permits the construction of larger vessels and the use of operating temperatures approaching 1150 °C (2100 °F). This system incorporates a second vacuum vessel outside the vacuum retort to maintain a roughing vacuum during the heating cycle. This removes the stress of the atmospheric pressure on the heated retort or vacuum vessel.

Bell-Type Furnace. A bell-type hot-wall furnace is shown in Fig. 2. The workload is placed on an elevated refractory metal hearth that rests on an insulated base clad with an alloy plate material. A water-cooled circumferential flange and vacuum gasket are located on the vacuum-tight base cover adjacent to the heated zone but in an unheated area. A retort made with a heavy-walled heat-resisting alloy covers the work load. A flange at the bottom of the retort fits on top of the base gasket to provide a vacuum-tight enclosure. The bell-shaped furnace equipped with internal electrical heating elements is lowered into position over the retort by a vertical hoist. The vacuum pumping system is connected through the insulated base.

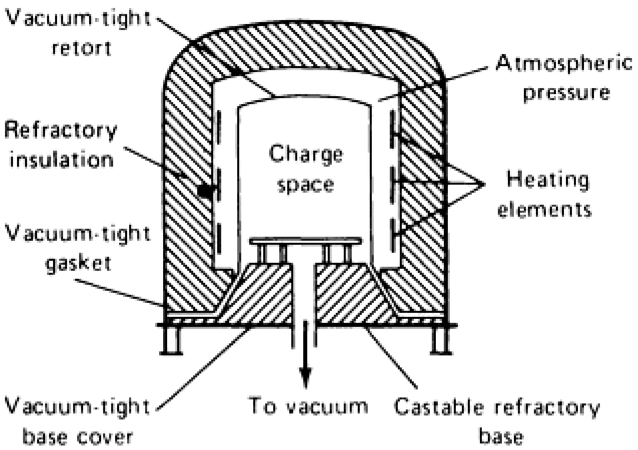

Fig. 2 Bell-type hot-wall vacuum furnace

Because this furnace cannot be heated or cooled rapidly, even when the bell-shaped vessel is removed, production rates and the number of thermal cycles within a given time period are limited. Moreover, because the hot retort must support the entire pressure of the external atmosphere, its wall must be quite heavy. Practical operating temperatures for a furnace of this type are generally limited to approximately 925 °C (1700 °F).

Pit-Type Furnace. Figure 3 shows a pit-type hot-wall furnace. The work load is placed in a top-loading muffle or retort made from a heat-resisting alloy. The upper end of the retort is provided with a water-cooled flange and vacuum gasket that interlock with a flange on the upper part of the furnace above the heated zone. The muffle is lowered into the furnace by an overhead hoist, providing vacuum connections for the furnace and retort.

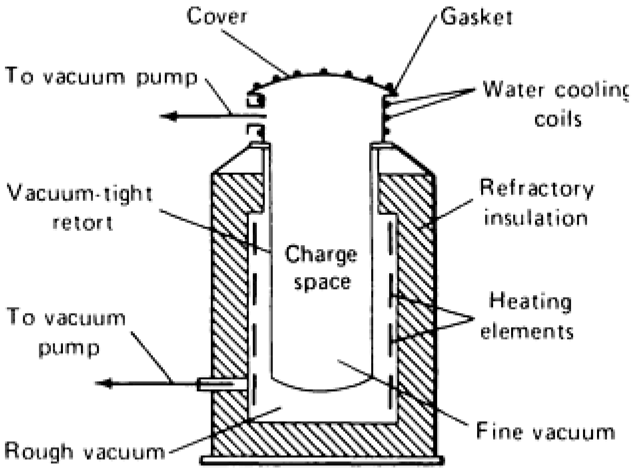

Fig. 3 Pit-type hot-wall vacuum furnace

With this construction, the space between the muffle and heating furnace can be evacuated by a roughing pump so that the pressure at the exterior surface of the muffle is essentially 0. This evacuation permits the use of a muffle with a much thinner wall and raises the maximum operating temperature of the system to approximately 1175 °C (2150 °F). When the heating cycle is completed, inert gas is bled into the retort, and air is bled simultaneously into the heating furnace so that the pressures remain balanced on both sides of the retort. The retort then can be removed from the furnace to a cooling stand, and another retort can be inserted in the hot furnace. This construction increases heating and cooling flexibility, which in turn increases cycle frequency and production.

Horizontal and vertical two-zone hot-wall vacuum furnaces are shown in Fig. 4 and 5. In both types, the heat-resisting alloy muffle is extended much further beyond the heating section of the furnace. This extended section has a water-cooled jacket to provide accelerated cooling. In the horizontal furnace, the charge is carried on an alloy hearth that can be moved in and out of the heated zone by a push rod extending through a seal in the outer fixed end of the muffle. This hearth has vertical heat baffles or multiple radiation shields at each end to confine the heat to the heated portion of the muffle. An equivalent means of transferring the work load is necessary in the vertical furnace as well, although this is not shown in Fig. 5. By using this technique, the charge can be cooled much faster because it is necessary to remove the heat from the hearth and work load only, not from the hot end of the muffle. This increased cooling rate permits the hardening of air-hardening steels and is adaptable to certain solution treatments not possible with other hot-wall furnaces.

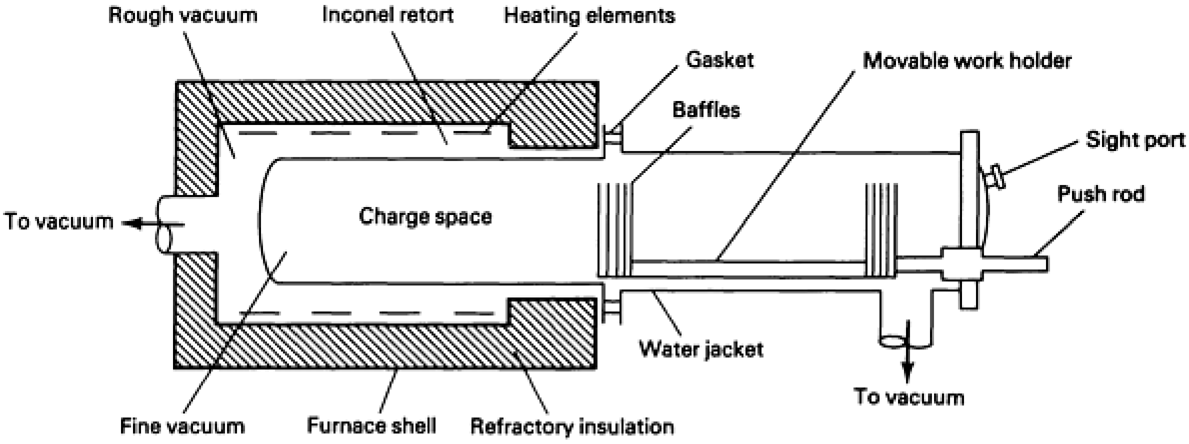

Fig. 4 Horizontal, two-zone, hot-wall vacuum furnace

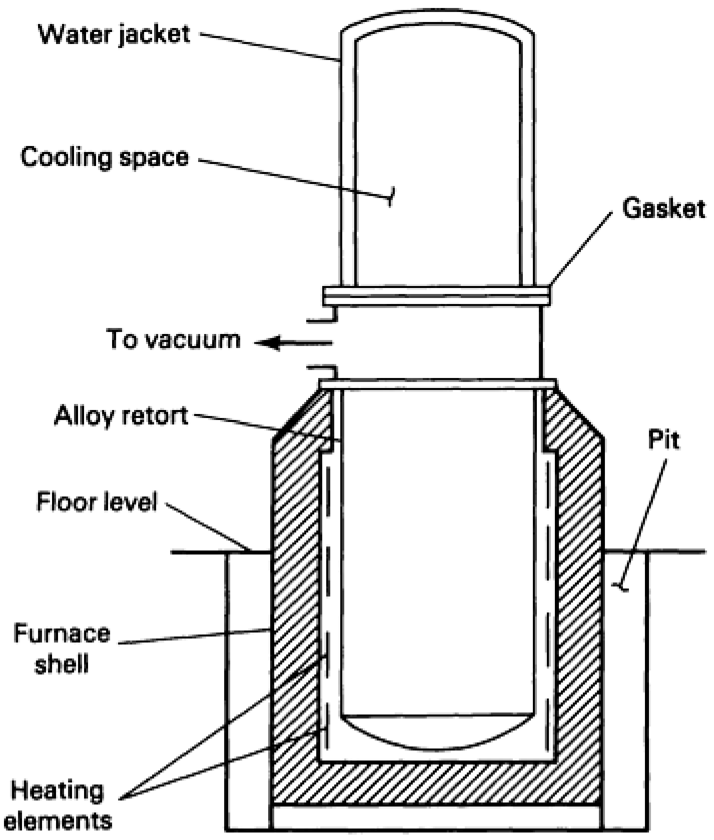

Fig. 5 Vertical, two-zone, hot-wall vacuum furnace

Cold-Wall Vacuum Furnaces

By far the most widely used, practical cold-wall furnace units consist of a water-cooled vacuum vessel maintained near ambient temperature during high-temperature operations. Consequently, because the operating temperature does not affect the strength of the vessel material, large units can be constructed for use at high operating temperatures.

In the cold-wall design, the water-cooled vacuum vessel contains and supports the internal insulation, the electrical heating elements, and the hearth upon which the work load rests. The vacuum acts as:

- A substitute for the normal heat-treating atmosphere to protect the work load
- An insulating medium in the furnace because the thermal conductivity of a vacuum is essentially 0
- An effective protective coating around the heating elements, heat shields, and supporting hearth

There are three forms of heat transfer in a furnace--radiation, conduction, and convection--but the only effective method of heat transfer in a vacuum is radiation. Heat transfer by conduction or convection is negligible because little or no gas is generated.

The use of a vacuum as the insulating medium has permitted the use of multiple radiation shields of very low mass or special lightweight ceramic, graphite laminate, or felt insulations that facilitate rapid heating and cooling. Rapid rates of heating and cooling are important because usually each treatment cycle is started at ambient temperature and must be cooled to near ambient temperature at completion. As the protective medium, vacuum has permitted the use of materials such as graphite, tungsten, molybdenum, and tantalum for heating elements and hot furnace structures. Such materials normally cannot be used in other furnace constructions without more elaborate, expensive, and sometimes hazardous protective-atmosphere environments.

Cold-wall vacuum furnaces can be classified as either batch vacuum furnaces or semicontinuous vacuum furnaces. In a batch operation, the work load remains stationary inside the furnace during heating. On the other hand, in semicontinuous

vacuum furnaces with multiple chambers, the work load is moved within the vacuum usually after completion of a processing step or segment.

Batch Vacuum Furnaces. By using high melting-point materials in furnace structures, extremely rapid rates of heating and high temperatures can be attained in batch furnaces. Heat is transferred to the work load almost entirely by radiation.

Radiation cooling in a hot batch vacuum furnace is extremely slow, however. To reduce furnace time and shorten quenching time, pressure in the vacuum chamber is usually increased to either just below atmospheric pressure or up to six times the atmospheric pressure by introducing a pure inert gas such as nitrogen or argon. This gas is rapidly recirculated within the furnace and then through cooling coils or through an external heat exchanger and back into the furnace, with high-powered large-capacity gas pumps.

The advantages of batch cold-wall vacuum furnaces over atmosphere furnaces include:

- Reliability
- Repeatability
- Cleanliness
- Bright, oxide-free treatment of most metals and alloys
- Outgassing and purging of entrapped volumes of gas
- Retained surface finish
- Removal of surface volatiles
- No heat added to local environment
- No chemical effect on furnace or work during treatment
- Easy control of furnace environment by controlling backfill gases
- Highest-quality workpiece produced
- No furnace conditioning
- Instant pushbutton start from cold
- Low pollution
- Wide operating temperature range in one unit
- Easy maintenance
- Safe operation
- Fully automatic processing
- Wide range of programmable heating and cooling rates
- Minimal distortion of treated work
- High heating rates and temperatures resulting from use of high-melting-point materials
- Complete shutdown when not in use; no need to maintain heat to maintain low dew point
- Blanketing gas usually not required during heating

Disadvantages of batch cold-wall vacuum furnaces over atmosphere furnaces include:

- Large amount of floor space required in relation to load size
- Lower productivity
- Longer cycle times
- Furnace must withstand atmospheric pressure and be free of leakage
- High capital cost
- High maintenance cost

Semicontinuous furnaces are constructed of modular units of three or more vacuum chambers. The heating chambers can be maintained at heat as required during loading and unloading. Each unit has a work carrier transfer system, an internal assembly of heating elements and shield package, pumping system, and temperature-controlled power system. Isolation locks or doors at each end of the vacuum heating or brazing environment separate these modular units from the entry and exit vacuum vestibules. These vestibules, in turn, have doors for access to and from atmospheric

pressure and other assembly operations. Usually included with the furnace are fans for fast cooling at the exit end of the furnace and an overhead conveyor system to transfer work carriers from the exit to the furnace entrance. Work carrier loading and unloading stations are incorporated in the external overhead conveyor system. A high-volume-production semicontinuous vacuum furnace is shown in Fig. 6. These furnaces are used for the fluxless brazing of aluminum heat exchangers at production rates of 100 to 250 parts per hour.

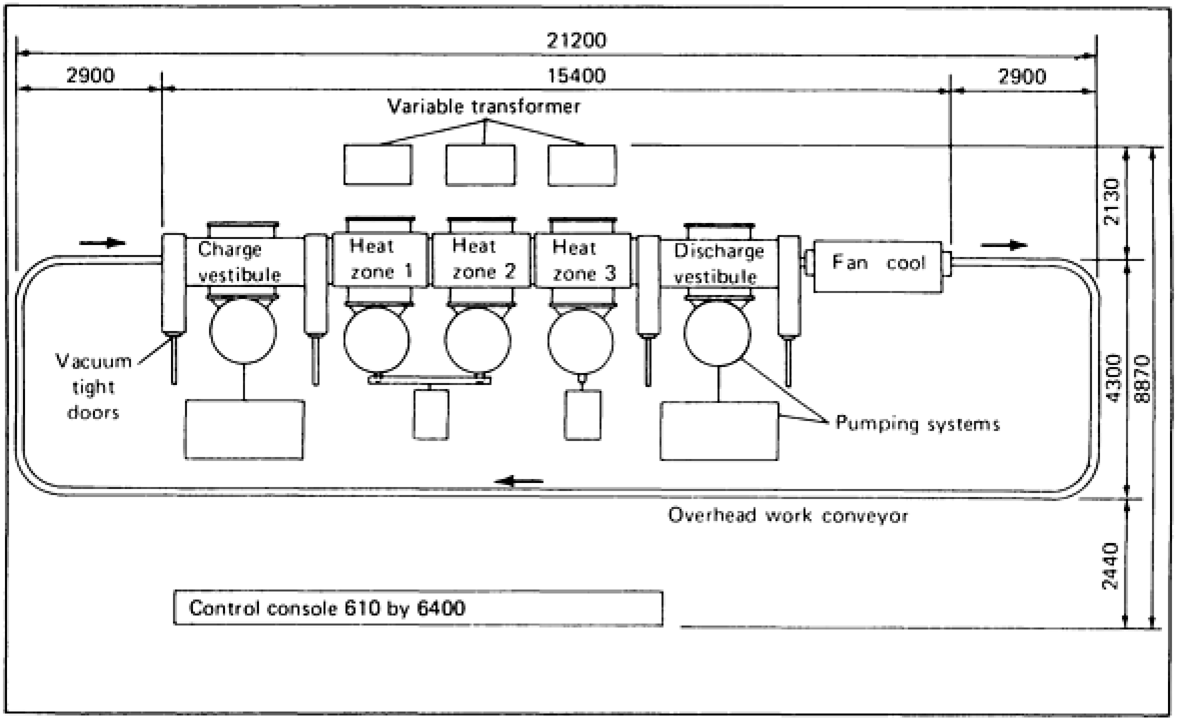

Fig. 6 Automatic vacuum furnace for fluxless aluminum brazing. Dimensions given in millimeters

For high-volume production and easy flow of work loads, semicontinuous vacuum furnaces are equipped with electrical controls that can also be computer programmed for automatic operation. The internal and external work carrier transfer systems, door operations, pumping systems, heating systems, gas backfill, and external cooling, loading, and unloading stations are all electrically interlocked and controlled for completely automatic operation. Automatically controlled mechanical loading and unloading of the work carriers can also be incorporated into the complete system.

Types of Cold-Wall Vacuum Furnaces. Cold-wall vacuum furnaces can be divided into bottom-loading, top-loading, and horizontally loading types.

Bottom-Loading Furnaces. As shown in Fig. 7, the furnace is stationary and elevated well above floor level. The bottom descends to floor level for ease of loading. The work is loaded on trays that are placed on the hearth by a fork lift when the bottom is in the lowered position. Such furnaces are built to handle large, heavy loads and are cooled rapidly by a high-velocity internal or external circulating-gas system.

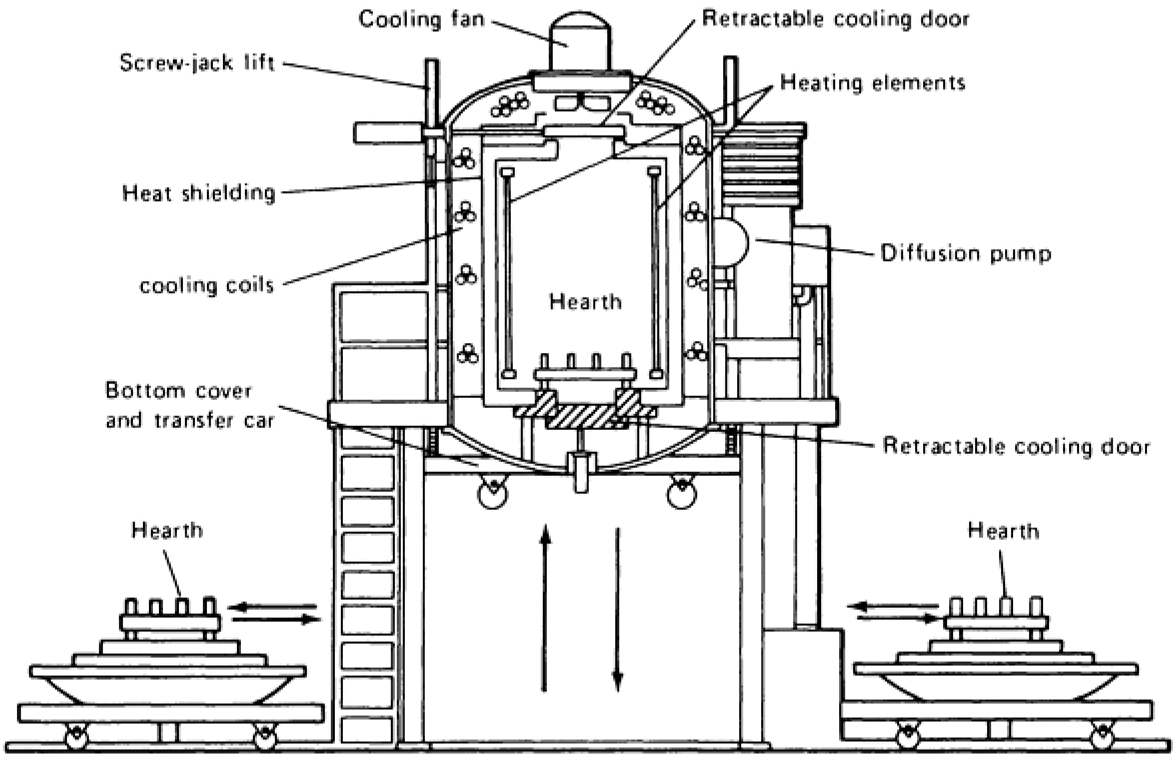

Fig. 7 Bottom-loading cold-wall vacuum furnace

Top-loading furnaces, as shown in Fig. 8, are not as widely used as bottom-loading furnaces. However, they are useful in processing long and relatively thin workpieces such as slender shafts. The workpieces are suspended vertically from hangers attached to the removable top of the furnace or placed on the hearth in the base. Adequate head room and a vertical hoist are required. These furnaces are cooled in the same way as bottom-loading units.

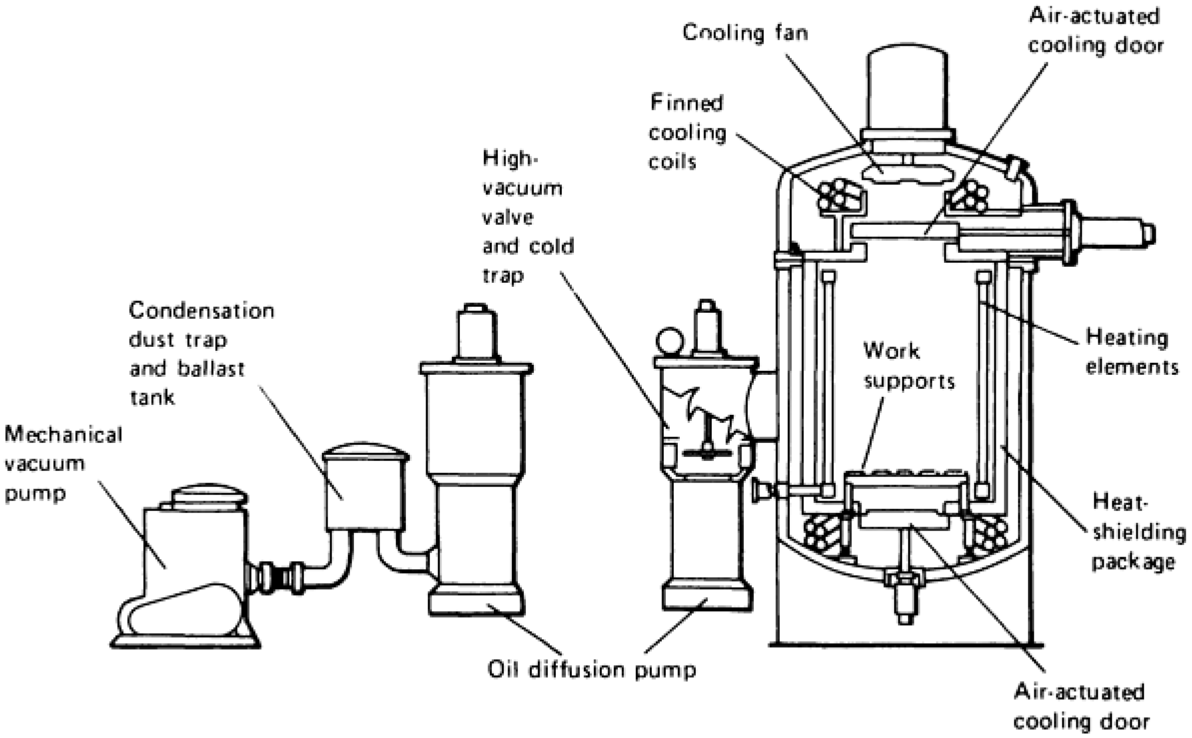

Fig. 8 Top-loading cold-wall vacuum furnace

Horizontally Loading Furnaces. A box-shaped or rounded design horizontally loaded furnace consists of a cylindrical shell free of gas leaks, with circular convex end plates or doors (Fig. 9). In some designs, both of the end plates are hinged to permit easy access to the furnace interior. Furnaces are also constructed with a stationary rear plate or with a second hinged access door at the front that is smaller than the main front plate. The cylindrical shell and the end plates are water cooled by copper coils soldered to the exterior surface or through the use of double-walled construction. The gastight shell is made of stainless or carbon steel, depending on the intended use. The movable end plates are sealed by O-rings at the end faces of the cylindrical section. The pressure of the outside atmosphere on the convex ends supplies the pressure for vacuum sealing. Usually, auxiliary clamps are provided to supply sealing pressure and to prevent the door from becoming unsealed when positive pressure inside the furnace is used during inert-gas quenching.

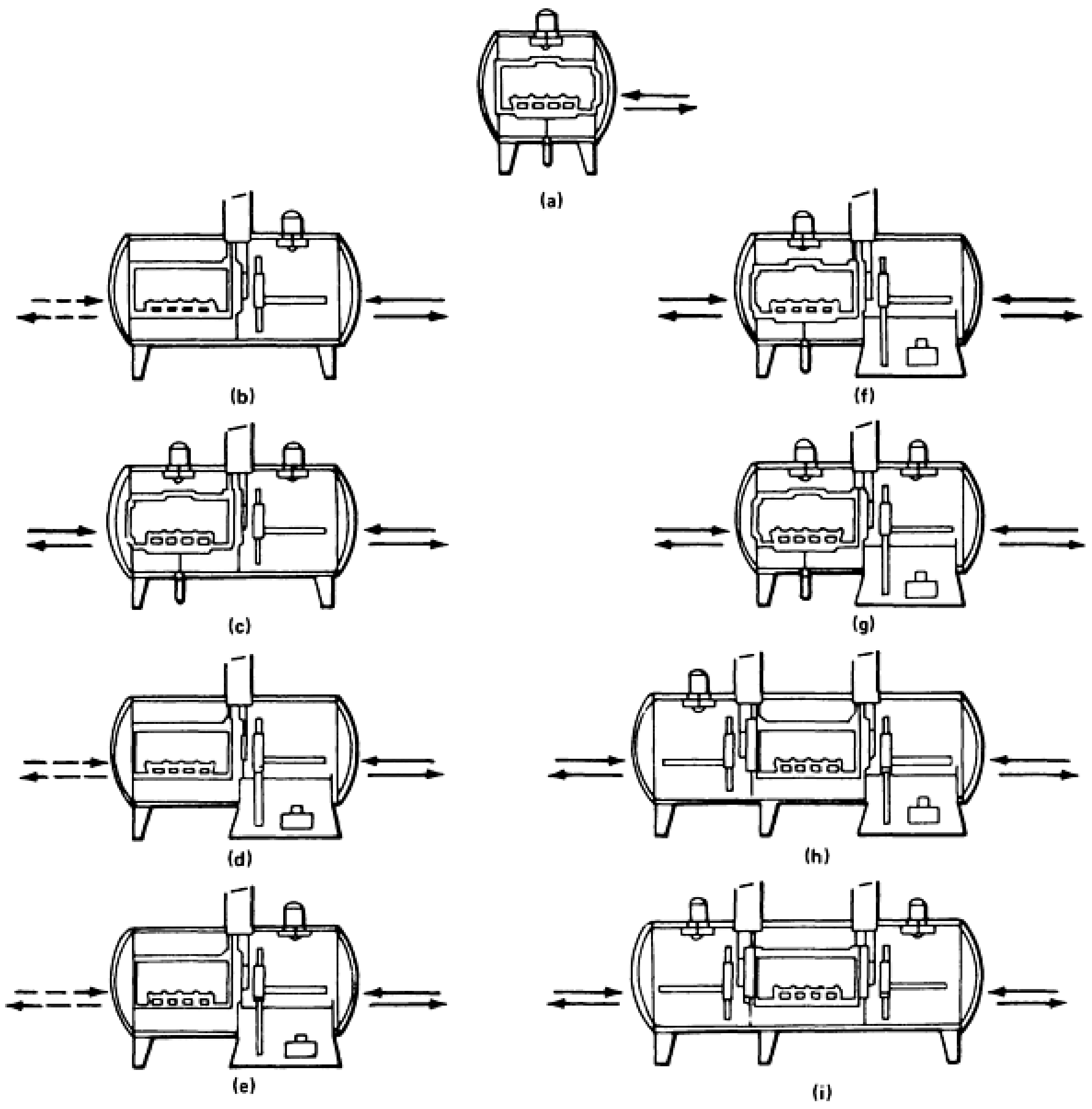

Fig. 9 Horizontal vacuum furnace configurations. (a) Single-chamber vacuum furnace with gas/fan quenching. (b) Two-chamber vacuum furnace; one chamber for heating, with integral second chamber for gas/fan quenching only and mechanism for internal in-and-out transverse movement of work load to and from heat chamber. Unit can be loaded and unloaded only from cooling or quenching chamber. (c) Same as (b) but gas/fan cooling is also included in heat chamber and unit can be loaded or unloaded from either chamber. (d)

Two-chamber vacuum furnace; one chamber for heating, with integral second chamber for oil quenching only and mechanism for internal movement of work load to and from heat zone. Unit can be loaded/unloaded from oil-quenching zone only. (e) Same as (d) but gas/fan cooling is also included only in quenching or cooling chamber. (f) Same as (d) but gas/fan cooling is also included only in the heating chamber and unit can be loaded or unloaded from either chamber. (g) Same as (d) but gas/fan cooling is included in both chambers and unit can be loaded or unloaded from either chamber. (h) Three-chamber vacuum furnace; middle chamber is for heating only. One end chamber contains gas/fan quenching only and internal mechanism for work movement to and from heat zone. Other end chamber contains oil quenching only and an internal mechanism for work movement to and from heat zone. Unit can be loaded or unloaded from either end chamber. (i) Three-chamber vacuum furnace with middle chamber for heating only. End chambers both contain gas/fan quenching only and internal mechanisms for workload movement to and from heat zone. Unit can be unloaded or loaded from either end.

Many horizontally loading furnaces are equipped with a special lifting and transfer truck that is stationed in front of the furnace. Frequently, this truck rolls on a track so that it is permanently aligned with the heating chamber. A hydraulic fork lift raises the work basket, and the truck moves forward to transfer the basket into the furnace, where it is lowered onto the hearth or work pedestal. This mechanism avoids damage to the interior of the furnace, which could occur if the transfer were attempted without controlled movement.

Horizontally loading furnaces may have several chambers, depending on the heat-treating operation to be performed (Fig. 9). Special systems have been designed to transfer work loads inside these furnaces. The conveyor, walking beam, roller-hearth, and pusher-type furnace designs can be adapted for vacuum furnaces.

The hearth is supported on wheels that roll on rails that are installed below and outside the heated zone and are protected by movable heat baffles. The longitudinal motion can be supplied by a sealed push rod extending through the furnace wall to an air or hydraulic cylinder or by an internal chain-driven conveyor in the cool area.

Another method of work transfer within a horizontally loaded furnace uses an internal rack-and-pinion drive. An overhead chain-driven conveyor can also be used. The work trays may also be transferred longitudinally to the second chamber hearth by a lifting mechanism installed in the unheated chamber that is exposed to the furnace heat only during the short transfer time. Rack-and-pinion drives and pneumatic cylinders are often used to execute vertical elevator movements into and out of liquid quench tanks, as well as to open and close internal heat shields and vertical doors.

A horizontally loaded vacuum furnace equipped with radiation shields is shown, in a vertical section, in Fig. 10. The work load is exposed directly to radiation from the electrical heating elements. The multiple radiation shields are made of thin sheets of heat-resisting material, such as molybdenum, in parallel layers between the heating elements and the chamber shell. An alternative construction using thermal insulating material instead of radiation shields is shown in Fig. 11. This insulation may be a fiber fill, graphite felt, or special low-density fiber ceramic material.

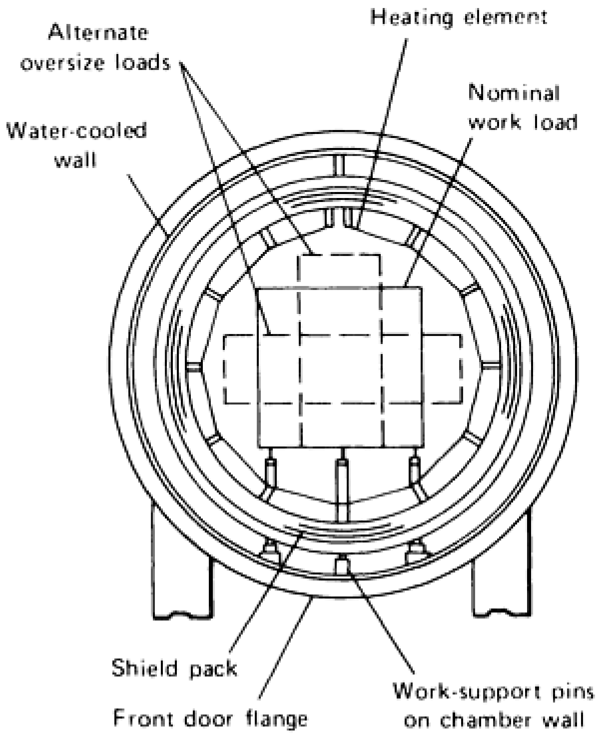

Fig. 10 Radiation shield cold-wall vacuum furnace

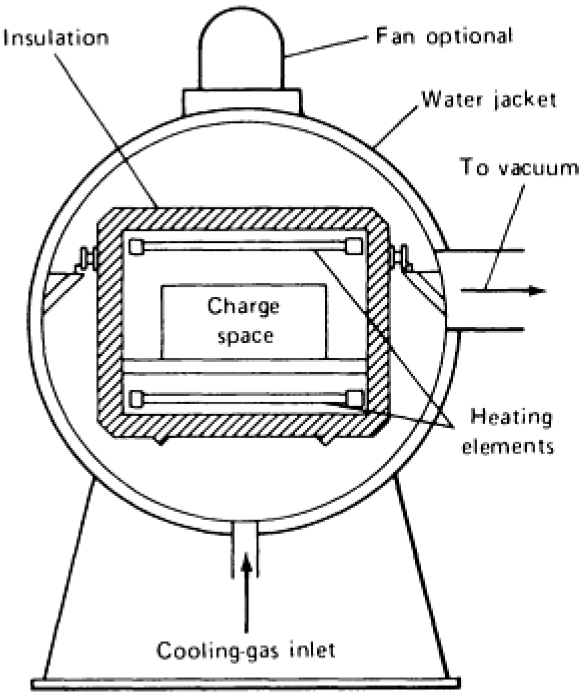

Fig. 11 Insulated cold-wall vacuum furnace

Cross-sectional views of a three-chamber oil quench furnace are shown in Fig. 12. The front chamber is equipped with internal cooling coils and a circulating fan for accelerated gas cooling. The center chamber is the heating chamber, which can be sealed at both ends during the heating cycle by internal moving heat shields and doors equipped with O-rings. The third chamber contains the oil quench and the vertical transport system required to immerse the work in the circulated quenching oil.

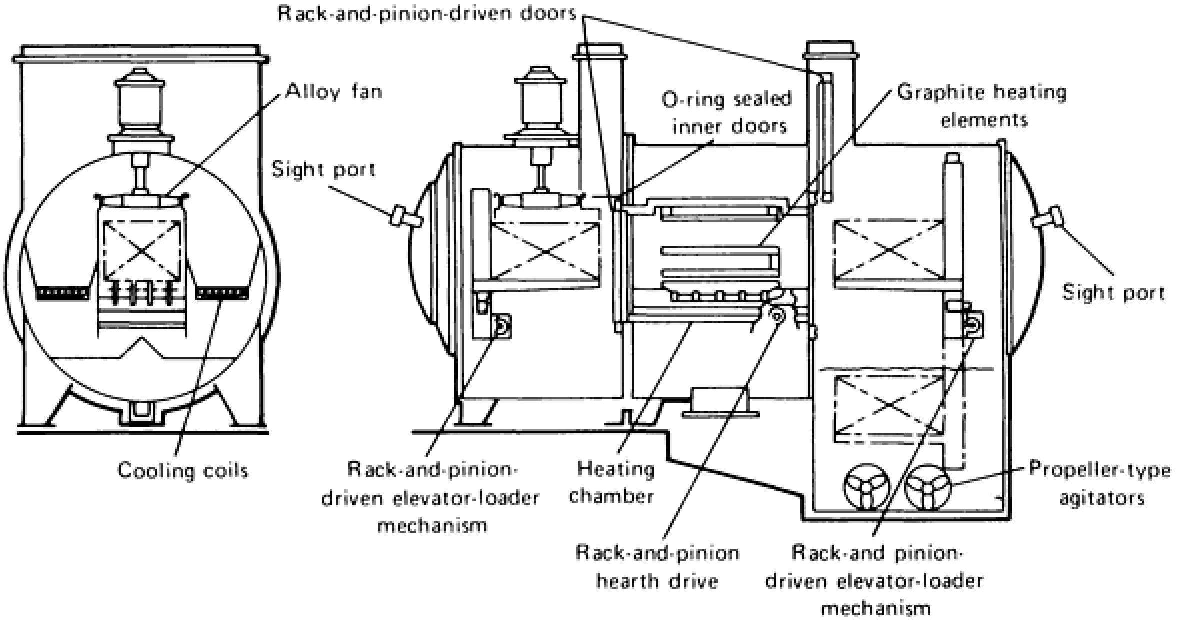

Fig. 12 Three chamber vacuum oil quench furnace

Two-chamber oil quench furnaces are also common. One chamber is used for heating, and the other for loading and oil quenching. A double high elevator in the quench chamber allows loading from either end of the unit.

Heating Elements

Resistance heating and induction heating were formerly the two most commonly used methods of heating within the cold-wall furnace; induction heating is now rarely used. When vacuum furnaces are heated inductively, a graphite cylinder is used as a susceptor; the graphite is heated by induction and radiates the heat to the work inside the cylinder. When heating is provided by the more common resistance elements, the heat transfer is also completed by radiation; therefore, the active heating surface should be large enough to effect a rapid and uniform transfer of heat.

Essentially all vacuum furnaces use three-phase 60 Hz power supplies. Three types of power supplies and controls are used:

- Controllable variable reactance transformers
- Saturable core reactors
- Silicon-controlled rectifiers

Low voltage (generally, <70 V or a maximum of 100 V at a pressure of 13 Pa, or 100 μm) should be used in the vacuum chamber because a high electrical potential can produce short circuiting of the elements by ionizing the residual gases within the chamber.

Resistance heating elements operating in a vacuum do not require oxidation-resistant properties equal to those required in oxidizing atmospheres. To improve operating efficiency, resistance heating elements are heated to higher temperatures than are the elements used in conventional furnaces because the transfer of radiant energy is proportional to the fourth power of the absolute temperature. Higher temperatures require heating elements with low vapor pressures to ensure long life. Materials meeting these requirements are:

- Refractory metals, such as tungsten, molybdenum, and tantalum
- Pure solid graphite in the form of bar, rod, or tube
- Pure graphite cloth woven from fine filaments of pyrolyzed graphite

- Chromium-nickel elements for operating temperatures of less than 980 °C (1800 °F)

Properties of these materials are compared with those of iron in Table 3.

Table 3 Characteristics of heating elements used in vacuum furnaces

Material	Melting point		Upper operating temperature limit		Vapor pressure at			
					1600 °C (2910 °F)		1800 °C (3270 °F)	
	°C	°F	°C	°F	Pa	torr	Pa	torr
Molybdenum	2617	4743	1705	3100	1.3×10^{-6}	10^{-8}	1.3×10^{-4}	10^{-6}
Tantalum	2996	5425	2500	4530	1.3×10^{-9}	10^{-11}	1.3×10^{-7}	10^{-9}
Tungsten	3410	6170	2800	5070	1.3×10^{-11}	10^{-13}	1.3×10^{-9}	10^{-11}
Graphite	3700	6700	2500	4530	1.3×10^{-11}	10^{-13}	1.3×10^{-8}	10^{-10}

Refractory Metals. The high melting points of tungsten, molybdenum, and tantalum make these metals ideal for use as heating elements in vacuum furnaces.

Tungsten is capable of withstanding higher operating temperatures than the other refractory metals (see Table 3). As a heating element material, it is used as wire or rod, thin sheet, or sections of woven wire screen. Wire screen is less likely to be damaged from thermal stresses that occur during heating or cooling.

Molybdenum in the form of solid rod, strip, or thin sheet material is the most widely used metallic element. Material in sheet form is normally preferred because the electrical power density (watts per square inch of radiating surface) is low compared to that of cylindrical rod, resulting in lower operating temperatures and thus longer service life for the elements. Also, thermal expansion and contraction and the resulting stresses are handled more easily from a design standpoint. However, thin sheets are subject to mechanical damage. Hangers and supports for metallic heating elements must have good insulating properties and must be chemically stable at the temperatures and pressures encountered in service. Heating elements must not be restrained by the support system from free movement during the thermal cycle.

Molybdenum exhibits extremely brittle characteristics at low temperatures after being in service. If deformed at low temperatures, molybdenum heating elements can fail because of the brittle nature of the metal.

Molybdenum undergoes a large change (500% increase) in electrical resistance between room temperature and the normal operating temperatures; consequently, the power supply must control the current during the early stages of heating to avoid damaging the elements, as well as the furnace heating systems.

Solid Graphite Heaters. All metals lose some strength when heated, whereas crystalline carbon in the form of graphite increases in strength as the temperature increases. Pure graphite in the form of flat bar or rod is less expensive than other high-temperature metallic resistors. Graphite also has a much lower heat expansion coefficient and is more resistant to thermal shock than most metallic materials.

As shown in Table 3, graphite also has a high melting point and a low vapor pressure; thus, it is an excellent choice for a vacuum furnace heating element material. In processes in which possible minute concentrations of carbonaceous material in the vacuum atmosphere will not have an adverse effect on workpieces, such as in the processing of the refractory alloys, where the use of graphite is not recommended (forbidden by most specifications), graphite resistors are commonly chosen. Moreover, the presence of incandescent carbon may provide additional cleansing or gettering action with respect to oxygen or water molecules in the residual vacuum atmosphere. This subtle action is not provided by any of the metallic resistors. The replacement of graphite resistors may be less expensive than the replacement of metallic ones because often graphite elements can be replaced without disturbing the surrounding insulation and because electrical connections are mechanical and require no welding.

Graphite has up to a 20% decrease in resistance as it heats, requiring wiring and power sources to be sized to handle the increased amperage should full power be applied to the cold elements.

Graphite Cloth Heaters. A third type of material used for vacuum heating elements is a cloth composed of fine graphite fibers. This material is made from rayon cloth pyrolyzed at high temperature to convert the carbon in the rayon to crystalline graphite. The cloth is strong and very flexible. It can be cut with ordinary scissors to the desired size and shape. Because the cloth is flexible, the supporting system can be considerably simplified. The ends are usually clamped in graphite electrodes. This graphite cloth is also available as a hollow cylinder with solid graphite ends of high electrical conductivity, forming a self-supporting electrode with a large radiating surface area.

The direction of the weave of cloth used in making elements is a critical factor in determining the resistance and voltage values of the graphite cloth. In most weave patterns, the fibers in one direction are straight, and those in the other direction are woven over and under the first. The actual cloth resistance obtained will exceed the calculated resistance value because the over-and-under cut length will exceed the straight cut length of the cloth.

Heat Insulation

Part of the insulation in a cold-wall vacuum furnace is provided by the vacuum itself. Where space is essentially void, there can be virtually no heating by convection or conduction. Radiant energy emitted by the resistors in all directions is generally confined to the desired heating zone by one of four designs of radiation shielding.

Metallic Shielding. Multiple concentric layers of thin heat-resisting sheet metal reflect the energy back into the heating chamber of the furnace. Approximately 6 mm ($\frac{1}{4}$ in.) spacing is maintained between these sheets. Thin wire coil springs are sometimes used as spacers between adjacent surfaces. Inner shields are sometimes fabricated from molybdenum because of its superior heat-resisting qualities; the next two layers may be stainless steel, and the outer layers are composed of nickel steel or plain carbon steel, depending on the maximum operating temperature of the furnace. As the number of shield layers (N) increases, the efficiency of the shielding increases; however, the insulating effect of each added shield decreases. Consequently, no more than five or six shields or layers are used. Approximately 85% efficiency can be achieved in this manner, even with a material of 0.5 emissivity. The effect on efficiency of the number of insulating layers and the emissivity of the sheeting material is shown in Fig. 13. Efficiency declines as the originally bright, clean metal surfaces become affected by the deposition of oxide or sooty films. This decline must be considered during the design of the furnace system.

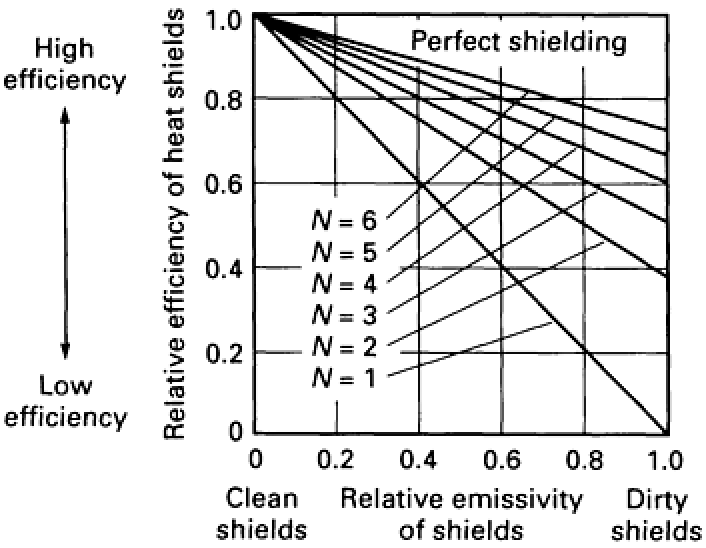

Fig. 13 Relationship between heat shield efficiency and emissivity of sheet metal for various numbers (*N*) of sheets

Slightly faster evacuation rates, higher ultimate vacuum levels, and cleaner work products are usually obtainable with designs incorporating radiation shields. These advantages are realized only if the furnace is subsequently used for a singular process application or is scrupulously maintained. These advantages readily revert to disadvantages when radiation-shielded units are used for multiprocess purposes or are not cleaned.

Sandwich construction, which resembles the wall of a conventional low-temperature furnace, has proved to be an efficient design. One or more layers of graphite felt or high-temperature refractory fiberfill are placed between the inner and outer sheet metal walls. For instance, the inner wall may be molybdenum, and the outer wall stainless steel. A vacuum between the fibers reduces the thermal conductivity of the wool packing to a fraction of the thermal conductivity in any atmosphere. Thermally insulated cold-wall vacuum furnaces are better suited to conventional vacuum heat treating involving multiple process and temperature requirements.

Pump rates for sandwich construction furnaces are slower than for conventional heat-treating multiple-process furnaces. Ultimate vacuum levels are not as high. The residual-gas load is not as clean as with radiant-shield designs because of higher internal outgassing loads. However, for most vacuum processing, thermally insulated vacuum furnace design is adequate. It is certainly less expensive in original cost, maintenance, thermal efficiency, and power consumption than conventional vacuum heat-treating multiple-process furnaces. Typically a radiant shield furnace with identical pump system runs a decade vacuum level lower than does a similar insulated furnace, that is, 1.3 mPa (1×10^{-5} torr) compared to 13 mPa (1×10^{-4} torr).

Multilayer Graphite. In this design, multiple layers of high-purity graphite felt are fastened to an outer cage of refractory metal by molybdenum clips. This material has a density of only about 0.08 g/cm^3 (0.003 lb/in.^{3}), and it functions as a thermal insulator in much the same way as refractory fiber fill. Because it is a felted material with inherent cohesion, it does not require support by sheet metal walls, as does the fiber-fill. Its emissivity is near unity--about 0.98 or better. Graphite felt is more economical than molybdenum and is easy to replace. This method, like sandwich construction, relies on an insulating material with low conductivity in a wall heated from one side.

Carbon-Bonded Carbon Fiber. This insulation material uses blocks or molded cylinders to form a structural lining. It has a density of approximately 0.19 g/cm^3 (0.0069 lb/in.^{3}) and is used to make a refractory lining that minimizes the use of molybdenum and is resistant to high-velocity erosion in gas quenching applications.

Insulation Maintenance. All types of insulation are subject to accidental contamination. In many cases, foreign materials, such as lubricants used in deep-drawing operations, volatile metals, or even cotton gloves, may be inadvertently carried into vacuum furnaces with the workload. Contamination can result in extensive damage to radiation shields and

considerable down-time if it necessitates the mechanical cleaning of the shields. In an insulated furnace that does not depend on reflectivity, a thorough outgassing normally returns the furnace to operating condition within several hours.

The efficiency of multiple radiation shields decreases rapidly as the shields become dirty and nonreflective and as emissivity increases. One method of cleaning molybdenum shields consists of heating the furnace to above the operating temperature after backfilling with dry hydrogen to a pressure of 130 Pa (1 torr).

An effective method of protecting the innermost radiation shield is to overlay the molybdenum with a layer of graphite foil. This material is essentially pure graphite that has been rolled into a thin sheet by a special process with dry hydrogen. It is held in place by mechanical fasteners. Any contamination from the splattering of brazing filler metal or the evaporation of volatile materials is deposited on this inert material rather than on the molybdenum shield. Graphite foil can be applied to almost any other metal lining surface as well.

Gas Quenching

The inability to obtain the high cooling rates necessary for many metallurgical operations proved to be a severe limitation to early hot-wall vacuum furnaces. The development of a retort that could be transferred from the hot furnace to a special cooling stand provided a somewhat inconvenient solution.

With the development of the cold-wall vacuum furnace, the cooling problem has been overcome to some extent by radiation shielding made of multiple thin metal sheets, thermal insulation of very low mass such as refractory fiber, special foam refractory brick, or graphite fiber felt. Because of the low heat content of these insulating media, most of the heat to be dissipated is contained in the work load itself. Cooling the work continues to be quite a slow process because of the absence of convective heat transfer in a vacuum. Backfilling the chamber with an inert gas is necessary to promote the conductive transfer of heat from the work to the water-cooled shell. Fans made from stainless steel or other heat-resisting alloys can be installed above the insulated work area to promote the convective circulation of the backfill atmosphere. Usually baffles or bungs of insulating material must be moved from above and below the work load to improve the access of the cooling atmosphere to the hot work. Finned copper coils cooled by circulating water can be installed between the insulating medium and the shell of the furnace to facilitate heat transfer, to avoid total reliance on the cold furnace shell as the transfer surface.

Circulation by an internal fan is often used because it provides the fastest gas cooling, but it is not as likely to provide uniform cooling throughout the load.

Cooling rate uniformity is not entirely due to the system used. It also depends on the size, shape, quantity, and distribution of the load being processed. Care must be exercised when loading a furnace to optimize the placement of parts for heating and cooling.

An inert-gas circulating system with an internal manifold is shown in Fig. 14. To increase the rate of heat removal, the mass-flow coefficient must be increased. Mass flow is the product of the mass of gas moved times its velocity. To increase this coefficient, either the velocity of the gas circulating through the load or the gas pressure in the system can be increased so that a greater number of gas molecules are present per unit volume.

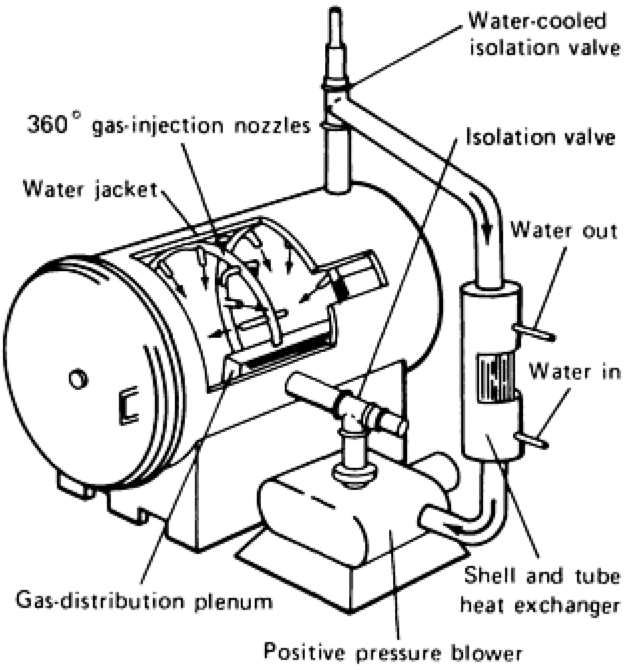

Fig. 14 Inert-gas recirculating system

Internal pressures used during inert gas quenching range from 13 to 86 kPa (100 to 650 torr) on furnaces that do not have positive-pressure clamps on the doors. For even more rapid gas cooling with the proper furnace construction, positive pressure up to six times atmospheric pressure have been used.

Because of technical advances in fan motors, door-sealing methods, and related equipment, it has become common to cool loads with gas fans at pressures up to 170 kPa (1275 torr) in conventional units and up to several times atmospheric pressure in furnaces with turbine recirculation systems. Because the cooling rate is proportional to absolute pressure, it is increased considerably by positive-pressure cooling.

By backfilling to pressures above atmospheric pressure, for example, 70 kPa (10 psi) gage, rather than slightly below atmospheric pressure, the cooling time can be shortened by as much as 30% (see Fig. 15). This development has greatly enhanced the use of vacuum equipment for air-hardening tool steels with decreased overall cycle time.

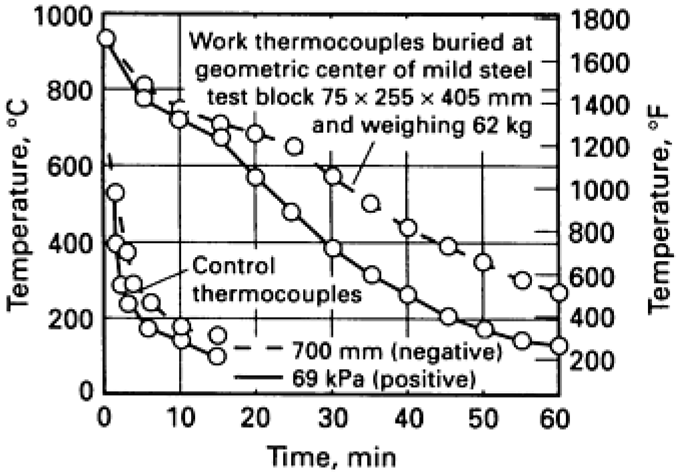

Fig. 15 Comparison of cooling rates and backfill pressures

The proportional increase of quenching speed with increasing gas pressure up to two times atmospheric pressure also applies to 500 kPa (5 bar) if the time delay in reaching this pressure and starting rapid gas circulation is minimal. Fast backfilling is promoted by a compact design and a special turbine system that builds up the forced circulation very rapidly. Figure 16 shows the effect of pressure on quenching speeds from a hardening temperature to 1010 °C (1850 °F). An increase in pressure from 100 to 200 kPa (1 to 2 bar) will decrease cooling time by 60 s, or 50%. An increase from four to five times atmospheric pressure would give a cooling-time decrease of 6 s, or 20%.

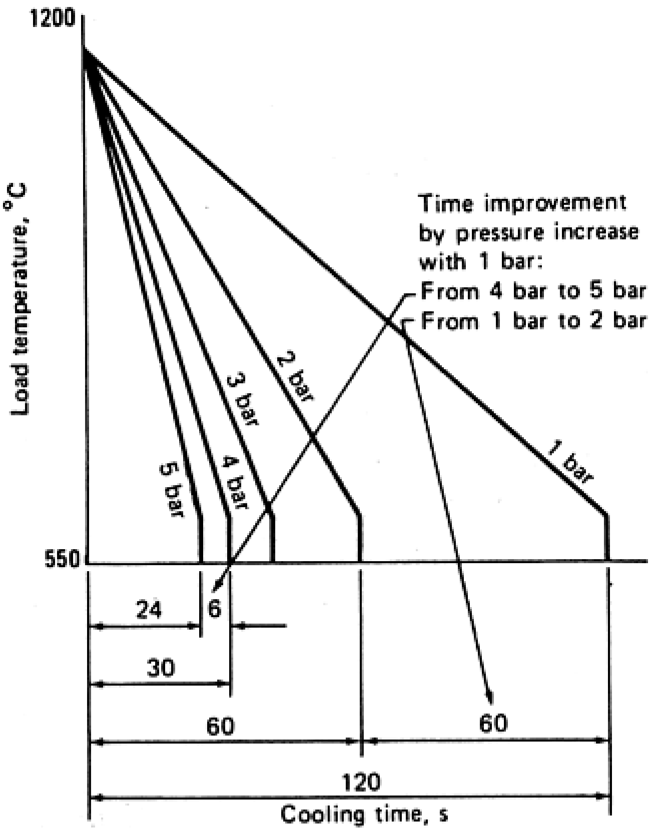

Fig. 16 Relationship between gas pressure and quenching rate

Liquid Quenching

When even faster cooling rates are needed, furnaces with liquid quench capabilities may be used. This usually requires an arrangement in which the quenching is done in a chamber isolated from the heating chamber. In one such design, a horizontal loading furnace has a rear heating chamber and a forward cooling chamber, with a vacuum sealing door between them. When the heating cycle is completed, the work is transferred to the front chamber. After the sealing door is closed, the work load is lowered into the quench tank by an elevator. The quenching liquid is agitated vigorously by propellers, and the heat absorbed by the quenching medium is removed by a heat exchanger similar to that used in many atmosphere heat-treating furnaces. The chamber that houses the quench tank can also be equipped with a circulating fan and cooling coils to provide forced convection gas cooling or liquid quenching. Quenching is usually completed at slightly below atmospheric pressure within an inert-gas backfill.

Precautions must be taken to ensure that the trays and fixtures that carry the work load into the heating chamber are degreased before reuse. Organic residues on trays and work load will outgas and make the pump-down time longer and give the interior of the furnace, and possibly the work, an undesirable appearance.

Gases Used for Backfilling

Gases used for backfilling vacuum furnaces are argon, nitrogen, helium, hydrogen, and natural gas. Argon and nitrogen can be obtained as compressed gases or as condensed liquids stored in cryogenic containers. Helium and hydrogen are readily available only as compressed gases. If appreciable amounts of argon or nitrogen are to be used, it is much less

expensive to purchase the gas in liquid form. Very high-purity gases are available, and some typical analyses of these gases are listed in Table 4.

Table 4 Typical analysis of backfill gases

Gas	Purity, %	Impurity, ppm							Dew point		Thermal conductivity (*k*) at 0 °C (32 °F)		Relative cooling rate[(a)]
		O_2	N_2	CO_2	CO	H_2	Hydro-carbons	Carbon-aceous gas	°C	°F	W/m · K	Btu · in./ft^2· h · °F	
Argon	99.9995	2	2	1	. . .	. . .	1	. . .	-79	-110	5.77	32.3	0.74
Nitrogen	99.9993	3	. . .	. . .	. . .	. . .	. . .	1	-79	-110	8.65	48.4	1.0
Helium	99.998	1	10	. . .	. . .	1	1	. . .	-62	-80	49.0	274	1.03
Hydrogen	99.9	10	1500	1	2	. .	25	. . .	-	-75	60.6	339	1.4

(a) Relative to nitrogen as 1.0

When a gas is purchased in a liquid state, it is stored under pressure in a large tank with a safety pressure relief value that allows gas to escape to the atmosphere if the internal pressure exceeds a set value. Liquid gas leaves the tank through a vaporizer, where ambient heat supplies the necessary heat for vaporization. Frequently, this vaporizer is a series of finned coils used to increase heat transfer. Because of the excellent insulation provided for the tank, usually very little gas is lost by venting. Sometimes a reservoir or storage tank of appreciable volume is used to store the vaporized gas at a nominal pressure to avoid sudden surges of pressure in the cryogenic system and to ensure that sufficient volume is available when backfilling is in progress.

Work Load Support

The work load in most vacuum furnaces is placed on a tray or in a basket to facilitate loading. Because such fixtures are heated and cooled at fairly rapid rates during processing, the material and design must allow for the cycles of thermal stresses. Molybdenum is often used for these support fixtures. If moderately high temperatures are used, as with many tool and die steels, austenitic stainless steel trays may be used. However, work baskets of Inconel alloys are often used in the processing of high-speed tool steels.

The work-supporting tray usually rests on a graphite or metallic hearth. Frequently this hearth consists of three or four horizontal molybdenum or graphite bars supported by heat-resisting piers from the furnace shell below. Some hearths use ceramic bars, and others use ceramic alumina wheels on which the work tray can be rolled.

It is essential that possible reactions between the hearth support and the work baskets be taken into consideration. Graphite hearths react with stainless steel and Inconel alloys to form a eutectic melting at approximately 1125 °C (2060 °F). To prevent a graphite hearth from reacting with a work basket or work load placed directly on the hearth, a thin sheet of a ceramic material capable of resisting high temperatures can be placed between the hearth and the workpiece. Some graphite hearth blocks have a longitudinal groove at the top. An alumina ceramic rod or tube is placed in the groove and supports the work or the work basket, thus separating the graphite and the metallic workpiece.

Molybdenum reacts with nickel to form a eutectic melting at approximately 1315 °C (2400 °F). Therefore, it is necessary to separate nickel-bearing alloys from a molybdenum hearth at this temperature. Slabs of honeycomb alumina ceramic are available for this purpose. Nickel and titanium form a eutectic melting at approximately 955 °C (1750 °F), and alloys of these metals must be kept separated if temperatures this high are contemplated. Table 5 is a listing of metal combinations and their compatibility.

Table 5 Maximum temperatures at which selected pure metals and metallic oxides are compatible in a 13 to 1.3 mPa (10^{-3} to 10^{-4} mm Hg) vacuum

Support fixture material	Temperature of workpiece material																									
	W		Mo		Al_2O_3		BeO		MgO		SiO_2		ThO_2		ZrO_2		Ta		Ti		Ni		Fe		C	
	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F	°C	°F
W	2540	4600	1925	3500	1815	3300	1760	3200	1370	2500	1370	2500	2205	4000	1595	2900	. . .	. . .	. . .	. . .	1260	2300	1205	2200	1480	2700
Mo	1925	3500	1925	3500	1815	3300	1760	3200	1370	2500	1370	2500	1900	3450	1900	3450	1925	3500	1260	2300	1260	2300	1205	2200	1480	2700
Al_2O_3	1815	3300	1815	3300	1815	3300	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	1815	3300	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
BeO	1760	3200	1760	3200	. . .	. . .	1760	3200	1370	2500	. . .	. . .	1760	3200	1760	3200	1595	2900	. . .	. . .	. . .	. . .	. . .	. . .	1760	3200
MgO	1370	2500	1370	2500	. . .	. . .	1370	2500	1370	2500	. . .	. . .	1370	2500	1370	2500	1370	2500	. . .	. . .	. . .	. . .	. . .	. . .	1370	2500
SiO_2	1370	2500	1370	2500	. . .	. . .	. . .	. . .	. . .	. . .	1370	2500	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	1370	2500
ThO_2	2205	4000	1900	3450	. . .	. . .	1760	3200	1370	2500	. . .	. . .	1980	3600	2205	4000	1900	3450	. . .	. . .	. . .	. . .	. . .	. . .	1980	3600
ZrO_2	1595	2900	1900	3450	. . .	. . .	1760	3200	1370	2500	. . .	. . .	2205	4000	2040	3700	1595	2900	. . .	. . .	. . .	. . .	. . .	. . .	1595	2900
Ta	. . .	. . .	1925	3500	1815	3300	1595	2900	1370	2500	. . .	. . .	1900	3450	1595	2900	2345	4250	1260	2300	1260	2300	1205	2200	1925	3500
Ti	. . .	. . .	1260	2300	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	1260	2300	1260	2300	925	1700	1040	1900	1260	2300
Ni	1260	2300	1260	2300	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	1260	2300	925	1700	1260	2300	1205	2200	1260	2300

Fe	1260	2300	1205	2200	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	1205	2200	1040	1900	1205	2200	1205	2200	1095	2000
C	1480	2700	1480	2700	. . .	. . .	1760	3200	1370	2500	1370	2500	1980	3600	1595	2900	1925	3500	1260	2300	1260	2300	1205	2200	2205	4000

Note: Although various materials may be compatible at a given temperature, a particular material may be unstable at this range of vacuum.

Vacuum Chambers

The prime requisites in the design, fabrication, and operation of a vacuum chamber are the prevention of leakage from the outside atmosphere and the assurance that the planned material processing will be completed without damage to the chamber or product. Leakage is a serious consideration even though the pressure within the vessel may be held at the required vacuum because the continual entrance of air into the evacuated chamber can be harmful to the product or internal components. If a high-capacity pump is used, the pump may well be able to maintain a low pressure inside the furnace regardless of a substantial air leak that causes a constant influx of oxygen, which can react with the surface of the work load. Many operators of vacuum equipment routinely conduct leak tests before energizing the heating elements. This is particularly useful when the work load consists of very expensive material. For example, a furnace is evacuated to 13 mPa (10^{-4} torr) for at least 1 h. The vacuum valve connecting the furnace to the pump is closed, and the rise in internal furnace pressure in a specified time interval is checked. It is difficult to set specific limits on leakage tolerance because this tolerance depends on the type of material being processed, the dew point of the air, and the length of time the furnace door is open. Common industrial practice with vacuum furnaces is to establish permissible leakage rates in terms of microns or micrometers per hour. A rate of rise between 1.3 and 3.3 Pa (10 and 25 μm Hg) per hour is generally an acceptable specification for most industrial work, but more stringent applications may require a lower rate. A more dependable method for discovering air leakage prior to or even during a run is to use a residual-gas analyzer. A residual-gas analyzer will indicate whether the leak is air, quench gas, water, solvent, or oil.

Generally, equipment manufacturers specify rate-of-rise measurements of 1.3 Pa (10 μm Hg) per hour or less for an empty, clean, cold, and thoroughly outgassed system. This measurement is usually obtained by checking the furnace after a gas cooling or vacuum cooling from a heat-up to a temperature sufficient to dry out or bake out the internal components. This procedure almost completely eliminates the out-gassing effects of work load and furnace components on rate-of-rise measurements.

Once a vacuum furnace has been properly installed and put into operation, the heat treater usually need only be concerned with preventing or correcting the leakage of air at seals around the doors, sight ports, pumping ports, electrical and water feed lines, mechanical rotating and sliding seals for introducing mechanical force and motion into the chamber, and any other point on the vessel that is subject to opening and closing.

Unless a vacuum furnace has been built for service at vacuum levels of 0.13 mPa (10^{-6} torr) or less, typical elastomer seals used in most applications will be worn out if subjected to overheating, to repeated openings and closings, or to rotating or sliding motions. When seals are replaced, all flanges must be properly aligned to ensure complete seating of the seal, and sharp edges or burrs must be removed to prevent physical damage. A good grade of vacuum grease lubricant should be used sparingly to facilitate placement of the seals and to obtain optimum sealing.

The best and most expensive vacuum chambers are constructed of an oxidation-resistant material such as a 300-series stainless steel. This material may be used for vacuum service at approximately 0.13 mPa (10^{-6} torr) pressure or less or when the vacuum chambers must operate as a hot-wall or retort unit. A less expensive carbon steel, adequately epoxy coated, is effective in cold-wall chambers for most heat-treating applications. However, unprotected carbon steel should not be used in the construction of a vacuum chamber. When carbon steel is exposed to a vacuum, it can be so thoroughly degassed that oxidation occurs very rapidly when reexposed to atmospheric conditions. Oxidation that occurs in a carbon steel chamber is permanent and progressive because the chamber is completely water-jacketed and does not achieve the temperatures necessary for surface cleaning.

The efficiency of the pumping system can be affected by the material used to build the vacuum chamber. For example, a stainless steel chamber with a total volume of 0.3 m^3 (10 ft^3) will require 10 min for evacuation to a pressure of 1.3 mPa (10^{-5} torr) by a 152 mm (6 in.) diffusion pump. A chamber with the same volume constructed of unprotected carbon steel can require evacuation times of up to 30 min to achieve the same pressure. If the carbon steel surfaces are oxidized, evacuation times of up to 2 h can be required.

Pumping Systems

Vacuum vessels are evacuated by various types of pumping systems that depend, to a great extent, on the pressure range needed for processing. An adequate vacuum pumping system must attain the specified pressure and must have sufficient capacity to handle the processing gas load, not only at the ultimate pressure but at all intermediate pressures during the pump-down cycle. Pumping systems are usually divided into two subsystems: the roughing pump and the high-vacuum pump. For certain requirements, a single pumping system is sufficient for the entire range and cycle. Pumps are usually

classified as mechanical or diffusion pumps. The choice of pump or combination of pumps depends largely on the pressure and gas volume or pumping rates required for a specific process and size of vacuum vessel. The vacuum system shown in Fig. 17 consists of a mechanical forepump that can be connected directly to the vacuum vessel by closing the high-vacuum valve, opening the roughing valve, and closing the foreline valve. This procedure isolates the diffusion pump from the rest of the system. The diffusion pump interior can then be pumped free of air by its mechanical holding pump.

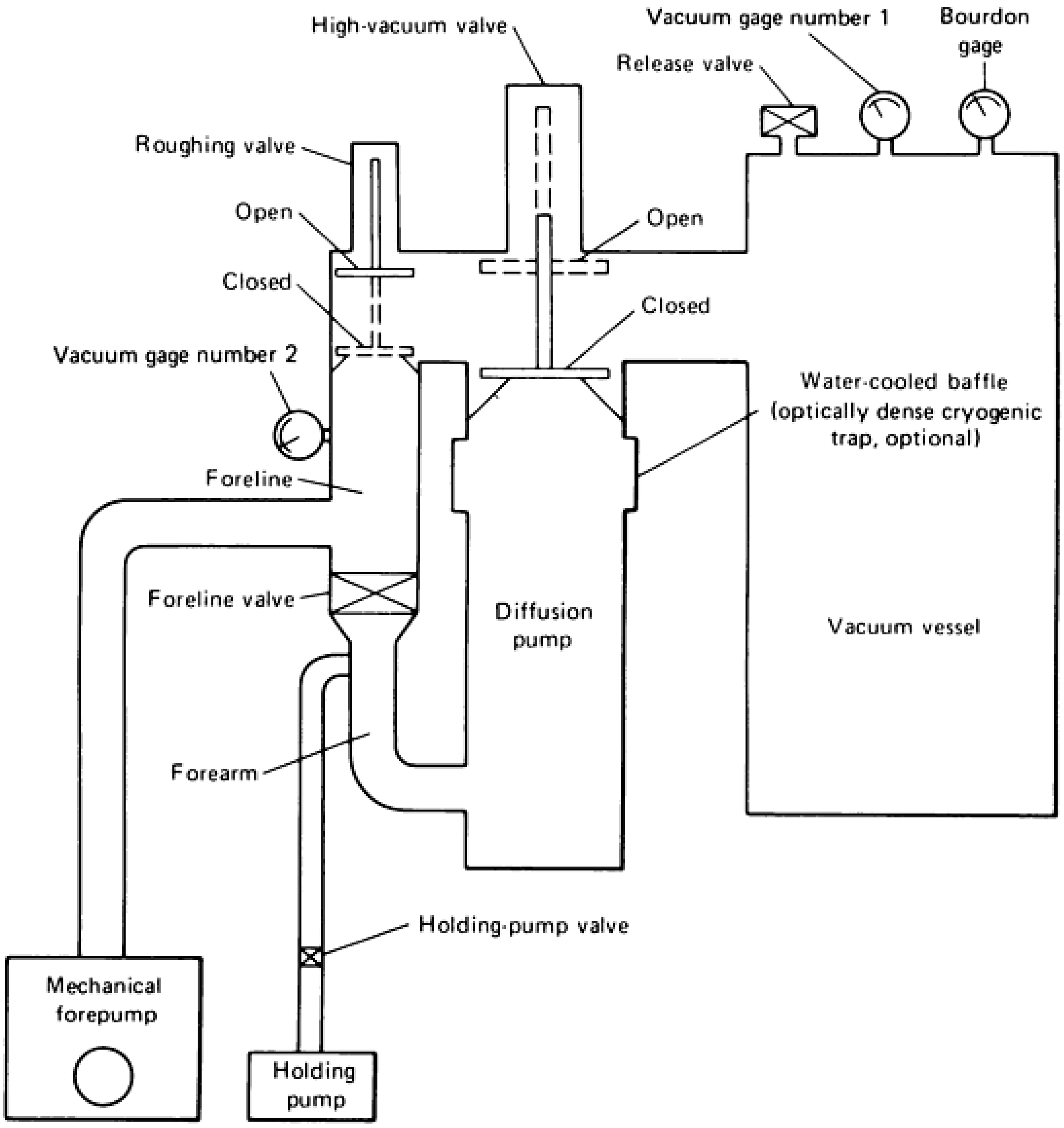

Fig. 17 Typical vacuum system containing mechanical and vapor pumps with interconnected valving and piping

When the pressure as shown on vacuum gage 2 has been reduced to a level at which the diffusion pump can operate efficiently, the roughing valve is closed and the foreline valve and high-vacuum valve are opened. The residual gas in the vacuum vessel can then expand continuously into the region of the diffusion pump, then through the foreline to the forepump, and finally to the atmosphere. The water-cooled baffle or other optically dense trap on top of the diffusion pump prevents diffusion pump oil from diffusing backward into the vacuum system. Vapors from the system are condensed in the liquid nitrogen cryogenic trap, if one is used, when a very high vacuum (very low pressure) of 0.13 mPa (10^{-6} torr) or below is desired. Vacuum gage 1 measures the pressure in the vacuum vessel. This gage should be more sensitive than vacuum gage 2. The release valve controls backfilling of the system to atmospheric pressure up to the high-vacuum valve.

Mechanical pumps operate on the fluid-flow principle and are primarily positive-displacement pumps with suitable seals to permit operation at low pressures. Piston pumps or rotary blowers in various pumping-speed ratings are available. Vacuum system levels down to 3.3 Pa (25 μm Hg) can be obtained with oil-sealed rotary mechanical pumps. Depending on the application, they may be called roughing or forepumps. They can discharge directly into the air against normal atmospheric pressure. A portion of air in the closed system expands into and is trapped within a chamber of the pump. This volume of air is then compressed by the movement of vanes or a piston in the interior of the pump and is expelled through a port equipped with a check valve. This process is repeated and, with each cycle, a portion of the remaining air volume in the closed system is expelled. When the back leakage through the pump or the leaks in the wall of the container equal the rate of air removal by the pump, the closed-vessel internal pressure remains constant.

A nonmechanical limitation on the ultimate pressure of a mechanical pump is the vapor pressure of the oil itself. Most commercial pump oils are controlled grades of petroleum type SAE 20, which have a vapor pressure of about 130 mPa (1 μm Hg).

When air containing moisture is compressed in the interior of the pump, water may condense and contaminate the oil, affecting the attainable ultimate pressure. One method used to prevent condensation is to introduce enough pure, dry air at the beginning of the cycle to ensure that the resulting moisture level of the trapped air is below the level at which compressive condensation can occur. Air is introduced during the pump compression cycle to prevent condensation of water vapor to water and to revaporize the water during the expansion cycle. During the expansion, the water may be pumped out as a vapor but not as a liquid. Called gas ballasting, this method alleviates the moisture condensation problem.

Diffusion Pumps. When the pressure in the vacuum chamber becomes so low and the molecules so few that the path typically traversed by a gas molecule exceeds the dimensions of the chamber, the remaining gas molecules collide more often with the walls than with each other. At higher pressures, the constant and frequent collisions of adjacent gas molecules and the resulting elastic rebounding effectively scatter and expand the gas such that it quickly fills any new volume created. At lower pressures, this effect nearly disappears, and the remaining gas is difficult to pump with fluid-flow positive-displacement mechanical pumps.

At these pressures, it is necessary to allow molecules to diffuse randomly into the throat of the pump, and to impart a preferred direction of motion to the molecules by momentum transfer. For pumping at a vacuum system level below 130 mPa (10^{-3} torr), a vapor diffusion pump is generally used. Pumping action is directed by a high-velocity stream of heavy molecules in the form of a pump fluid, usually oil. The heavy molecules strike the gas molecules and push them in the desired downward direction toward the outlet of the pump. To be effective, the inlet pressure of the diffusion pump should be below 130 mPa (1 μm Hg) so that the vapor stream is operating in nearly empty space except for the occasional diffusing gas molecule.

A diagram of a three-nozzle vapor diffusion pump is shown in Fig. 18. Vapor from a liquid held in a closed boiler heated at the bottom is forced upward inside the boiler. The vapor passes quickly at a downward angle through narrow, circumferential openings in the nozzles. Molecules of gas that stray from the vacuum chamber above the pump toward the vapor jet streaming from the nozzles encounter the downward-directed stream of heavy molecules. The overall effect is to compress the gas molecules and force them downward to a point at which they can be removed by the mechanical forepump.

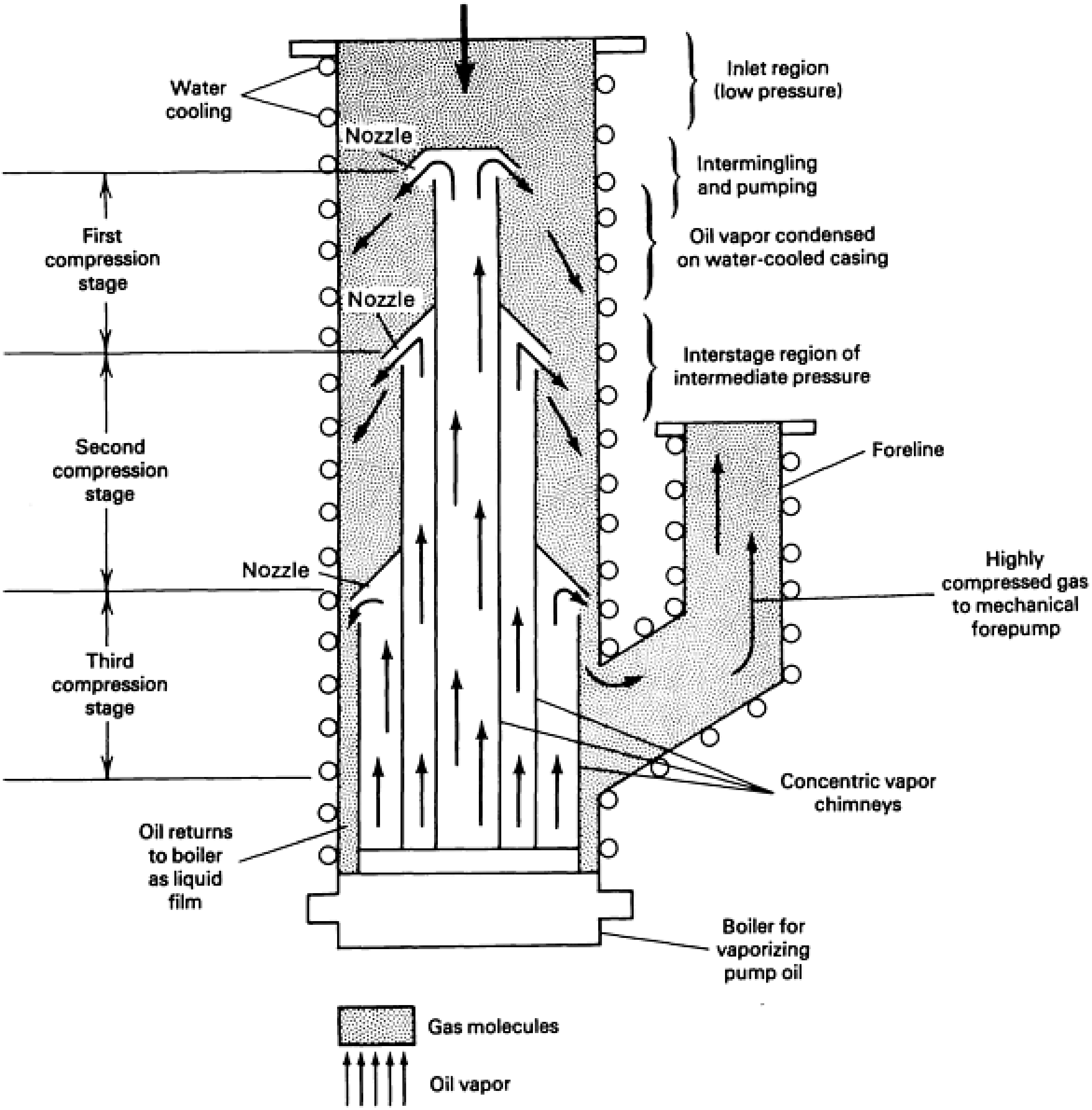

Fig. 18 Oil vapor diffusion pump

Pump vapor is condensed on the cooled inner walls of the pump and returns as a liquid to the boiler. Maximum velocity is imparted to the gas molecules by using a liquid composed of heavy molecules in the boiler. Efficiency is improved by using several nozzles in line, one above the other. Special highly stable liquids with very low vapor pressure are required for such diffusion pumps.

Backstreaming is the movement of the molecules of the pump fluid above the inlet flange of the diffusion pump and in the direction of the vacuum chamber. The rate of backstreaming increases rapidly as the inlet pressure exceeds 130 mPa (1 μm Hg) and depends on the size and type of diffusion pump. Backstreaming can also be caused by exceeding the fore pressure limit, which is about 65 Pa (500 μm Hg), of most diffusion pumps. Backstreaming can be reduced by interposing opaque baffles between the diffusion pump throat and the vacuum chamber. Most backstreaming originates at the top jet of the pump and can be reduced by placing a water-cooled cap above the jet. The oil vapor condenses on the cap and drips back into the pump.

By using a cold trap placed above the throat of the diffusion pump, it is possible to reduce oil backstreaming further. The cold trap consists of an arrangement of baffles and water-cooled or refrigerant-cooled walls that provide an opaque path through the trap. A refrigerant such as liquid nitrogen may be used. Molecules of oil condense on the surface of the cooled baffle and remain trapped. Such traps also attract condensable vapors that may be present in the vacuum chamber.

Water vapor, the most common contaminant present in high-vacuum systems, may be removed successfully in this way. The capability of the trap to serve as a pump for condensable vapors increases as the temperature of the refrigerant decreases.

Other Pumping Systems. Many types of vacuum pumps may be used, depending on the pressure to be maintained for a given vacuum process. The rotary mechanical pump and the oil vapor diffusion pump are typically used for most vacuum metallurgical processes. Other types of pumps include steam ejector, oil booster, liquid ring, turbomolecular, and cryogenic pumps. These pumps are used in vacuum processing for such functions as degassing and drying in conjunction with a rotary pump.

Steam ejector pumps have an operating range from 0.13 to 1.3 Pa (1 to 10 μm Hg). Although steam ejector pumps eliminate the need for a mechanical pump, they require a large volume of steam to operate. Because their principal advantage is the capability of removing large volumes of gas vapor at low vacuum levels, they are suitable for laboratory work and for very large vacuum vessels, especially if noxious vapors are to be pumped.

Oil booster pumps have an operating range from 130 to 0.13 Pa (1000 to 1 μm Hg) and require a backing pump. These pumps tend to introduce the excessive backstreaming of oil vapor into the vacuum vessel and are used mainly when high pumping capacities are desired above 1.3 Pa (10 μm Hg). They can be used in conjunction with an oil diffusion pump to achieve lower pressures while maintaining high pumping capacities.

Cryogenic pumps condense gas molecules on refrigerated surfaces at -195 °C (-320 °F) or lower. These pumps are regenerated periodically by heating the condensing surfaces to vent the accumulation of condensed gases. Cryogenic pumps are often used instead of diffusion pumps to pump high volumes of water vapor and other condensable gases in the 130 to 0.013 mPa (10^{-3} to 10^{-8} mm Hg) range. Cryogenic pumps capture the gas instead of pumping it. Consequently, they must be shut off occasionally for gas removal.

Gas Flow Valves. Gas flow of the vacuum pumping system is controlled by three specific types of valves, as shown in Fig. 19. High-vacuum valves isolate the oil diffusion pumps from the vessel, and butterfly and gate valves are used as roughing, foreline, and holding-line valves. All of these valves have apertures that provide minimal gas flow impedance and special seals for vacuum service.

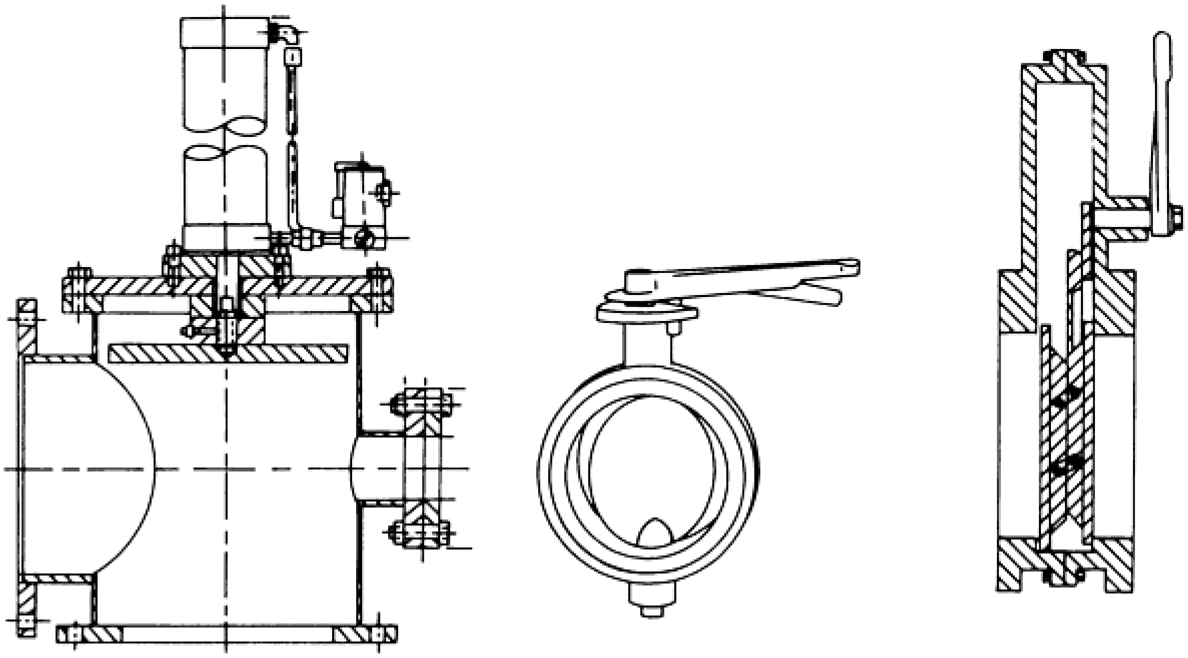

Fig. 19 Typical vacuum valves

Process Control Instrumentation

Except for vacuum-gaging instruments, the instruments used in vacuum equipment processing are similar to those used in other heat-treating operations. Once vacuum control has been attained, heating cycles can be initiated, either manually or automatically, by a temperature-sensing instrument.

Temperature Control Systems

Temperature control systems consist of a primary sensing device, the control instrument, and the final control element.

Pyrometers. The total radiation pyrometer is adaptable to automatic control, but its accuracy may be impaired by intervening media such as gas, smoke, or a discolored sight-glass window. Sublimation of materials within the furnace may cause the deposition of metallic vapors on the sight-glass window, thereby reducing the radiation reaching the detector.

Thermocouples are typically used as temperature-sensing devices, although their performance varies with the environment (from a vacuum to an oxidizing atmosphere). Unless the hot junction of the thermocouple is attached to the part being measured, heat transfer to the thermocouple is based almost completely on radiation. In air or other furnace atmosphere, a thermocouple receives heat by conduction and convection. For this reason, the response time of a thermocouple in a vacuum is slower than in air. A change in air gap of 0.03 mm (0.001 in.) between the hot junction of the thermocouple and the part being measured can change the response time of the thermocouple significantly.

Control thermocouples made from nickel-nickel molybdenum are satisfactory for many heat-treating applications up to 1290 °C (2350 °F) (see Table 6 and Fig. 20). Noble metal thermocouples such as platinum-platinum rhodium are used up to 1650 °C (3000 °F) (see Table 7 and Fig. 21). Refractory metal thermocouples such as those of tungsten-rhenium are used up to 2205 °C (4000 °F) (see Table 8 and Fig. 22). Thermocouples are sometimes used with unsheathed (bare wire) hot junctions, reducing lag time tremendously. In many applications, particularly with platinum, thermocouples are sheathed in an adequate ceramic or metal protection tube. Below 1095 °C (2000 °F), sheathed base-metal thermocouples can be used to measure different locations in the load.

Table 6 Properties of 19 alloy/20 alloy nonstandard thermocouple

Property	**Thermoelement**	
	Negative 19 alloy	**Positive 20 alloy**
Nominal composition	Ni-1Co	Ni-18Mo
Melting point, °C (°F)	1450 (2640)	1425 (2595)
Specific gravity	8.9	9.1
Thermal conductivity, W/m · K (Btu · in./ft^2 · h · °F) at 20 °C (68 °F)	50 (350)	15 (105)
Coefficient of thermal expansion, μm/m · K (μin./in. · °F) (20 to 100 °C, or 68 to 212 °F)	13.6 (7.56)	11.9 (6.62)
Magnetic susceptibility	Magnetic	Magnetic
Resistivity, nΩ · m at 20 °C (68 °F)	80	1650
Temperature coefficient of resistance, μΩ/Ω · °C (20 to 100 °C, or 68 to 212 °F)	3050	290

Tensile strength, MPa (ksi)	415 (60)	895 (130)
Yield strength, MPa (ksi)	170 (25)	515 (75)
Elongation, %	35	35

Table 7 Properties of standard thermocouples

Type	Thermo-elements	Base composition	Melting point		Resistivity, nΩ · m	Recommended service	Maximum temperature	
			°C	°F			°C	°F
K	KP	90Ni-9Cr	1350	2460	700	Oxidizing	1260	2300
	KN	94Ni-Al, Mn, Fe, Si, Co	1400	2550	320			
R	RP	87Pt-13Rh	1860	3380	196	Oxidizing or inert	1480	2700
	RN	Pt	1769	3216	104			
S	SP	90Pt-10Rh	1850	3362	189	Oxidizing or inert	1480	2700
	SN	Pt	1769	3216	104			
B	BP	70Pt-30Rh	1927	3501	190	Oxidizing, vacuum, or inert	1705	3100

Table 8 Properties of tungsten-rhenium thermocouples

	Thermocouple type		
	W versus W-26Re	W-3Re versus W-25Re	W-5Re versus W-26Re
Nominal operating temperature range, °C (°F)(a)	2760 (5000)	2760 (5000)	2760 (5000)
Maximum short-time temperature, °C (°F)	3000 (5430)	3000 (5430)	3000 (5430)
Approximate thermoelectric output, μV/°C (μV/°F)			

Mean, over nominal operating range 0 to 2315 °C (32 to 4200 °F)	16.7 (9.3)	17.1 (9.5)	16.0 (8.9)
At 2315 °C (4200 °F)	12.1 (6.7)	9.9 (5.5)	8.8 (4.9)
Nominal melting temperature, °C (°F)			
Of positive thermoelement	3410 (6170)	3360 (6080)	3350 (6062)
Of negative thermoelement	3120 (5648)	3120 (5648)	3120 (5648)
Stability with thermal cycling	Good	Good	Good
High-temperature tensile properties	Good	Good	Good
Stability under mechanical working	Fair	Fair	Fair
Ductility (of most brittle thermoelement) after use	Poor	Poor to good depending on degree of vacuum	Poor to good depending on degree of vacuum
Resistance to handling contamination	Good	Good	Good
Extension wire	Available	Available	Available

(a) Preferential vaporization of rhenium may occur when bare (unsheathed) couple is used at high temperatures and high vacuum. Vapor pressure of rhenium at operating temperature and vacuum should be checked before bare couple is used.

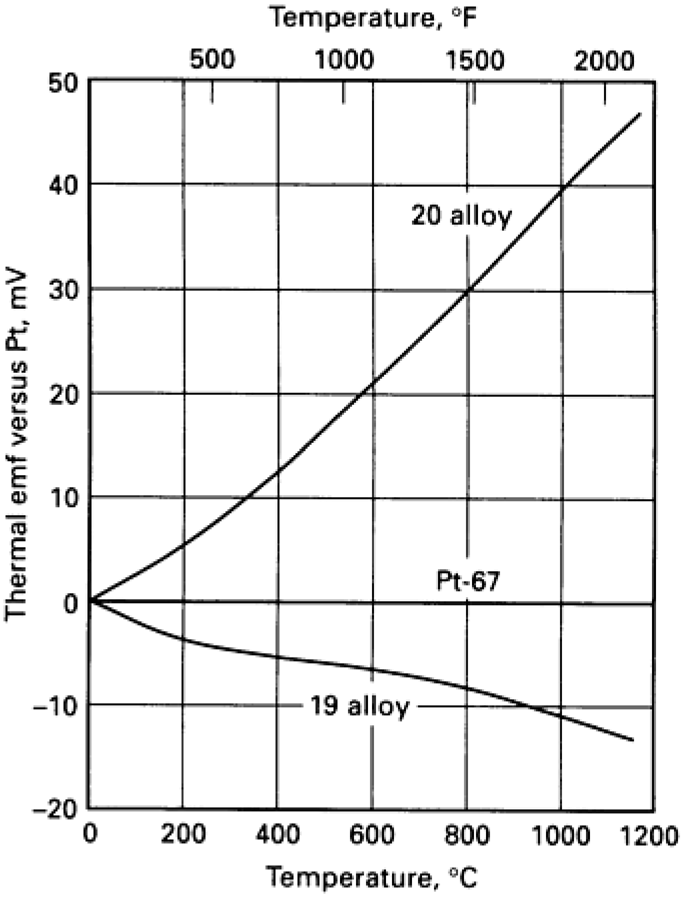

Fig. 20 Thermal electromotive force (emf) of 19 alloy and 20 alloy versus Pt-67

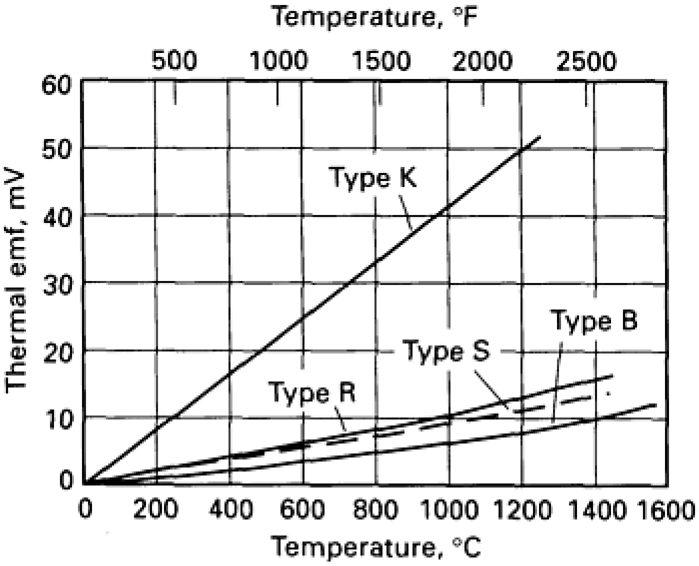

Fig. 21 Thermal emf curves for Instrument Society of America (ISA) standard thermocouples. Thermal emf plots are based on the International Practical Temperature Scale (IPTS) 1968 (amended 1975).

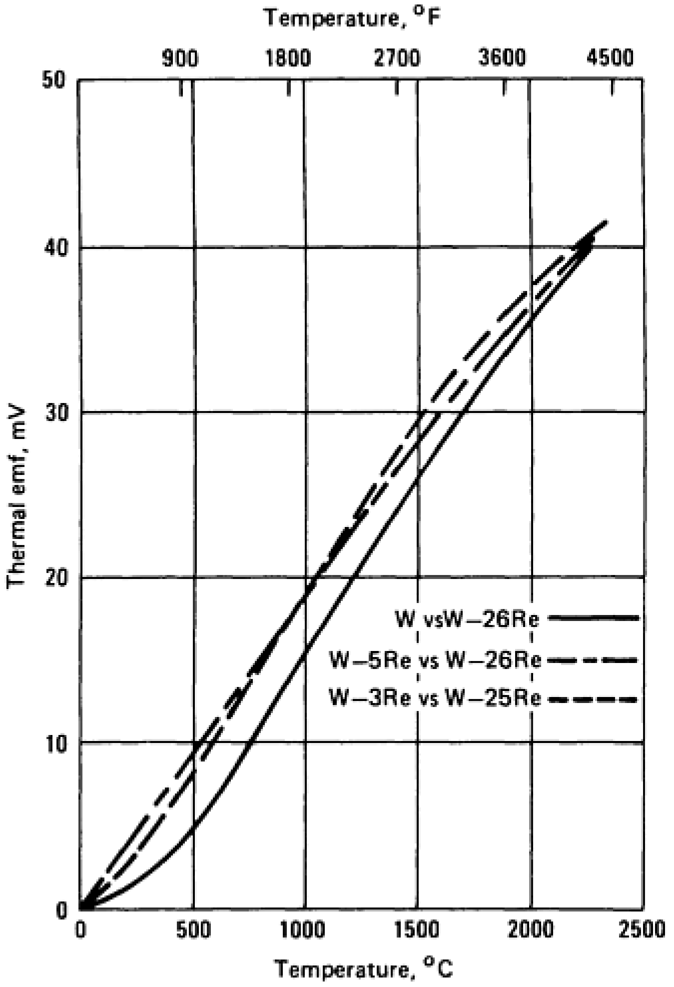

Fig. 22 Thermal emf of tungsten-rhenium thermocouples

Because rapid heating rates can be achieved in most vacuum furnaces, it is important to determine temperatures at various locations in the work load. For instance, a large die may overheat in certain locations within the furnace. Information on heating uniformity is also required when processing smaller parts loaded in baskets.

To bring thermocouple lead wires through the exterior shell of the furnace, special feed-through fixtures are provided. These fixtures are electrically insulated and vacuum tight, and they constitute a permanent portion of the furnace. The ends of the lead wires inside the furnace have ceramic-insulated quick-disconnecting terminals to which workpiece thermocouples can be connected. Type K chromel-alumel thermocouples are often used to monitor workpieces if the temperature to be measured is not above 1175 °C (2150 °F) and the time at temperatures above 980 °C (1800 °F) is not excessively long (see Table 7 and Fig. 21).

Additional information is available in the article "Furnace Temperature Control" in this Volume.

Pressure Control Systems

Instruments used to measure and record the pressure inside a vacuum processing chamber fall into two classifications: those that measure the pressure hydrostatically, and those that sense some physical characteristic of the gas that bears a definite relationship to the pressure.

Hydrostatic Measuring Devices. The Bourdon pressure gage and the McLeod gage are two hydrostatic measuring devices.

The Bourdon gage (Fig. 23) accurately and continuously indicates the pressure from 100 kPa (1 atm) to approximately 1 kPa (0.01 atm) and can be used effectively to monitor the roughing cycle and the performance of the roughing pump.

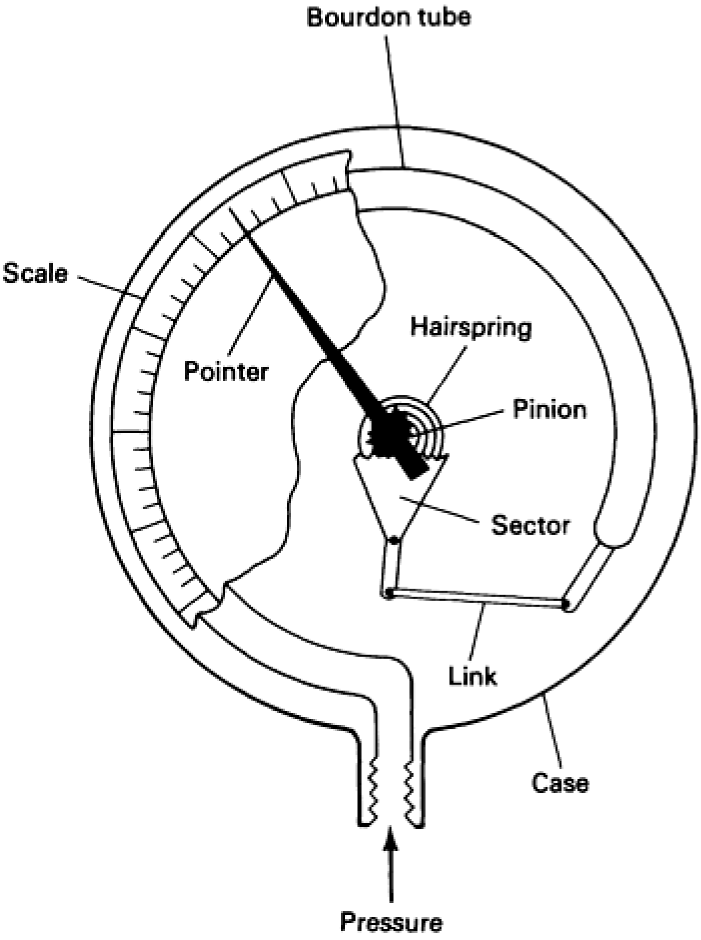

Fig. 23 Spriral Bourdon tube gage

McLeod Gage. Special, expensive diaphragm gages are available for measuring pressures continuously from atmospheric pressure down to approximately 13 mPa (10^{-4} torr). Pressures from a few torr down to 13 mPa (10^{-4} torr) can be measured periodically with a McLeod gage (Fig. 24), which samples the gas and compresses it to a small, calibrated volume. It then registers the ratio of the initial and final volumes, and this ratio is an indication of the pressure at which the gas sample was taken. McLeod gages are manual units that are usually used to monitor the accuracy of other gages.

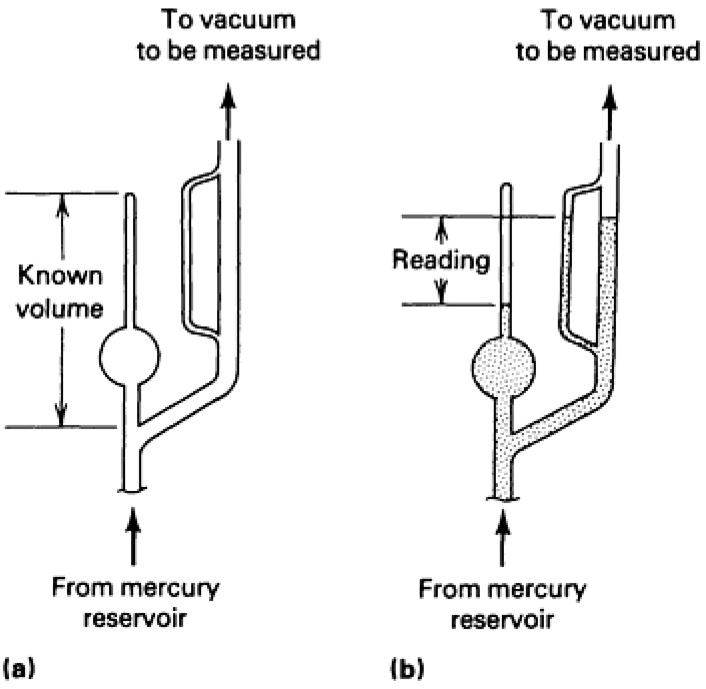

Fig. 24 McLeod gage. (a) In filling (charging) position. (b) In measuring position

Thermal and Electrical-Conductivity Measuring Devices. The second classification of gages includes those that sense the thermal and electrical conductivity of the gas. These physical characteristics bear a direct relationship to pressure and to the specific type of gas.

The thermal-conductivity gages are widely used for most vacuum metallurgical processing because they are relatively inexpensive and can continuously monitor vacuum levels between 130 and 0.13 Pa (1 and 10^{-3} torr). The thermal conductivity, or convective heat transfer, of a gas is essentially constant as pressure is reduced until a pressure of about 130 Pa (1 torr) is reached. From that point, the conductivity declines until, at a pressure somewhat less than 0.13 Pa (10^{-3} torr), there is almost no heat transfer by the gas molecules to the surface of the gage walls, and thermal conductivity becomes virtually 0. This trend is shown for a typical common gas in Fig. 25.

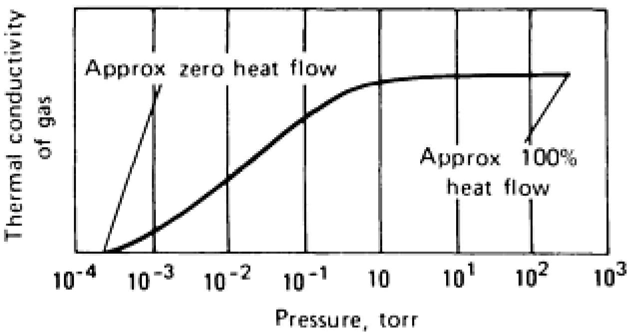

Fig. 25 Relationship between the thermal conductivity of gas and pressure

Thermal conductivity varies considerably from 0.13 to 130 Pa (10^{-3} to 1 torr), but varies little above that pressure; this behavior constitutes the operational principle of the thermal-conductivity gage. Two gages use this principle, the thermocouple and the Pirani.

The radiation or thermocouple gage is based on the principle that, as the amount of gas in a vessel decreases, the temperature of a constantly heated wire increases because less heat is radiated to the surrounding environment. The thermocouple gage is the most commonly used measuring device used with vacuum furnaces.

Wire temperature is measured by a fine wire thermocouple attached to the midpoint of the heated wire. The maximum temperature of the wire is about 115 °C (240 °F), a temperature reached at pressures of 130 mPa (1 μm Hg) or less. A typical thermocouple gage is shown in Fig. 26. Advantages of this gage are:

- Circuitry and tubes are comparatively inexpensive
- It samples temperature continuously
- Because of the relatively low wire temperature, it can be exposed to air for years without damage or danger of burnout
- The signal can be used to activate relays or other remote controls

Disadvantages of this gage are:

- Because different gases have different thermal-conductivity values, the gage requires calibration for each type of gas
- The scale is markedly nonlinear; at low pressures, the marks on the scale are spread widely; in higher ranges, the marks are closely spaced (Fig. 25)
- Output depends somewhat on the ambient temperature of the tube
- The useful range is from 0.13 to 130 Pa (1 to 1000 μm Hg)

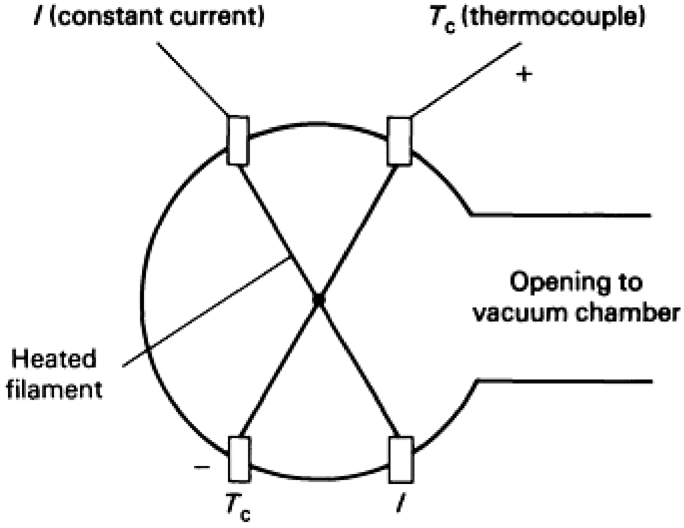

Fig. 26 Thermocouple-type thermal-conductivity vacuum gage

The Pirani gage (Fig. 27) uses the same thermal conductivity principle as the radiation or thermocouple gage. Operation is based on the change of heat conductivity of a gas with pressure and the change of electrical resistance of a wire with temperature. When the wire is electrically heated with a constant current, its temperature changes with pressure, producing a voltage across the bridge network. The compensating cell corrects for changes in room temperature. The vacuum pressure is thus measured in terms of the bridge imbalance. The system is somewhat more expensive and complicated than the thermocouple gage, with essentially the same advantages and disadvantages.

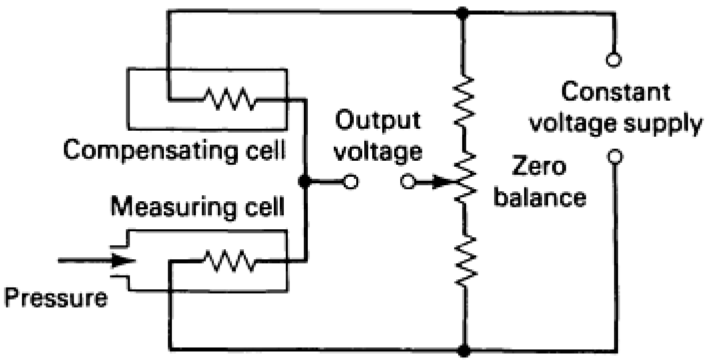

Fig. 27 Schematic of a Pirani gage

Hot-Filament Ionization Gage. The thermocouple and Pirani gages do not measure pressures of less than 0.13 Pa (1 μm Hg); therefore, a different type of gage is necessary for systems operating below this level. For vacuums from 130 mPa to 0.13 μPa (10^{-3} to 10^{-9} torr), the hot-filament ionization gage can be used. The sensing element of the gage resembles a triode vacuum tube. Figure 28 shows the three elements of a hot-filament ionization gage. A heated filament emits electrons that are attracted to the loosely wound and positively charged grid. The electrons strike residual molecules of gas in the vacuum. These collisions may remove an electron from the gas molecule, resulting in a positively charged gas ion, which is attracted to the collector. The positive ion current flow from the collector to ground is a measure of the gas pressure or vacuum.

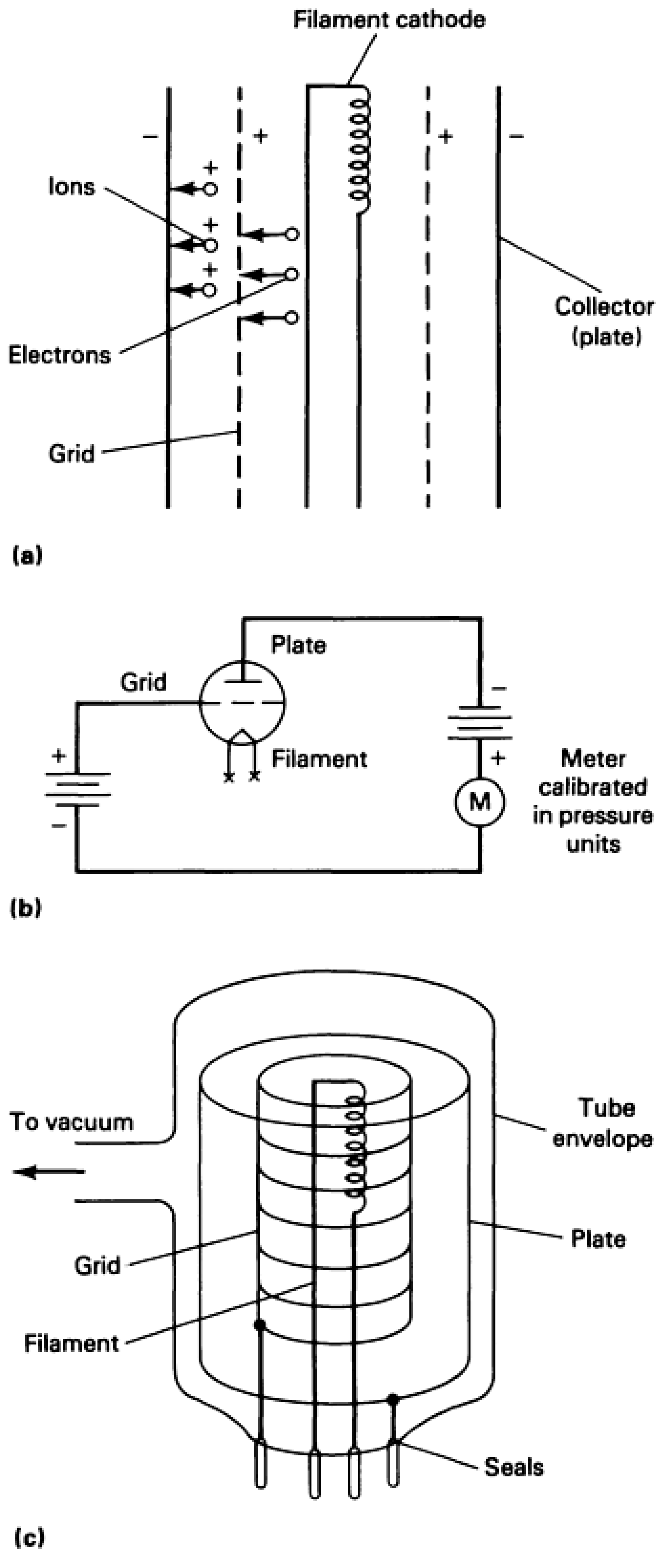

Fig. 28 Components of a hot-filament ionization gage. (a) Movement of electrons and ions in relation to filament cathode. (b) Simplified electrical circuit of the device. (c) Typical gage construction. A tungsten or thoria-coated filament cathode emits a current of approximately 5 mA. The electrons are accelerated toward a cylindrical grid operated at approximately 150 V.

The glass ionization gage, which originated in the radio tube industry, is usually calibrated with dry nitrogen. Its response varies slightly with other gases, and this must be considered when great accuracy is required. The filament can deteriorate, with a resulting loss of accuracy and subsequent burnout.

Cold-Cathode Ionization Gage. Another type of ion gage is the cold-cathode gage (Fig. 29), which depends on the measurement of an ion current produced by a high-voltage discharge. The cathode in the sensing element releases electrons that spiral through a magnetic field toward the anode. This spiralling motion lengthens the distance that electrons travel between cathode and anode, increasing the probability of collision with gas molecules and the formation of positive ions. The formation of ions varies linearly with pressure, and the ion current indirectly indicates the pressure. These rugged gages are well suited for production applications. They cannot be degassed as easily, however, and they are more readily contaminated and less accurate than hot-filament gages. Output is linear below 130 mPa (10^{-3} torr), and the usable range for measuring vacuum is between 1300 and 0.13 mPa (10^{-2} and 10^{-6} torr).

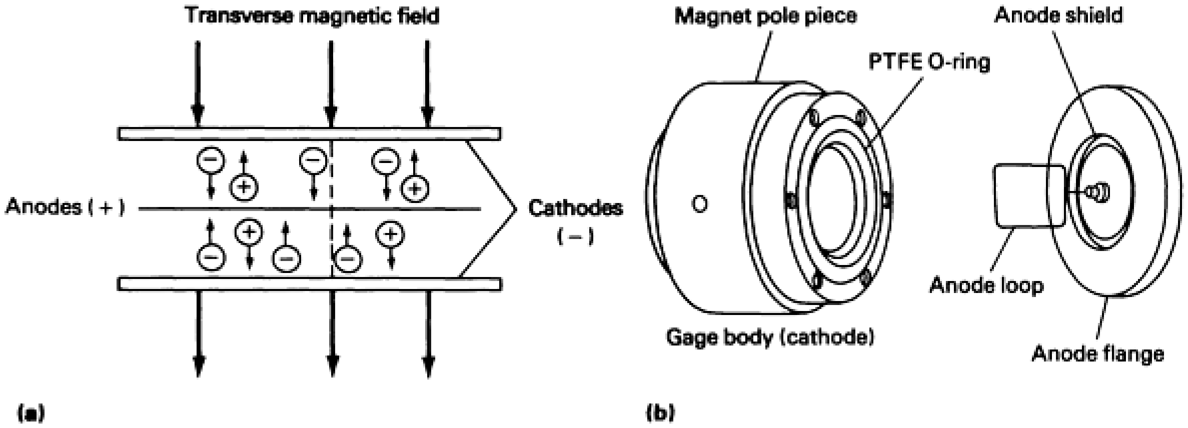

Fig. 29 Components of a cold-cathode discharge gage. (a) Movement of electrons in relation to magnetic field. (b) Typical gage construction showing cathode body and anode flange. PTFE, polytetrafluoroethylene

Whether the ionization gage is the hot-filament or the cold-cathode type, vacuum gas is used for vacuum pressures below 130 mPa (10^{-3} torr).

Heat-Resistant Materials for Heat-Treating Furnace Parts, Trays, and Fixtures

Revised by G.Y. Lai, Haynes International, Inc.

Introduction

TRAYS AND FIXTURES made of heat-resistant alloys are among the many parts used in industrial heat-treating furnaces that operate at temperatures from 540 to 1200 °C (1000 to 2200 °F). Coverage of heat-resistant structural materials may be found in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook*, together with room-temperature and high-temperature mechanical properties.

Basic Metallurgy and Product Forms

A partial list of typical products can be divided into two categories: The first consists of parts that go through the furnaces and are therefore subjected to thermal and/or mechanical shock; these include trays, fixtures, conveyor chains and belts, and quenching fixtures. The second comprises parts that remain in the furnace with less thermal or mechanical shock; these include support beams, hearth plates, combustion tubes, radiant tubes, burners, thermowells, roller and skid rails, conveyor rolls, walking beams, rotary retorts, pit-type retorts, muffles, recuperators, fans, and drive and idler drums.

These heat-resistant alloys are supplied in either wrought or cast forms. In some situations, they may be a combination of the two. The properties and costs of the two forms vary, even though their chemical compositions are similar. Because

there are many foundries and fabricators experienced in the design and application of these products, it is important to seek their advice when purchasing high-alloy parts.

Five types of heat-resistant alloys are listed in Vol 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook*:

- Iron-chromium alloys
- Iron-chromium-nickel alloys
- Iron-nickel-chromium alloys
- Nickel-base alloys
- Cobalt-base alloys

The great majority of heat-treating furnaces use only the second and third types because the iron-chromium alloys do not have sufficient high-temperature strength to be useful. Some iron-chromium alloys (more than 13% Cr) are susceptible to so-called 475 °C (885 °F) embrittlement. Because of increasing temperatures (for example, >980 °C, or 1800 °F), more and more applications use nickel-base alloys because of their improved creep-rupture strengths and oxidation resistance. Cobalt-base alloys are generally too expensive except for very special applications. Therefore, this discussion will be limited to the use and properties of the iron-chromium-nickel, iron-nickel-chromium, and nickel-base alloys.

Room-temperature mechanical properties have limited value when selecting materials or designing for high-temperature use, but they may be useful in checking the quality of the alloys. These properties are shown in Vol 1 and also may be found in ASTM specification A 297. The useful high-temperature properties of these alloys are summarized in Table 1 for castings and Table 2 for wrought products. The tables include nominal composition of the alloys and the stress required to produce 1% creep in 10,000 h and rupture in 10,000 h and 100,000 h, at temperatures of 650, 760, 870, and 980 °C (1200, 1400, 1600, and 1800 °F). A design stress figure commonly used for uniformly heated parts not subjected to thermal or mechanical shock is 50% of the stress to produce 1% creep in 10,000 h, but this should be used carefully and should be verified with the supplier.

Table 1 Composition and elevated-temperature properties of selected cast heat-resistant alloys

Grade	UNS number	Approximate composition, %			Temperature		Creep stress to produce 1% creep in 10,000 h		Stress to rupture in 10,000 h		Stress to rupture in 100,000 h	
		C	Cr	Ni	°C	°F	MPa	ksi	MPa	ksi	MPa	ksi
Iron-chromium-nickel alloys												
HF	J92603	0.20-0.40	19-23	9-12	650	1200	124	18.0	114	16.5	76	11.0
					760	1400	47	6.8	42	6.1	28	4.0
					870	1600	27	3.9	19	2.7	12	1.7
					980	1800	. . .	. . .	. . .	. . .	. . .	. . .
HH	J93503	0.20-0.50	24-28	11-14	650	1200	124	18.0	97	14.0	62	9.0
					760	1400	43	6.3	33	4.8	19	2.8

					870	1600	27	3.9	15	2.2	8	1.2
					980	1800	14	2.1	6	0.9	3	0.4
HK	J94224	0.20-0.60	24-28	18-22	650	1200	. . .	. . .	. . .	. . .	. . .	. . .
					760	1400	70	10.2	61	8.8	43	6.2
					870	1600	41	6.0	26	3.8	17	2.5
					980	1800	17	2.5	12	1.7	7	1.0
Iron-nickel-chromium alloys												
HN	J94213	0.20-0.50	19-23	23-27	650	1200	. . .	. . .	. . .	. . .	. . .	. . .
					760	1400	. . .	. . .	. . .	. . .	. . .	. . .
					870	1600	43	6.3	33	4.8	22	3.2
					980	1800	16	2.4	14	2.1	9	1.3
HT	J94605	0.35-0.75	15-19	33-37	650	1200	. . .	. . .	. . .	. . .	. . .	. . .
					760	1400	55	8.0	58	8.4	39	5.6
					870	1600	31	4.5	26	3.7	16	2.4
					980	1800	14	2.0	12	1.7	8	1.1
HU	. . .	0.35-0.75	17-21	37-41	650	1200	. . .	. . .	. . .	. . .	. . .	. . .
					760	1400	59	8.5	. . .	. . .	. . .	. . .
					870	1600	34	5.0	23	3.3	. . .	. . .
					980	1800	15	2.2	12	1.8	. . .	. . .
HX	. . .	0.35-0.75	15-19	64-68	650	1200	. . .	. . .	. . .	. . .	. . .	. . .
					760	1400	44	6.4	. . .	. . .	. . .	. . .

					870	1600	22	3.2	. . .	. . .	. . .	. . .
					980	1800	11	1.6	. . .	. . .	. . .	. . .

Note: Some stress values are extrapolated.

Table 2 Composition and elevated-temperature properties of selected wrought heat-resistant alloys

Grade	UNS number	Approximate composition, %				Temperature		Creep stress to produce 1% creep in 10,000 h		Stress to rupture in 10,000 h	
		C	Cr	Ni	Other	°C	°F	MPa	ksi	MPa	ksi
Iron-chromium-nickel alloys											
309S	S30908	0.08 max	22-24	12-15	. . .	650	1200	48	7.0	. . .	. . .
						760	1400	14	2.0	. . .	. . .
						870	1600	3	0.5	10	1.45
						980	1800	. . .	. . .	3	0.5
310S	S31008	0.08 max	24-26	19-22	. . .	650	1200	63	9.2	. . .	. . .
						760	1400	17	2.5	. . .	. . .
						870	1600	9	1.3	13.5	1.95
						980	1800	. . .	. . .	4	0.6
Iron-nickel-chromium alloys											
RA 330	N08330	0.08 max	17-20	34-37	. . .	760	1400	25	3.6	30	4.4
						870	1600	13	1.9	12	1.8
						980	1800	3.5	0.52	4.5	0.65
RA 330 HC	. . .	0.4 max	17-22	34-37	. . .	760	1400	47	6.8	54	7.8
						870	1600	18	2.6	18	2.6

						980	1800	5	0.7	5	0.7
RA 333	N06333	0.08 max	24-27	44-47	3 Mo, 3 Co, 3 W	760	1400	43	6.2	65	9.4
						870	1600	21	3.1	21	3.1
						980	1800	6	0.9	7	1.05
Incoloy 800	N08800	0.1 max	19-23	30-35	0.15-0.60 Al, 0.15-0.60 Ti	760	1400	19	2.8	23	3.3
						870	1600	4	0.61	12	1.7
						980	1800	1	0.23	6	0.8
Incoloy 802	N08802	0.2-0.5	19-23	30-35	. . .	760	1400	83	12.0	79	11.5
						870	1600	30	4.4	33	4.8
						980	1800	8	1.1	11.5	1.65
Nickel-based alloys											
Inconel 600	N06600	0.15 max	14-17	72 min	. . .	760	1400	28	4.1	41	6.0
						870	1600	14	2.0	16	2.3
						980	1800	4	0.56	8	1.15
Inconel 601	N06601	0.10 max	21-25	58-63	1.0-1.7 Al	760	1400	28	4.0	42	6.1
						870	1600	14	2.0	19	2.7
						980	1800	5.5	0.79	8	1.2

In general, these materials contain iron, nickel, and chromium as the major alloying elements. Carbon, silicon, and manganese also are present and affect the foundry pouring and rolling characteristics of these alloys, as well as their properties at elevated temperature. Nickel influences primarily high-temperature strength and toughness. Chromium increases oxidation resistance by the formation of a protective scale of chromium oxide on the surface. An increase in carbon content increases strength.

Since the mid to late 1970s, a number of heat-resistant wrought alloys have been developed and are now being used in the heat-treating industry. Some of these alloys, such as Haynes alloys 230 (UNS N06230) and 556 (UNS R30556) and Inconel alloy 617 (UNS N06617), were originally developed for gas turbines, which require alloys with high creep-rupture strengths, good oxidation resistance, good fabricability, and good thermal stability. These alloys, commonly

referred to as solid-solution-strengthened alloys, use molybdenum and/or tungsten for strengthening. The alloys are also strengthened by carbides. Another high creep strength alloy, originally developed for gas turbine combustors, is Incoloy alloy MA 956, which is strengthened by oxide dispersion. This alloy is produced by a mechanical alloying process, using the high-energy milling of metal powders. These wrought heat-resistant alloys, along with chemical compositions and major characteristics, are tabulated in Table 3.

Table 3 New heat-resistant wrought alloys developed from about 1975 to 1990

Alloy	UNS number	Composition, wt%								Major characteristics
		Fe	Ni	Co	Cr	Mo	W	C	Other	
253 MA[(a)]	S30815	Bal	11	. . .	21	. . .	. . .	0.08	1.7 Si, 0.17 N, 0.04 Ce	Oxidation resistance
RA85H[(b)]	S30615	Bal	14.5	. . .	18.5	. . .	. . .	0.2	3.6 Si, 1.0 Al	Carburization resistance
Fecralloy A[(c)]	. . .	Bal	. . .	. . .	15.8	. . .	. . .	0.03	4.8 Al, 0.3 Y	Oxidation resistance
HR-120[(d)]	. . .	Bal	37	. . .	25	. . .	. . .	0.05	0.7 Nb, 0.2 N	Creep-rupture strength
556[(d)]	R30556	Bal	20	18	22	3	2.5	0.1	0.6 Ta, 0.2 N, 0.02 La	Creep-rupture strength
HR-160[(d)]	. . .	2	Bal	29	28	. . .	. . .	0.05	2.75 Si	Sulfidation resistance
214[(d)]	. . .	3	Bal	. . .	16	. . .	. . .	0.05	4.5 Al, Y (present)	Oxidation resistance
230[(d)]	N06230	. . .	Bal	. . .	22	2	14	0.1	0.005 B, 0.02 La	Creep-rupture strength/oxidation resistance
Inconel 617[(e)]	N06617	1.5	Bal	12.5	22	9	. . .	0.07	1.2 Al	Creep-rupture strength/oxidation resistance
Incoloy MA	. . .	Bal	. . .	. . .	20	. . .	. . .	. . .	0.5 Y_2O_3, 4.5 Al,	Creep-rupture strength/oxidation

(a) 253 MA is a registered trademark of Avesta Jernverks Aktiebolag.

(b) RA85H is a registered trademark of Rolled Alloys, Inc.

(c) Fecralloy A is a trademark of UK Atomic Energy.

(d) HR-120, HR-160, 556, 214, and 230 are trademarks of Haynes International, Inc.

(e) Inconel and Incoloy are registered trademarks of Inco family of companies.

All of the alloys commonly used in castings for furnace parts have essentially an austenitic structure. The iron-chromium-nickel alloys (HF, HH, HI, HK, and HL) may contain some ferrite, depending on composition balance. If exposed to a temperature in the range of 540 to 900 °C (1000 to 1650 °F), these compositions may convert to the embrittling σ phase. This can be avoided by using the proper proportions of nickel, chromium, carbon, and associated minor elements. Chromium and silicon promote ferrite, whereas nickel, carbon, and manganese favor austenite. Use of the iron-chromium-nickel types should be limited to applications in which temperatures are steady and are not within the σ-forming temperature range. Transformation from ferrite to σ phase at elevated temperature is accompanied by a change from ferromagnetic material and from a soft to a very hard, brittle material. All heat-resistant alloys of the iron-nickel-chromium group are wholly austenitic and are not as sensitive to composition balance as is the iron-chromium-nickel group. Also, the iron-nickel-chromium alloys contain large primary chromium carbides in the austenitic matrix and, after exposure to service temperature, show fine, precipitated carbides. The iron-nickel-chromium alloys are considerably stronger than the iron-chromium-nickel alloys and may be less expensive per part if the increased strength is considered when designing for a known load.

The life expectancy of trays and fixtures is best measured in cycles rather than hours, particularly if the parts are quenched. It may be cheaper to replace all trays after a certain number of cycles to avoid expensive shutdowns caused by wrecks in the furnace. Chains or belts that cycle from room temperature to operating temperature several times a shift will not last as long as stationary parts that do not fluctuate in temperature. Parts for carburizing furnaces will not last as long as those used for straight annealing.

Finally, alloy parts represent a sizable portion of the total cost of a heat-treating operation. Alloys should be selected carefully, designed properly, and operated with good controls throughout to keep costs at a minimum.

Material Comparison for Heat-Resistant Cast and Wrought Components

The selection of a cast or fabricated component for furnace parts and fixtures depends primarily on the operating conditions associated with heat-treating equipment in the specific processes, and secondarily on the stresses that may be involved. The factors of temperature, loading conditions, work volume, rate of heating, and furnace cooling or quenching need to be examined for the operating and economic trade-offs. Other factors that enter into the selection include furnace and fixture design, type of furnace atmosphere, length of service life, and pattern availability or justification.

Some of the factors affecting the service life of alloy furnace parts, not necessarily in order of importance, are alloy selection, design, maintenance procedures, furnace and temperature control, atmosphere, contamination of atmosphere or work load, accidents, number of shifts operated, thermal cycle, and overloading. High-alloy parts may last from a few months to many years, depending on operating conditions. In the selection of a heat-resistant alloy for a given application, all properties should be considered in relation to the operating requirements to obtain the most economical life.

If either cast or wrought alloy fabrications can be used practically, both should be considered. Similar alloy compositions in cast or wrought form may have varying mechanical properties, different initial costs, and inherent advantages and disadvantages. Castings are more adaptable to complicated shapes, and fabrications to similar parts, but a careful comparison should be made to determine the overall costs of cast and fabricated parts. Initial costs, including pattern or tooling costs; maintenance expenses; and estimated life are among the factors to be included in such a comparison. Lighter-weight trays and fixtures will use less fuel in heating. Cast forms are stronger than wrought forms of similar chemical composition. They will deform less rapidly than wrought products, but may crack more rapidly under conditions of fluctuating temperatures. Selection should be based on the practical advantages, with all facts considered.

General Considerations. Both cast and wrought alloys are well accepted by the designers and users of furnaces requiring high-temperature furnace load-carrying components. Heating elements are also manufactured in either cast or wrought form (Fig. 1).

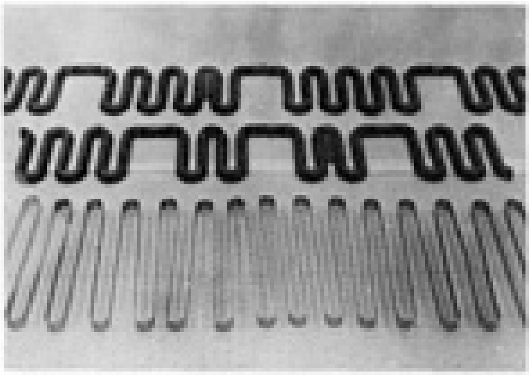

Fig. 1 Cast grid heating element (top) and ribbon heating element (bottom). Courtesy of the Electric Furnace Company

There are certain advantages for each type of manufactured component; often, the compositions are similar, if the carbon and silicon levels in the castings versus the wrought material are ignored. In general, the specifications of the wrought grades have carbon contents below 0.25%, and many are nominally near 0.05% C. In contrast, the cast alloys have from 0.25 to 0.50% C. This difference has an effect on hot strength. The difficulty in hot working the higher-carbon alloys accounts for their scarcity in the wrought series. Castings and fabricated parts are not always competitive; each product has advantages, which include:

Advantages of cast alloys

- *Initial cost:* A casting is essentially a finished product as-cast; its cost per pound is frequently less than that of a fabricated item
- *Strength:* Similar alloy compositions are inherently stronger at elevated temperatures than are wrought alloys
- *Shape:* Some designs can be cast that may not be available in wrought form; also, even if wrought material is available, it may not be able to be fabricated economically
- *Composition:* Some alloy compositions are available only in castings; they may lack sufficient ductility to be worked into wrought material configurations

Advantages of wrought alloys

- *Section size:* There is practically no limit to section sizes available in wrought form
- *Thermal-fatigue resistance:* The ductility of the fine-grain microstructure of wrought alloys may promote better thermal fatigue resistance
- *Soundness:* Wrought alloys are normally free of internal or external defects; they have smoother surfaces that may be beneficial for avoiding local hot spots
- *Availability:* Wrought alloys are frequently available in many forms from stock

Shape, complexity, and number of duplicate parts (eventually affecting cost) usually determine the choice between casting or wrought part. Where section thickness and configuration permit, castings are usually cheaper. The cost per pound of the casting metal is comparable to that of a fabricated part. The total projected cost of the fabrication is usually higher because the cost of forming, joining, and/or assembling must be added to the cost of the material. However, when only one or two types of parts are to be made, the pattern cost precludes the use of a casting.

In energy-intensive heat-treating industries, the use of wrought fabrications allows fuel savings through reduced heat-treating time cycles. At the present level of energy costs, wrought fabrications may be economically preferable because of improvements in thermal efficiency.

Fabrications are preferred for thin sections and for parts where less weight or greater heat transfer may be required. Where thick walls are necessary for strength or where heavy loads are transported or pushed, the cost of fabricated sections may be prohibitive. Wrought materials have a greater degree of acceptance in fabricated baskets used under carburizing or carbonitriding conditions.

A factor that must be considered in evaluating castings and fabrications is the importance of good welding techniques, particularly for parts that are used in case hardening atmospheres. Castings have replaced fabricated products because of weld failures in multiwelded fabrications.

Although cast alloys exhibit greater high-temperature strength, it is possible to place too much emphasis on this characteristic in materials selection. Strength is rarely the only requisite and frequently is not the major one. More failures are due to brittle fracture from thermal fatigue than from stress rupture or creep. However, high-temperature strength is important where severe thermal cycling is required.

Specific Applications. Recommended alloy applications for parts and fixtures of various types of heat-treating furnaces, based on atmosphere and temperature, are summarized in Tables 4, 5, and 6. Where more than one alloy is recommended, each has proved adequate, although service life varies in different installations because of differences in exposure conditions.

Table 4 Recommended materials for furnace parts and fixtures for hardening, annealing, normalizing, brazing, and stress relieving

Retorts, muffles, radiant tubes		Mesh belts	Chain link		Sprockets, rolls, guides, trays	
Wrought	**Cast**	**Wrought**	**Wrought**	**Cast**	**Wrought**	**Cast**
595-675 °C (1100-1250 °F)						
430	HF	430	430	HF	430	HF
304		304	304		304	
675-760 °C (1250-1400 °F)						
304	HF	309	309	HF	304	HF
347	HH			HH	316	HH
309					309	
760-925 °C (1400-1700 °F)						
309	HH	309	314	HH	310	HH
310	HK	314	RA 330 HC	HL	RA 330	HK
253 MA	HT	253 MA	800H/800HT	HT	800H/800HT	HL

RA 330	HL	RA 330	HR-120		HR-120	HT
800H/800HT	HW					
HR-120						
600						
925-1010 °C (1700-1850 °F)						
RA 330	HK	314	314	HL	310	HL
800H/800HT	HL	RA 330	RA 330 HC	HT	RA 330	HT
HR-120	HW	600	802	HX	601	HX
600	HX	601	601		617	
601		214	617		X	
617			X		556	
X			556		230	
214			230			
556						
230						
1010-1095 °C (1850-2000 °F)						
601	HK	80-20	80-20	HL	601	HL
617	HL	600	617	HT	617	HX
X	HW	601	X	HX	X	
	HX	214	556		214	
556	NA22H		230		556	

230					230	
1095-1205 °C (2000-2200 °F)						
601	HL	601	601	HX	601	HL
617	HU	214	617		617	HX
230	HX		230		230	

Table 5 Recommended materials for parts and fixtures for carburizing and carbonitriding furnaces

Part	**815-1010 °C (1500-1850 °F)**	
	Wrought	**Cast**
Retorts, muffles, radiant tubes, structural parts	RA 330	HK
	800H/800HT	HT
	HR-120	HU
	600	HX
	601	
	617	
	X	
	214	
	556	
	230	
Pier caps, rails	RA 330	HT
	800H/800HT	
	HR-120	

	600	
	601	
Trays, baskets, fixtures	RA85H	HT
	RA 330	HT (Nb)
	800H/800HT	HU
	HR-120	HU (Nb)
	600	HX
	601	
	617	
HL	X	
HX	556	
	214	
	230	

Table 6 Recommended materials for parts and fixtures for salt baths

Process and temperature range	**Electrodes**	**Pots**	**Thermocouple protection tubes**
Salt quenching at 205-400 °C (400-750 °F)	Low-carbon steel	Low-carbon steel	Low-carbon steel, 446
Tempering at 400-675 °C (750-1250 °F)	Low-carbon steel, 446, 35-18[(a)]	Aluminized low-carbon steel, 309	Aluminized low-carbon steel, 446
Neutral hardening at 675-870 °C (1250-1600 °F)	446, 35-18[(a)]	35-18[(a)], HT, HU, Ceramic. 600, 556	446, 35-18[(a)]
Carburizing at 870-940 °C (1600-1720 °F)	446, 35-18[(a)]	Low-carbon steel[(b)], 35-18[(a)], HT	446, 35-18[(a)]
Tool steel hardening at 1010-1315 °C	Low-carbon steel[(c)], 446	Ceramic	446, 35-18[(a)], ceramic

(1850-2400 °F)			

Note: Where more than one material is recommended for a specific part and operating temperature, each has proved satisfactory in service. Multiple choices are listed in order of increasing alloy content (except ceramic parts).

(a) A series of alloys generally of the 35Ni-15Cr type or modifications that contain from 30 to 40% Ni and 15 to 23% Cr and include RA 330, 35-19, Incoloy, and other proprietary alloys.

(b) Immersed electrode furnaces only.

(c) Low-carbon steel is recommended for completely submerged electrodes only.

Typical Applications

Trays and Grids. Many parts to be heat treated are irregular in shape and as such must be conveyed through the continuous-heat-treating furnaces or loaded and unloaded from the batch furnaces on grids or trays (Fig. 2). These trays or grids must withstand exposure to the same furnace conditions as the product: They are subjected to repeated heating and cooling, as well as repeated compression and tensile loading. Heat-resistant alloys are used extensively for these parts, although there are instances in which dispensable carbon or low-alloy-steel fabricated trays are employed. In such instances, the choice is based on the economics of the particular situation, taking into account the cost of materials and the expected service life.

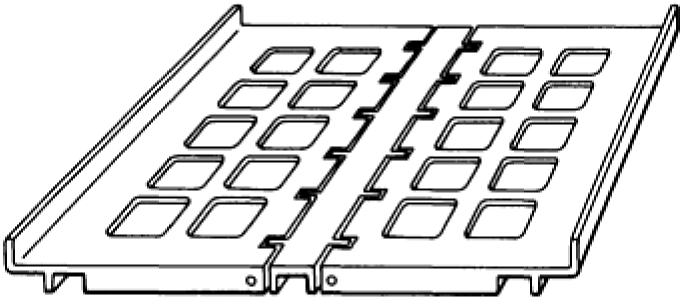

Fig. 2 Articulated tray for roller rail furnace

Two-thirds of the approximately 15 common heat-resistant alloy compositions find application in the heat-treating industry. Of these, half are recommended for use in trays and grids. The particular alloy chosen should be selected on the basis of required strength at temperature, ductility, and oxidation corrosion resistance.

Trays and grids made of austenitic stainless steels containing approximately 10% Ni may find an application at furnace temperatures of 650 to 870 °C (1200 to 1600 °F), but as the service temperature goes up, for example, to 1040 to 1150 °C (1900 to 2100 °F), an alloy with twice as much nickel would probably be selected. If the tray or fixture is to be subjected to the thermal shock of rapid heating and cooling, an even higher nickel content would probably be selected. The particular atmosphere surrounding the trays necessitates the consideration of varied amounts of chromium addition to enhance resistance to oxidation or high-temperature corrosion. If trays are to be used in an atmosphere with very high sulfur, an alloy with rather high chromium and moderate nickel would be selected. Some alloys contain relatively large amounts of silicon to fortify against carburization in carburizing applications (Fig. 3).

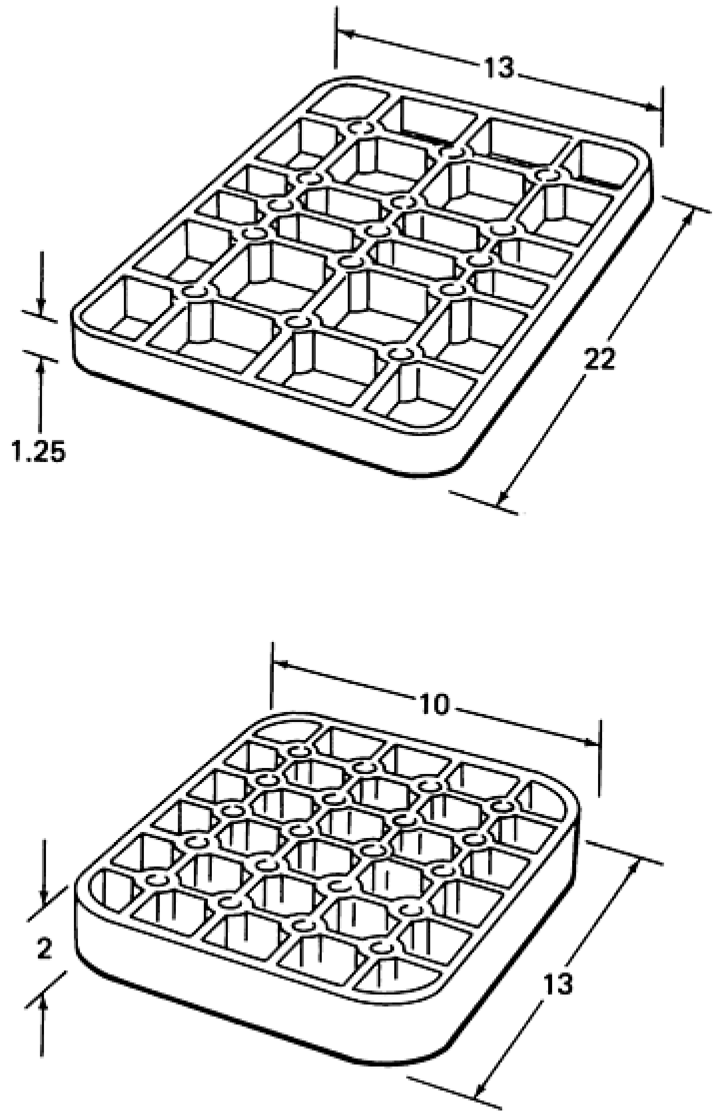

Fig. 3 Typical HT alloy carburizing furnace trays. Dimensions given in inches

Families of commercially available heat-resistant alloys provide sufficient selection so that an alloy that is optimized for each application and use can be specified. Alloy producers as well as vendors of trays and grids, both cast and fabricated, are an invaluable source of information regarding service life, design considerations, and fabrication. Generally, a tray or grid should be of sufficient section size to provide reasonable service life under specified loading conditions. An overly heavy tray may prolong service life, but the added energy cost to heat the tray through each cycle may offset any cost savings realized through added life. It is sometimes possible to combine materials in trays to provide sufficient strength yet maintain minimum weight. For example, in an articulated tray used in an extremely long pusher furnace, the tray grid that is subjected to the compressive force of the pusher bar is of a higher nickel content than are the vertical load supports that must bear the compressive load on a per-tray basis. This dual-alloy tray represents a compromise between weight, cost, and service life. In addition, service life is greatly affected by the tray-cooling process, and, in general, uniform section size throughout the tray is highly desirable to minimize thermal contraction/expansion stresses during cooling and heating.

All service conditions should be considered when selecting an alloy for trays and grids. Unlike furnace structural parts, a tray is subject to alternate heating and cooling during each cycle. The cooling can be rapid, as in quenching, or relatively slow, as in furnace-cooling applications. The selection of a proper alloy ensures adequate service life if all service conditions are known and considered.

Baskets and Fixtures. In many situations, parts being heat treated are of a size that does not permit them to be loaded directly on a furnace hearth, tray, or grid. They require some type of container, such as a basket. The design of these baskets varies because each product is developed for a specific application and loading and must function with a specific type of furnace equipment.

Baskets and fixtures can be produced from cast or wrought alloys. Fabricated parts are used in light-to-medium loading applications, intricate designs, complex shapes, and generally with lighter metal sections. Typically, these include the bar frame-type basket (Fig. 4) or corrugated box or shroud. In applications involving heavy loading and/or simple shapes and designs, cast alloys are commonly selected; typically they are large-pit-furnace baskets (Fig. 5).

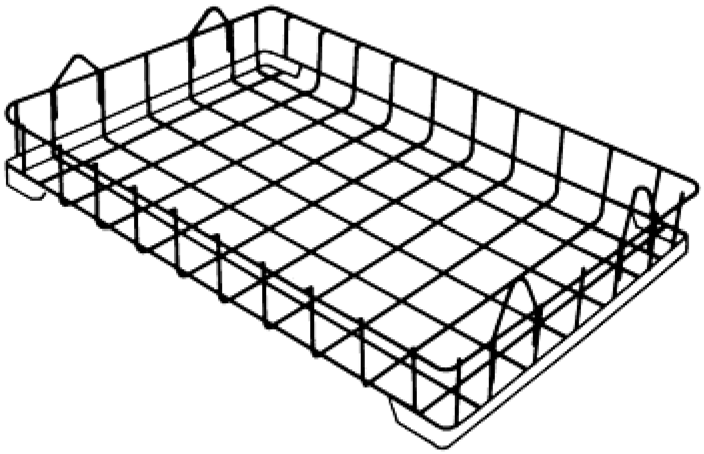

Fig. 4 Bar frame-type basket

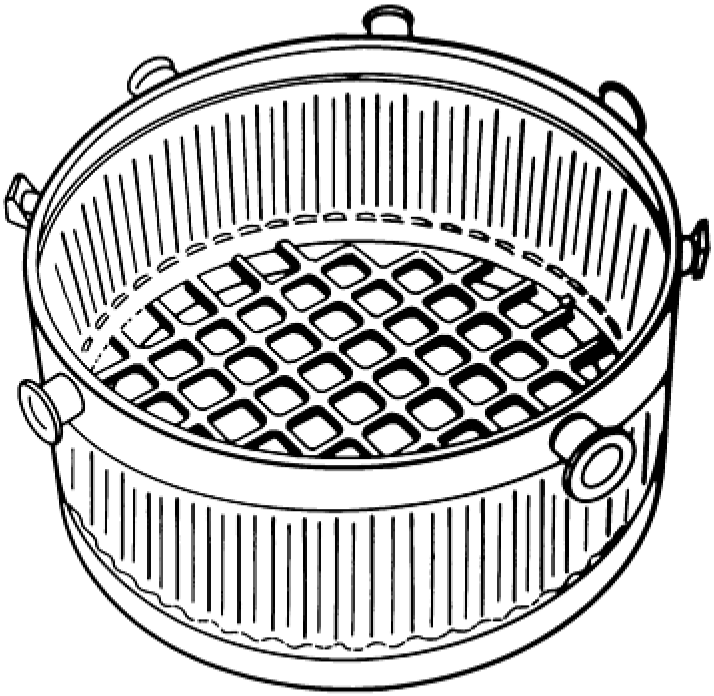

Fig. 5 Large-pit-furnace basket

In specific applications, a part may require special positioning. This is accomplished by using a fixture that is generally adaptable to an existing tray or grid or, in some instances, placed directly into a basket or container. These components can range from simple shapes, such as round, square, rectangular, or fluted bars, to extremely intricate shapes. Figures 6,

7, and 8 are examples of such fixtures. Figure 6 is a tray/fixture assembly used for carburizing pinions. Figure 7 was designed for heat treating lawn mower blades, and Fig. 8 was designed for heat treating shafts.

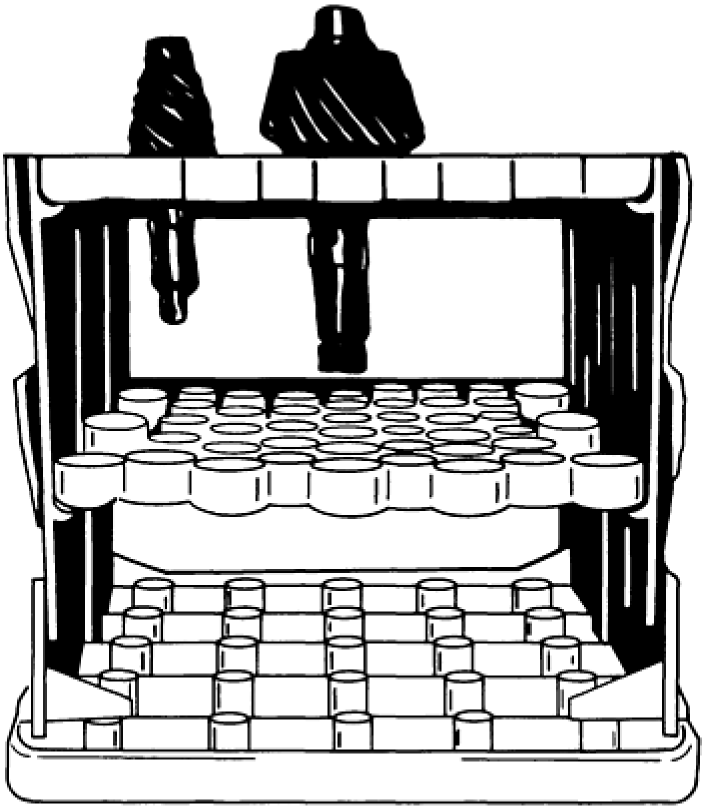

Fig. 6 Tray/fixture assembly for carburizing pinions

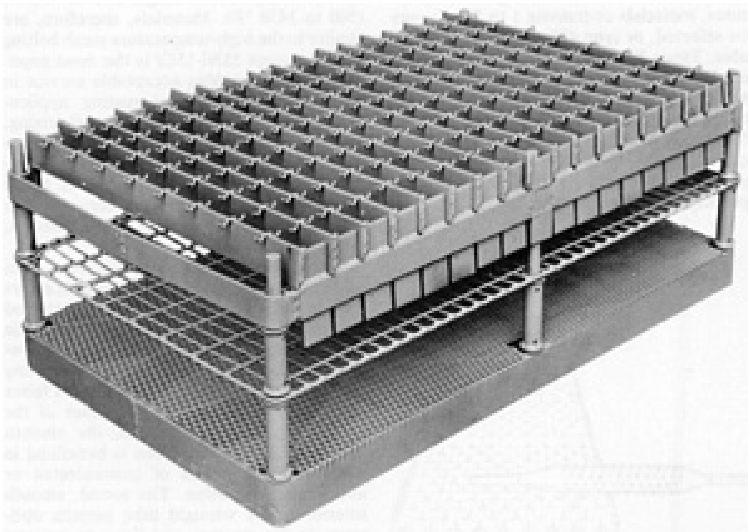

Fig. 7 Fixture designed for heat treating lawn mower blades

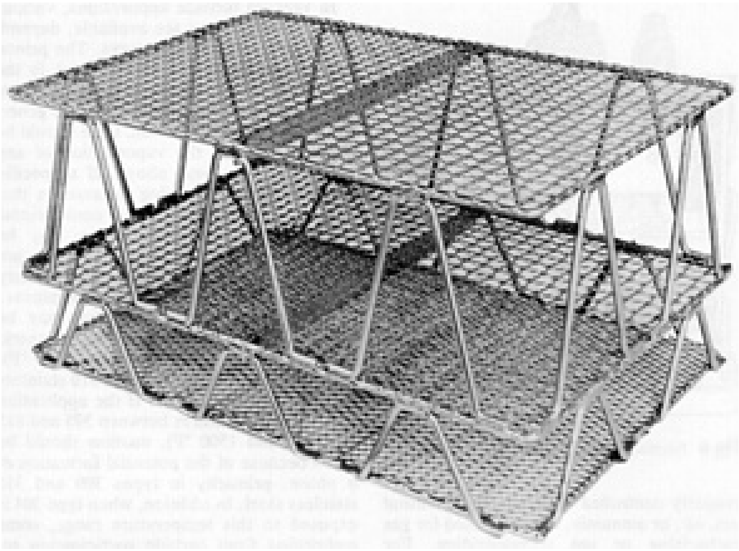

Fig. 8 Fixture designed for heat treating shafts

In most applications involving operating temperatures of 790 to 1010 °C (1450 to 1850 °F), the product is generally manufactured with a material having a nominal composition of 35Ni-15Cr, which provides a fully stable austenitic structure virtually free from any embrittling phases. In addition, it provides a reasonable cost-to-life ratio in applications involving endothermic, exothermic, and inert atmospheres even with properly controlled enrichments of natural gas, air, or ammonia, typically used for gas carburizing or gas carbonitriding. For quenching, a 35Ni-15Cr alloy provides acceptable life; however, in applications of severe quenching, higher-nickel alloys may be considered, depending on the cost-to-life ratio of the product. If applications involve higher temperatures, excessive oxidation, or carburization, consideration should be given to increasing the nickel-chromium content of the alloy. For nitriding, a higher nickel content provides the best cost-to-life ratio.

In vacuum furnace applications, various heat-resistant alloys are available, depending on operating temperatures. The principal controlling factor in this case is the creep-rupture strength of the alloy. A combination of distortion and warpage is generally the major failure mode. Care should be taken to prevent the vaporization of any element within these alloys. If a specific application has operating parameters that will not allow the use of a conventional alloy, molybdenum fabrications may be used, providing that air and oxygen are absent because catastrophic oxidation may become significant at higher temperatures.

For baskets and fixtures that may be restructured to lower-temperature operations of 260 to 595 °C (500 to 1100 °F), materials such as 304, 309, and 310 stainless steel may be acceptable. If the application involves temperatures between 595 and 815 °C (1100 and 1500 °F), caution should be taken because of the potential formation of σ phase, primarily in types 309 and 310 stainless steel. In addition, when type 304 is exposed to this temperature range, some embrittling from carbide participation results. Therefore, if the operating temperature is between 595 and 815 °C (1100 and 1500 °F), iron-nickel-chromium alloys, such as 35Ni-15Cr and 35Ni-20Cr, are generally suitable.

It should be noted that in the applications of baskets and fixtures, periodic straightening and rewelding can greatly enhance product life and improve the cost-to-life ratio.

Skid Rails, Hearth Components, and Rollers. Certain furnace parts are subjected to an additional service condition that must be considered when opting for a particular design or alloy selection. This group of parts includes components of the conveyance system in a continuous furnace that is subjected to wear as a result of interfacing with product or trays. Furthermore, this interfacing or wear occurs at elevated temperatures where alloy strength is diminished. The proper selection of an alloy for a specific high-temperature service involves consideration of many factors. One important factor is to avoid selecting the same composition for components that have sliding or rolling contact in order to minimize the possibility of galling or seizing. For example, when selecting an alloy to make skid rails (Fig. 9), it is necessary to consider whether the rail will be cooled and, if so, by what method; whether adequate expansion space has been specified; the amount of contact area present at the interface; and how the rail will be supported and at what

intervals. Thus, it can be inferred that the design of skid rails and selection of the alloy are an integral part of furnace design; the same principles apply to rollers and hearth components.

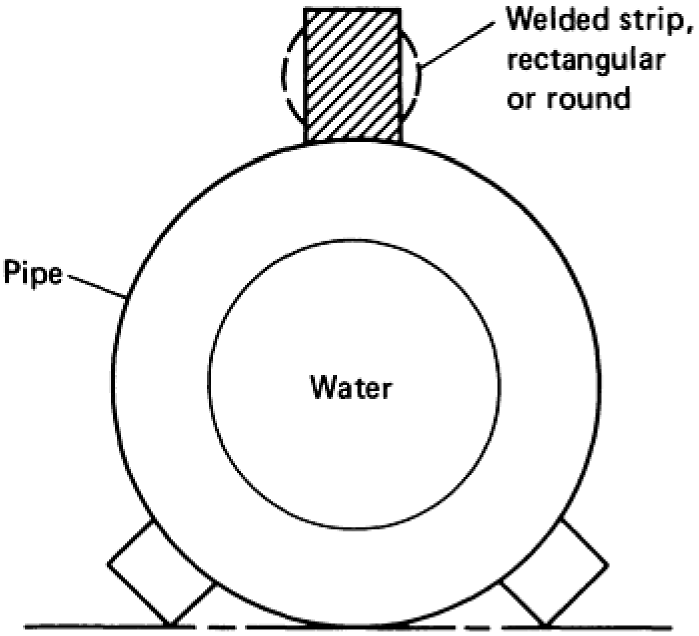

Fig. 9 Water-cooled skid pipe with welded strips

Perhaps the greatest single factor affecting a roller in a heat-treating-furnace application is the actual bearing or roller support of the roller. In roller hearth furnaces, the rollers protrude through the furnace walls, and the roller bearing can operate in a relatively reduced ambient temperature (Fig. 10). However, in some roller tray furnaces, the individual rollers operate within the furnace heated area, and the roller spindle or shaft must rotate on a roller support without aid of a precise, lubricated bearing. Hearth components are usually nonrotating or nonmoving parts and, in most situations, are well supported by refractory piers and/or ledges. Hearth components are almost always subjected to compressive loading, although they could on occasion be subjected to lateral thrust and/or bending. When selecting an alloy for these applications, it is necessary to consider the elevated-temperature mechanical properties required for the anticipated loading.

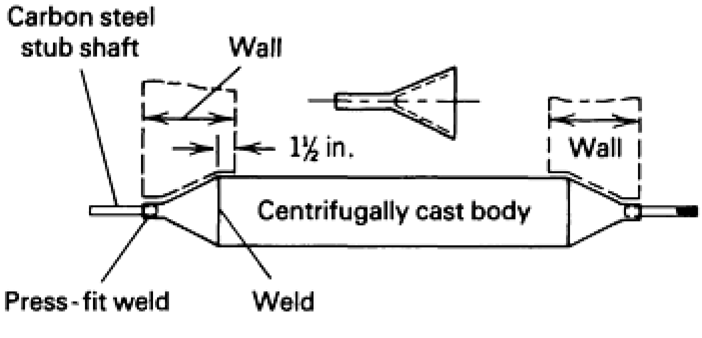

Fig. 10 Thin-walled furnace roller

Belting. Conveyor belts are used extensively in the design of furnaces used for the brazing, sintering, and hardening of carbonitriding applications. Woven belts or mesh belts are commonly used for light-duty loading, whereas cast link belts are designed for heavy-loading requirements. Figure 11 shows an assembled conveyor belt with a 100 mm (4 in.) pitch and the drive drum ready for installation.

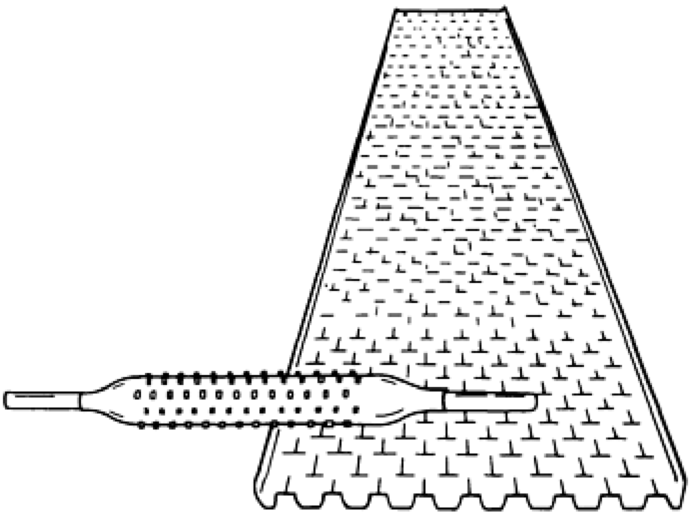

Fig. 11 Conveyor belt assembled with 100 mm (4 in.) pitch and drive drum ready for installation

When mesh belting is required for applications between 260 and 790 °C (500 and 1450 °F), medium-carbon steel (grades 1040 and 1055) can be selected for application up to 540 °C (1000 °F). For higher temperatures, materials containing 1 to 5% Cr may be selected, or type 430 stainless is acceptable. Types 304, 309, and 316 stainless steel tend to be susceptible to carbide participation or the formation of σ phase within this temperature range and therefore are not frequently selected. If stainless steel is required, type 347, which is stabilized with niobium and virtually free from carbide participation, may be selected.

Alloys commonly used for mesh belts in the temperature range of 790 to 1205 °C (1450 to 2200 °F) are 35Ni-15Cr; 80Ni-20Cr; type 314 stainless steel; and alloy 600, alloy 601, and 214 alloy, with the latter three nickel-base alloys servicing the high end of the temperature range (that is, 980 to 1205 °C, or 1800 to 2200 °F) The selection of the proper alloy is based on temperature, atmosphere, possible process contaminants, and cost-to-life ratios of the application. In addition to material selection, other key considerations for mesh belt applications are belt support, drive system, proper tension, and control of side travel.

In applications involving heavier loading, the cast link belt is often used. These applications tend to be in the temperature range of 790 to 1095 °C (1450 to 2000 °F) and not in the low-temperature range, 260 to 790 °C (500 to 1450 °F). Materials, therefore, are similar to the high-temperature mesh belting alloys, except 35Ni-15Cr is the most popular alloy. It provides acceptable service in most conventional heat-treating applications, such as hardening, gas carburizing, and gas carbonitriding. The cast links are generally assembled using a wrought 35Ni-15Cr alloy with a higher carbon level. In the application of cast link belts, consideration should be given to support, drive systems, tension, and side travel.

Radiant tubes can be manufactured from cast alloys or fabricated with wrought alloys and, in most applications, can be selected interchangeably depending on cost-to-life ratios. Fabrications may be selected because of the direct savings in fuel resulting from reductions in weight (fabricated tubes can weigh as much as one-quarter of the equivalent cast tubes). Also, the smooth surface of a fabricated tube is beneficial in avoiding focal points of concentrated or accelerated corrosion. The sound, smooth interior of the wrought tube permits optimum design stresses and helps to prevent the buildup of soot deposit. Figure 12 shows a typical U-shaped radiant tube used in carburizing furnaces. Some furnaces use a straight radiant tube.

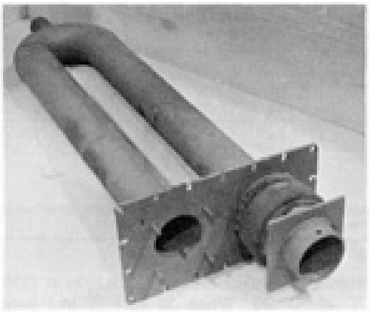

Fig. 12 U-shaped radiant tube

Wrought alloys for radiant tubes include type 309, type 310, RA 330 alloy, alloy 800H, alloy 601, 230 alloy, and 214 alloy. Most radiant tubes are fired with natural gas in the inner diameter. The inner diameter of the radiant tube is subject to oxidation. The outer diameter of the tube is exposed to the furnace atmosphere; thus, the furnace atmosphere can also influence the selection of alloys. For example, nickel-base alloys are preferred for nitriding atmospheres. However, nickel-base alloys are not recommended for use with gases having a high sulfur content.

In addition to temperature and atmosphere, consideration should be given to tube design for proper expansion and contraction, support for horizontal mounting, and burner positioning to prevent flame impingement. These considerations, as well as dissipation rates, affect service life as severely as the material selection.

Pots. Furnace design is the most important consideration in the selection of material for pots holding molten lead or salt. Externally heated pots act as a muffle or barrier between the heating and work zones. This type of service is severe because of the great difference between outside and inside temperatures, especially while the furnace is being heated to the operating temperature, when the outside of the pot is subjected to maximum heat input and the lead or salt it contains is still solid.

When the furnace is heated by immersed or submerged electrodes, the pot is completely sealed from the outside air, and the inside of the pot is protected by the molten bath. A pot in this type of installation lasts much longer than an externally heated pot. For environmental reasons, salt operations, such as those using cyanide salts, have diminished greatly. The most popular operations remaining generally involve neutral salt and lead. The specific alloy selected for pots used in salt operations is directly related to salt composition.

Pots are available in both cast alloys and fabricated wrought alloys. However, because the availability of cast pots has become somewhat limited, fabricated pots are more widely used. Carbon steel pots can be used within a temperature range of 260 to 540 °C (500 to 1000 °F). For applications between 540 and 815 °C (1000 and 1500 °F), type 309 stainless, 35Ni-15Cr, and higher-nickel alloys can be applied.

Electrodes. The choice of heat-resistant alloys used for electrodes depends chiefly on the type of furnace in which they are used. The most popular alloy for neutral salt pot electrodes is type 446 stainless steel. Immersed electrodes deteriorate rapidly along the line where the surface of the salt bath comes in contact with them. This is known as air-line attack. Submerged electrodes, entering the bath through the side of the furnace, are never exposed to air and last much longer. This type of electrode is used only with ceramic pots.

Electrodes deteriorate badly at the salt line during the start-up period. Better service is obtained by maintaining them at a temperature just above the freezing point of the salt during short pauses in operation. This practice not only prolongs the life of electrodes, but also eliminates the tedious task of starting a cold bath. Very little power is required to hold a well-insulated, unused furnace at about 700 °C (1300 °F).

Retorts and muffles are used in heat-treating furnaces to separate materials being heated from the products of combustion and, in some instances, to contain atmospheres that would otherwise escape through more porous containment vessels. In most situations, a muffle may be made either of metallic or nonmetallic materials. A typical D-shaped muffle with internal hearth is shown in Fig. 13.

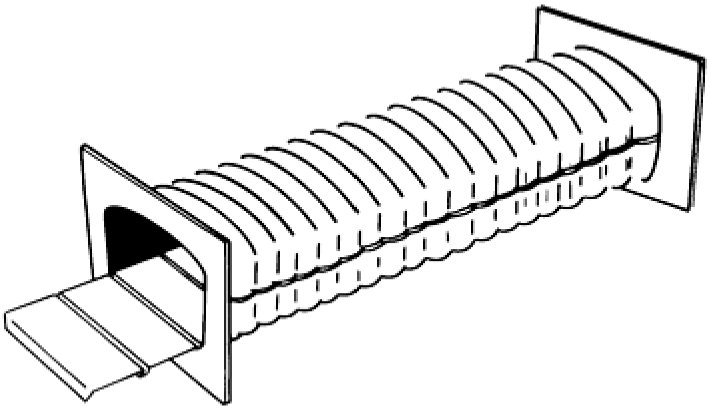

Fig. 13 Typical fabricated D-shaped muffle with internal hearth

Muffles are treated as a separate category of HT alloy applications. An important and different set of constraints apply because the heat necessary to raise the inside of a muffle to the proper process temperature is applied from without. Materials and designs must be selected that will not only withstand the rigors of furnace temperature and corrosion conditions, but will also not significantly prevent heat transfer. Designs must provide for expansion and contraction, be atmosphere tight, and provide maximum area for radiating surfaces because most muffles do not include internal recirculation features. For this reason, many cast or fabricated muffles are corrugated in design. This corrugated construction increases the radiating area while assisting in accommodating expansion and contraction as the muffle is cycled to and from operating temperature. Heat is transmitted by conduction to the inner-wall radiating surface of a muffle. In order to transfer heat, there must be a temperature drop across the wall of the muffle. The temperature drop is directly proportional to the thickness of the muffle wall. With heavy wall construction, the outside temperature must be raised to effect a given temperature within the muffle. Muffle material should be selected to provide a balance between alloy content (which represents strength), cost, and wall thickness.

Cost of any specific furnace part or fixture increases as the alloy content increases, although not necessarily in the same proportion as the base cost of the alloy. Some cost items will be approximately the same regardless of the type of alloy used.

To be meaningful, computations of cost for furnace parts and fixtures must be based on the number of hours of operation. In many instances, the more expensive alloys prove to be more economical. For example, service comparisons show that HU may be less expensive than HT for oil-quenched carburizing trays, and HW may be less expensive than HT for oil-quenched carburizing fixtures. On the other hand, some examples, such as brazing belts, show that the alloy of lower initial cost may also be less expensive when judged by cost per service hour.

From a practical standpoint, even cost-per-service hour data may be incomplete. Other factors should be considered for some components, notably the labor cost of replacement, the loss of productivity during downtime, and the possibility of damage to other components when failure occurs.

Nonmetallic Material Radiant Tubes (Ref 1, 2)

Silicon-silicon carbide composite radiant tubes having a density of 2.80 g/cm^3 (0.088 lb/in.^{3}) have undergone field trials in gas-fired indirect heating applications in a variety of atmospheres. One manufacturer installed these composite tubes in a pusher-type carburizing furnace in place of previously used mullite tubes in 1988 and the silicon-silicon carbides tubes were still operational after 26 months of continuous operation (24 1-h cycles/day at 980 °C (1800 °F). Another manufacturer indicates that the life expectancy of the silicon-silicon carbide tubes averaged 16 months while the life expectancy of the mullite tubes averaged 1 month.

These ceramic radiant tubes have been used in the following heat-treating processes:

- Annealing

- Carburizing
- Carbide solution treating
- Neutral hardening
- Carbonitriding
- Ferritic nitrocarburizing

Furnace atmospheres have included:

- Endothermic (both lean and rich)
- Carbon-enriched gases
- Ammonia-enriched gases
- Nitrogen
- Mixed endothermic and ammonia (50/50)

The composite radiant tubes are produced by using a moving hot zone (induction coil) to progressively melt the silicon and cause the particulate silicon to infiltrate the coarse-grained silicon carbide. The end product is a material that contains reaction-bonded silicon carbide grains in a silicon matrix. Tube composition is 53 wt% C and 47 wt% Si. An exothermic chemical reaction yields a composite material tube having excellent oxidation resistance, creep resistance, thermal shock resistance, and heat transfer properties.

Figure 14 demonstrates the results of a compression creep test run on tube sections of the silicon-silicon carbide composite material and a Ni-Cr-Fe alloy (8.51 g/cm^3, or 0.307 lb/in.^{3}, density). The Inconel 600 tube section actually melted after 1 h at 1350 °C (2460 °F) while the composite material showed no effect even after 2 weeks at 1350 °C (2460 °F). When 50 mm (2 in.) long samples of both materials were tested in compression for 2 weeks at 1200 °C (2190 °F), Inconel 600 showed 1.6% (0.79 mm, or 0.031 in.) creep while the silicon-silicon carbide composite creep was negligible at <0.03 mm (<0.001 in.).

Fig. 14 Comparison of high-temperature (1350 °C, or 2460 °F) creep testing of radiant tube sections. (a) Silicon-silicon carbide composite after 360 h. (b) Ni-Cr-Fe alloy after <1 h

Table 7 provides strength and fracture toughness data for the silicon-silicon carbide composite material at selected temperatures.

Table 7 Strength and fracture toughness properties of silicon-silicon carbide composite for radiant tubes used in gas-fired indirect heating applications

Temperature	Strength[a]		Fracture toughness
	C-ring configuration	O-ring configuration	

	MPa	ksi	MPa	ksi	MPa $\sqrt{m}$	ksi $\sqrt{in}$
RT[(b)]	58.7	8.52	59.8	8.67	2.09	1.90
1000	59.4	8.62	77.7	11.27	2.78	2.53
1250	69.6	10.10	92.6	13.43	. . .	. . .
1350	72	10.49	90.5	13.13	. . .	. . .

(a) Fracture stress is calculated on the basis of elastic beam theory, which is an overestimate of the actual fracture stress.

(b) RT, room temperature

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Energy-Efficient Heat-Treating Furnace Design and Operation

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Introduction

ENERGY EFFICIENCY AND COST of heat-treating operations are related concerns that are substantially affected by the method of converting stored energy into molecular kinetic energy (temperature) of the workpiece(s). In electric furnaces, for example, high relative efficiencies between 85 and 100% are feasible, but the cost of electric energy has a substantially higher rate than that of fuels such as natural gas. Consequently, gas-fired furnaces are often more economical than electric heating, even though their efficiencies (which can range from 5 to 70% depending on operating temperatures and furnace design) are generally lower than electric heating methods.

The sources of heat loss in fuel-fired furnaces result from flue losses and furnace losses (Fig. 1). Flue losses, which can be the most significant component of energy inefficiency, occur from either incomplete combustion or the loss of sensible heat due to the discharge of hot flue gas. Furnace losses depend on the particular furnace design and method of operation. For example, batch processing can be less efficient than continuous processing because the heating and cooling cycles require expenditure of unused energy. Other typical types of furnace losses are illustrated in Fig. 1. All forms of heat loss become more significant as furnace temperature increases.

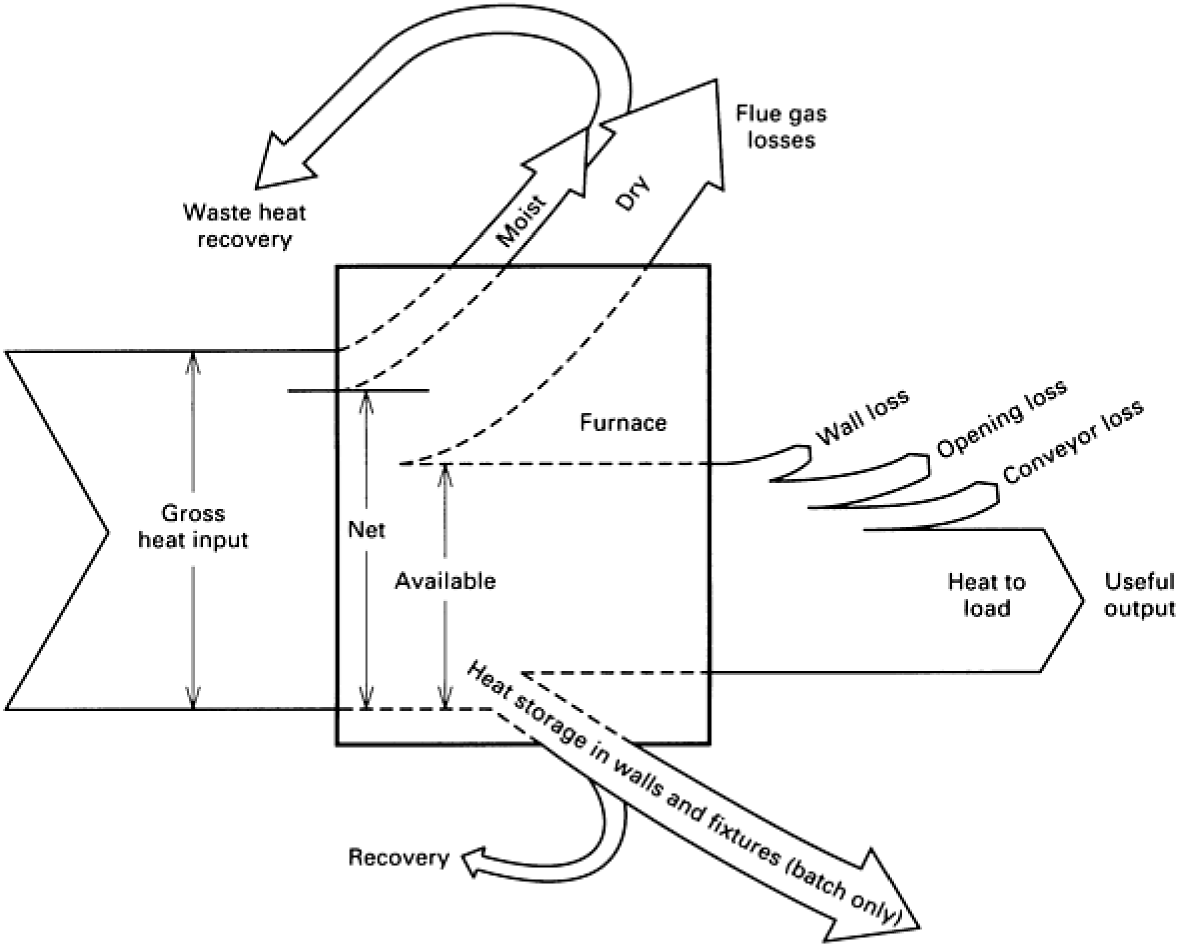

Fig. 1 Sankey diagram of heat loss in a fuel-fired furnace

This article briefly reviews some of the methods used to improve the efficiency of gas-fired furnaces. The methods are classified into three areas:

- Combustion control
- Waste-heat recovery
- Furnace design and operation

Of these methods, recovery of flue gas heat can have a significant impact on efficiency, particularly at higher temperatures. For example, if flue gases are discharged at 1300 °C (2400 °F) from a natural gas burner, about 70% of the energy input is lost in flue discharge. If incomplete combustion or an improper air/gas ratio occurs, then losses will be even higher. These losses can be reduced by recovery of heat from flue gases and/or improved combustion control.

At high furnace temperatures (≥ 1040 °C, or 1900 °F), electric heating may also become more effective because electric heating elements may require less maintenance than metallic radiant tubes. The higher relative efficiency of electrical heating may also be an advantage at higher temperatures. However, with advances in the technology of gas-fired heating, gas is becoming more competitive at higher temperatures. In particular, ceramic radiant tubes (reaction-bonded SiC) with recuperative burners can operate up to 1200 °C (2200 °F) with efficiencies of about 60%. High-alloy metallic tubes with regenerative burners also can provide economic life-cycle costs at higher temperatures.

Combustion Control

Combustion control is a basic factor in reducing flue losses, which are closely related to the fuel/air ratio prior to combustion. Too much excess air decreases efficiency because the energy expended to heat this air is wasted up the stack. Too little excess air results in fuel being unburned and also wasted up the stack. Consequently, the best efficiency theoretically occurs when the fuel/air ratio is closest to stoichiometric combustion conditions. In practice, however, some level of excess air is required to completely burn the fuel because of imperfect fuel/air mixing conditions in any commercial burner.

In most processes, efficiency is lost because the fuel/air ratio is too lean (too much excess air). The effect of this type of loss is shown in Fig. 2 in which the percent fuel required is plotted as a function of excess oxygen for several values of exhaust gas temperature. It is clear from this figure that the potential savings are greatest in high-temperature processes. For example, a reduction of excess oxygen from 6 to 5% for a process with 815 °C (1500 °F) exhaust gases produces a fuel savings of more than 5%.

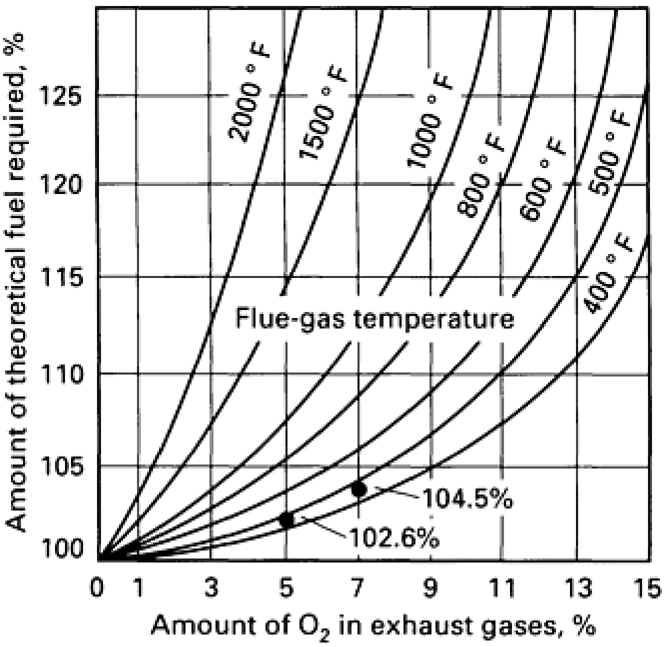

Fig. 2 Efficiency losses due to excess air in a typical gas-fired combustion process. Source: Ref 1

Control of Fuel/Air Ratio. There are two well-known methods of determining fuel/air ratios in gas-fired furnaces:

- Metering of gas and air flow rates into the furnace or burner unit
- Determining O_2 and CO content of flue gases

Currently flue gas analysis is becoming increasingly attractive with the availability of lower cost instruments, particularly oxygen analyzers. The sensor most widely favored for measuring O_2 uses a solid electrochemical zirconium oxide cell, which has an output directly related to the product of the absolute temperature and the logarithmic difference in the partial pressure of O_2 across the cell. One side of the cell is connected to a reference air supply that provides a quantified supply of oxygen ions. There are several methods of determining CO content, including a catalytic method that can be incorporated into the same assembly as the O_2 sensor. Because O_2 sensors have been prone to maintenance problems, flue gas analyzers are often supplemented with flow meters for backup.

The control of fuel/air ratios depends, in part, on whether the furnace provides direct heating of the workpiece or indirect heating with radiant tubes. Because direct heating involves the exposure of workpieces to the hot flue gases, the control of fuel/air ratios in direct heating furnaces may be slightly on either the oxidizing side or the reducing side of stoichiometric conditions depending on the application. In the iron and steel industry, for example, slab reheating furnaces are supposed to be run at about 1% excess oxygen to avoid tight scaling on the surface. Other processes must be run slightly on the

reducing side to avoid oxidation. For heat treating of steel and copper, direct heating furnaces are controlled at or near stoichiometric conditions to avoid oxidation.

Depending on the specific combustion process, the optimum oxygen content in terms of efficiency is 1 to 3% excess O_2. The optimum value of CO is in the range of 200 to 250 ppm. (As a regulated pollutant, however, 60 ppm of CO is an industry standard.) For combustion on the reducing side, efficiency drops off more rapidly than for combustion on the oxidizing side for an equal change in the fuel/air ratio (Fig. 3). Therefore, if a reducing atmosphere is required, then indirect heating with radiant tubes may be more efficient because the combustion process could be run more efficiently near the oxidizing side of stoichiometric conditions.

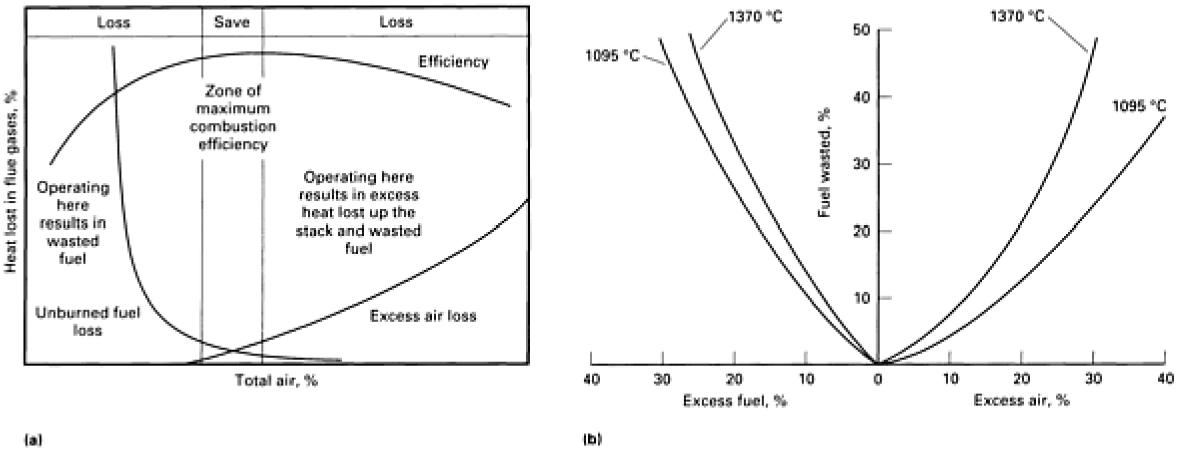

Fig. 3 Effects of excess air or fuel on combustion efficiency. (a) General effect on efficiency. (b) Effect on percent of fuel wasted

Heat transfer from the combustion flame is due to a combination of convection and radiation in the flue gases. With natural gas flames, for example, heat transfer by radiation is low because of the transparent nature of natural gas flame. Therefore, convection of flue gases is an important factor in both direct-fired and indirect-fired gas furnaces. Efforts to increase the heat transfer of combustion flames also include increasing the flame temperature with a preheat of combustion air (see the sections on recuperators and regenerative burners in this article).

High-velocity burners represent a recent development to improve convective heat transfer in direct-fired furnaces. The use of high-velocity burners create vigorous circulation of gases in the furnace and thereby promote uniform heat transfer. A small number of high-velocity burners therefore provides an efficient alternative to burner arrays, which require individual adjustment of a large number of burners so as to achieve uniform heating.

A potential limitation of high-velocity burners is that the circulating flow diminishes when the burners are turned down. Using excess air (to reduce temperature and increase the velocity of circulating) also leads to a reduction in thermal efficiency. Therefore, pulse firing can be useful in achieving lower temperatures and adequate circulation without resorting to the use of excess air (see the section "Pulse Firing" in this article).

Heat Transfer in Radiant Tubes. When a controlled furnace atmosphere is required, indirect heating is performed with radiant tubes. Inside the tube, heat transfer to the tube surface is governed by radiation and convection. Improvements in heat transfer inside radiant tubes can be attained by the use of axial fins (Ref 2).

Pulse techniques include two distinct methods known as pulse firing and pulse combustion. Pulse firing involves on-off cycling of burners, while pulse combustion is a resonant technique that depends on oscillations in a suitably designed combustion container.

Pulse firing is a method of controlling temperature by cycling the fuel or fuel/air supply so that a burner is either off or operating at full capacity. Temperature is thus controlled by varying the frequency of the on-off cycle, which typically has a period of about 3 to 6 s. This method of frequency modulation differs from conventional combustion control, which involves the control of heating by varying the amplitude of the flame.

Pulse firing has several advantages such as:

- Improved efficiency because fuel burns more effectively with maximum flame velocity
- Turndown ratios as high as 20:1 or even 30:1 as compared to a typical turndown ratio of 8:1 in an amplitude controlled system
- Improved convective heat transfer from the turbulence created by pulsing

Pulse firing also has other potential benefits, depending on the particular firing practice and furnace. In direct-fired furnaces, for example, pulse firing allows the reduction in the operating temperature of high-velocity burners without the addition of excess air. Pulse firing thus allows improved energy efficiency, which is the main motivation for its use in high-velocity burners.

In other applications, pulse firing can have other advantages that are more important than improved energy efficiency. In radiant tubes, for example, the pulsing provides more uniform heating of the tube and promotes the extension of tube life. The high turndown ratios also provide better furnace control. If energy efficiency of radiant tubes is a concern, pulse firing can be incorporated with regenerative burners (see Example 1 in this article).

Pulse Combustion. The basic principle of pulse combustion involves the enhancement of heat transfer by creating oscillation of gas flow within the combustion system. This oscillation follows a pattern of periodic combustion, which in many cases can have a cycling frequency up to 150 Hz. Specific advantages of pulse combustors include: ability to burn various fuels; high combustion intensities; low NO_x formation; low excess air requirements; and self aspiration, which eliminates the need for compressors or fans to pump the air and combustion products through the system. Additionally, the presence of pulsations in the exhaust flow enhances the rates of mass, momentum, and heat transfer in the process.

To date, pulse combustors have been utilized in such applications as drying, steam raising, water heating, and domestic space heating (Ref 3). In heat treatment furnaces, however, there are some potential drawbacks of pulsed combustion. One disadvantage is that the furnace (or combustion chamber) must be designed around the burner so that oscillations are sustained adequately. The heat-transfer enhancement resulting from the pulsations will also decrease as distance from the pulse combustor discharge is increased. The greatest heat transfer enhancement occurs within the combustor and is related to the acoustic intensity. The pressure and velocity fluctuations decrease as the gases expand outward from the discharge of the system. There is not an extensive body of data on the pressure and velocity fluctuations downstream from the combustor, but there are some indications that the pressure levels may decease by 3 to 5 dB within 3 m (10 ft) of the outlet (Ref 4).

Nevertheless, radiant tube burners might be a potential application of pulse combustion technology. In this application, the benefit of pulse combustion would be to improve convective heat transfer from the burner to the tube. A theoretical estimate relates heat transfer enhancement with tube efficiency (Ref 5). Another possible advantage is reduced NO_x emissions, which may be a more important factor with future environmental restrictions.

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Recovery of Waste Heat

Recovery of waste heat is a basic objective that can be implemented in a variety of ways. Waste heat can be used to heat water, or it can even be used to generate electricity. The main objective, however, is the most efficient utilization of the waste heat for the given energy needs of a particular plant.

This section focuses exclusively on the use of recuperators and regenerative burners for the preheating of combustion air with hot flue gases. Preheating combustion air improves combustion efficiency (Fig. 4) and is common to many fuel-fired furnaces. Other recovery methods depend on the specific plant operations. For example, the heat stored in a batch furnace can be partially recovered to preheat another batch furnace or another load.

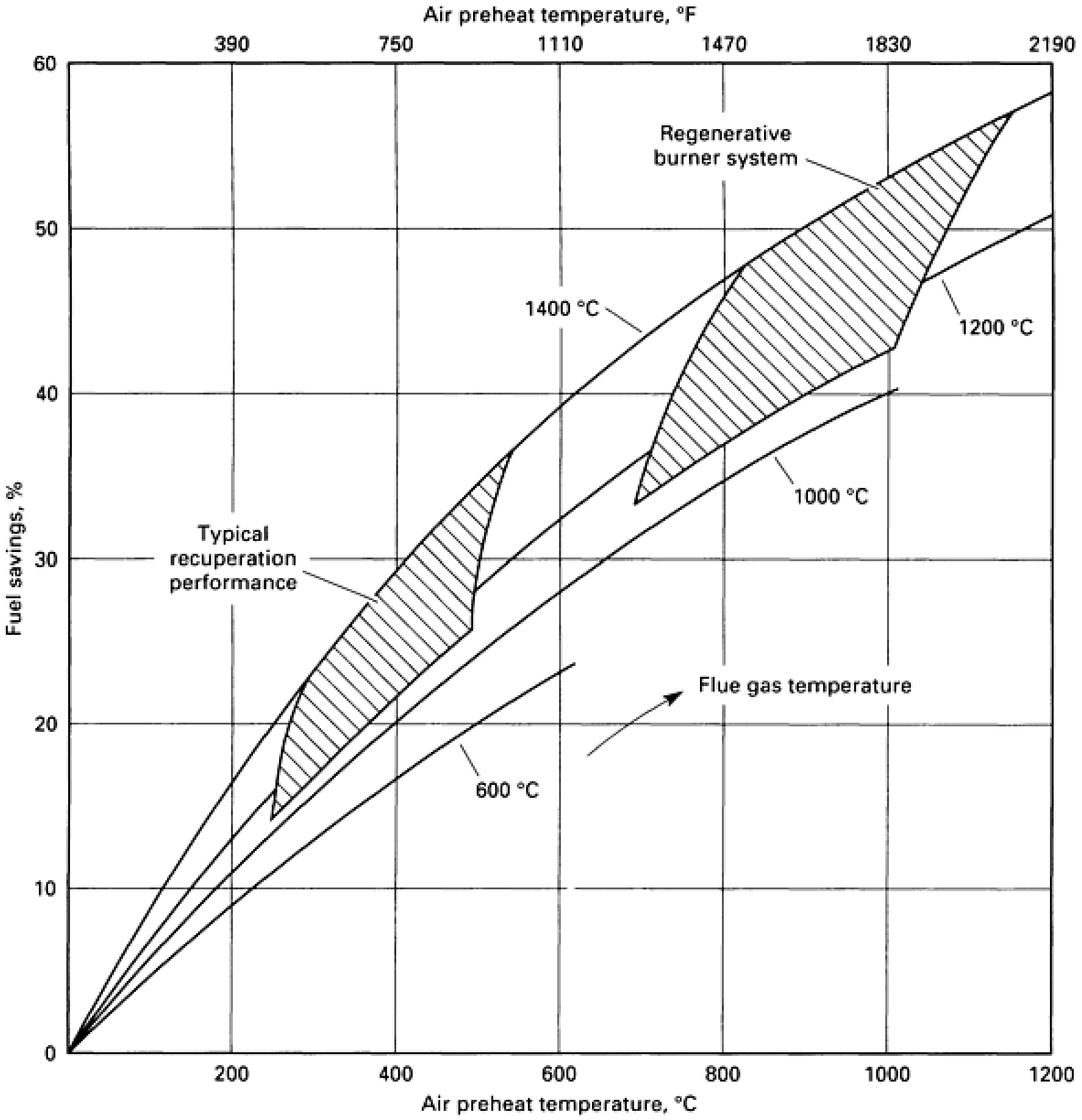
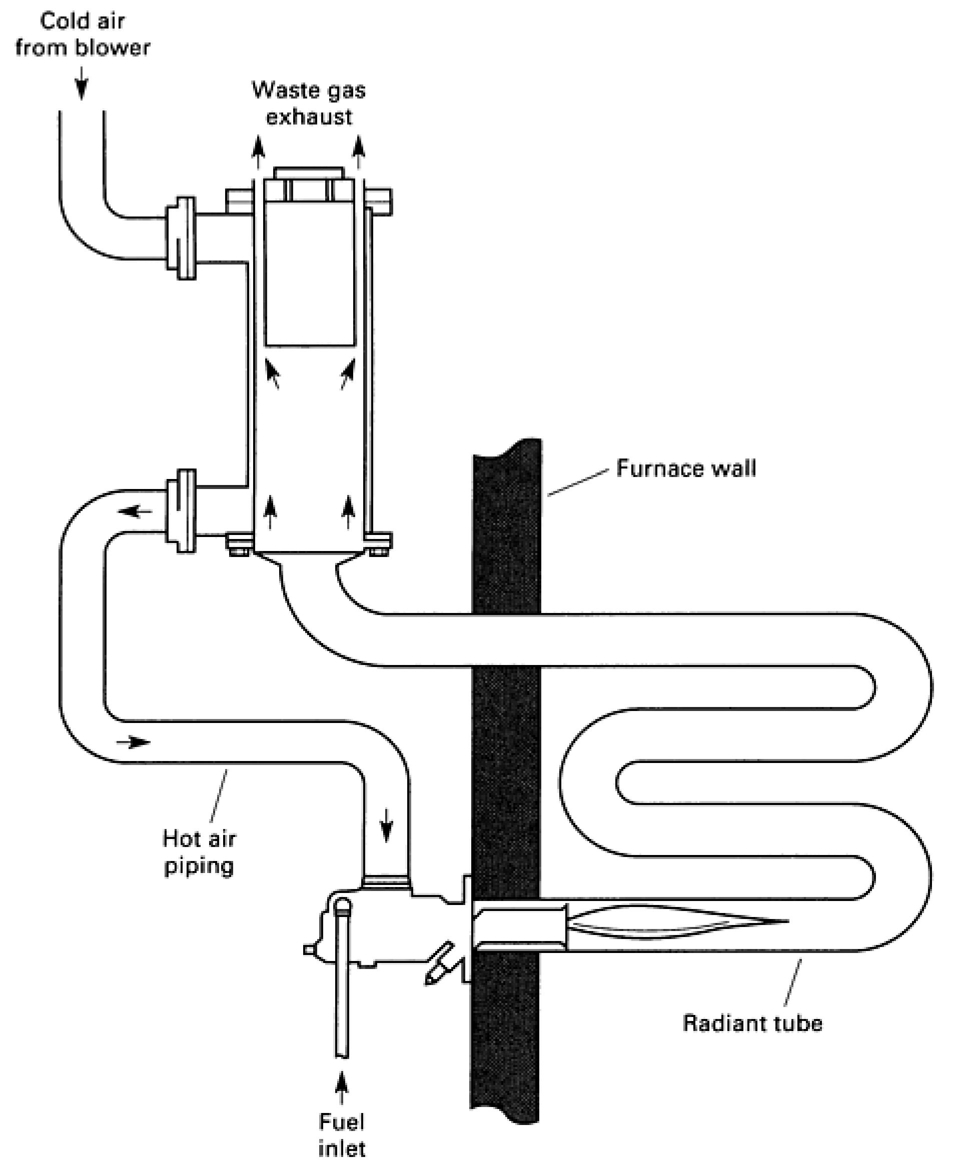


Fig. 4 Effect of air preheat on conbustion efficiency. Source: Ref 6

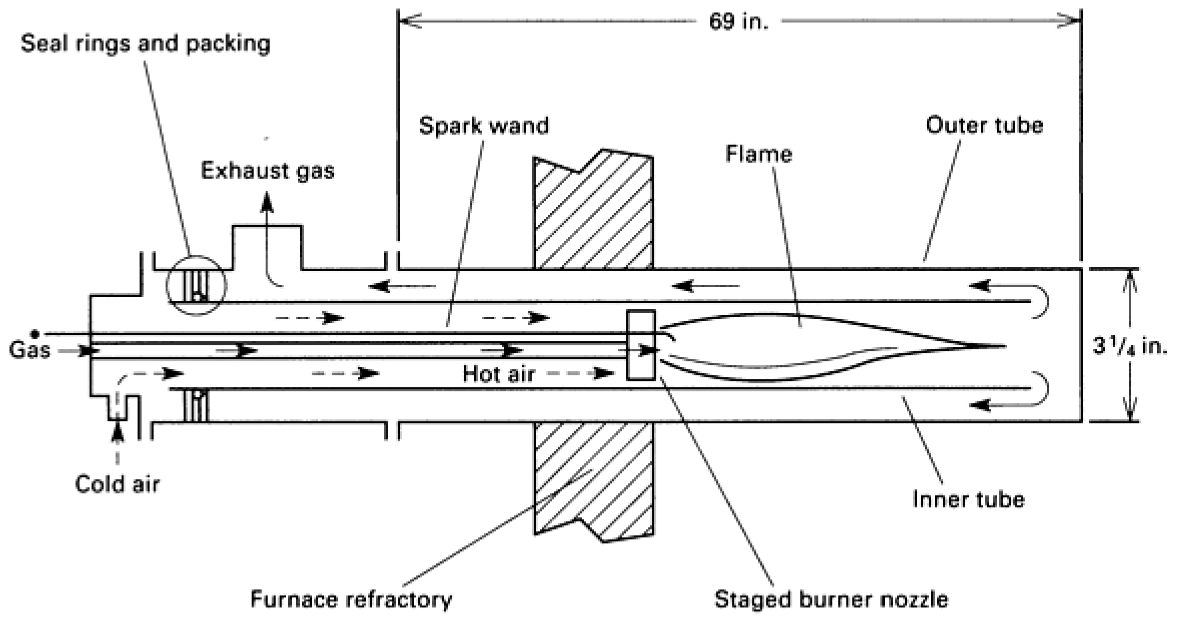
Recuperators preheat combustion air by transferring heat from the hot flue gases to the inlet air. In a direct-fired furnace, for example, tubes can carry the combustion air directly through the main flow of flue gases. This type of recuperator design transfers heat by convection. Convective recuperators, which are typically used with flue temperatures up to about 1000 °C (1850 °F), can preheat combustion air up to about 450 °C (850 °F). This would provide a fuel savings of about 25% (Fig. 4).

Conventional recuperators are also designed with inlet air passages placed alongside flue ducts (Fig. 5). Conventional recuperators, which can be based on metallic or ceramic tube design, are used with flue temperatures up to about 1500 °C (2700 °F) with ceramic materials (Ref 7). Wrought metallic radiant tubes with recuperation can be used up to about 1000 °C (1850 °F), but the tube life is limited to less than six months at these temperatures. Cast radiant tubes, which do not require a tradeoff between strength and workability, can operate satisfactorily at temperatures in excess of 1200 °C (2200 °F) (Ref 8).



Cold air
from blower
Waste gas
exhaust
Furnace wall
Hot air
piping
Radiant tube
Fuel
inlet

(a)



69 in.
Seal rings and packing
Spark wand
Outer tube
Flame
Exhaust gas
Gas
Hot air
$3^1/_4$ in.
Cold air
Inner tube
Furnace refractory
Staged burner nozzle

(b)

Fig. 5 Radiant tube recuperator systems. (a) External recuperation with U tubes. (b) Single-ended recuperation with inner and outer tubes made of reaction-bonded silicon carbide

The amount of air preheat from conventional recuperation depends on the design of the heat exchanger and flue gas temperatures. For an external recuperator (Fig. 5a) with wrought metallic radiant tubes, the combustion air is commonly preheated up to about 590 °C (1100 °F). A single-ended ceramic tube with recuperation (as shown in Fig. 5b), which has a maximum operating temperature of 1260 °C (2300 °F), can preheat combustion air to 650 °C (1200 °F) (Ref 9). A special two-stage recuperator with a metallic stage and a ceramic stage (Ref 10) preheated combustion air up to 1100 °C (2000 °F). This can provide fuel savings comparable to that of regenerators (Fig. 4).

Self-Recuperative Burners. Because conventional recuperators (Fig. 6) are generally large and confined to large-scale plants, self-recuperative burners have been developed. Self-recuperative burners are compact units that combine the function of burning and recuperation into a single integral unit (Fig. 6).

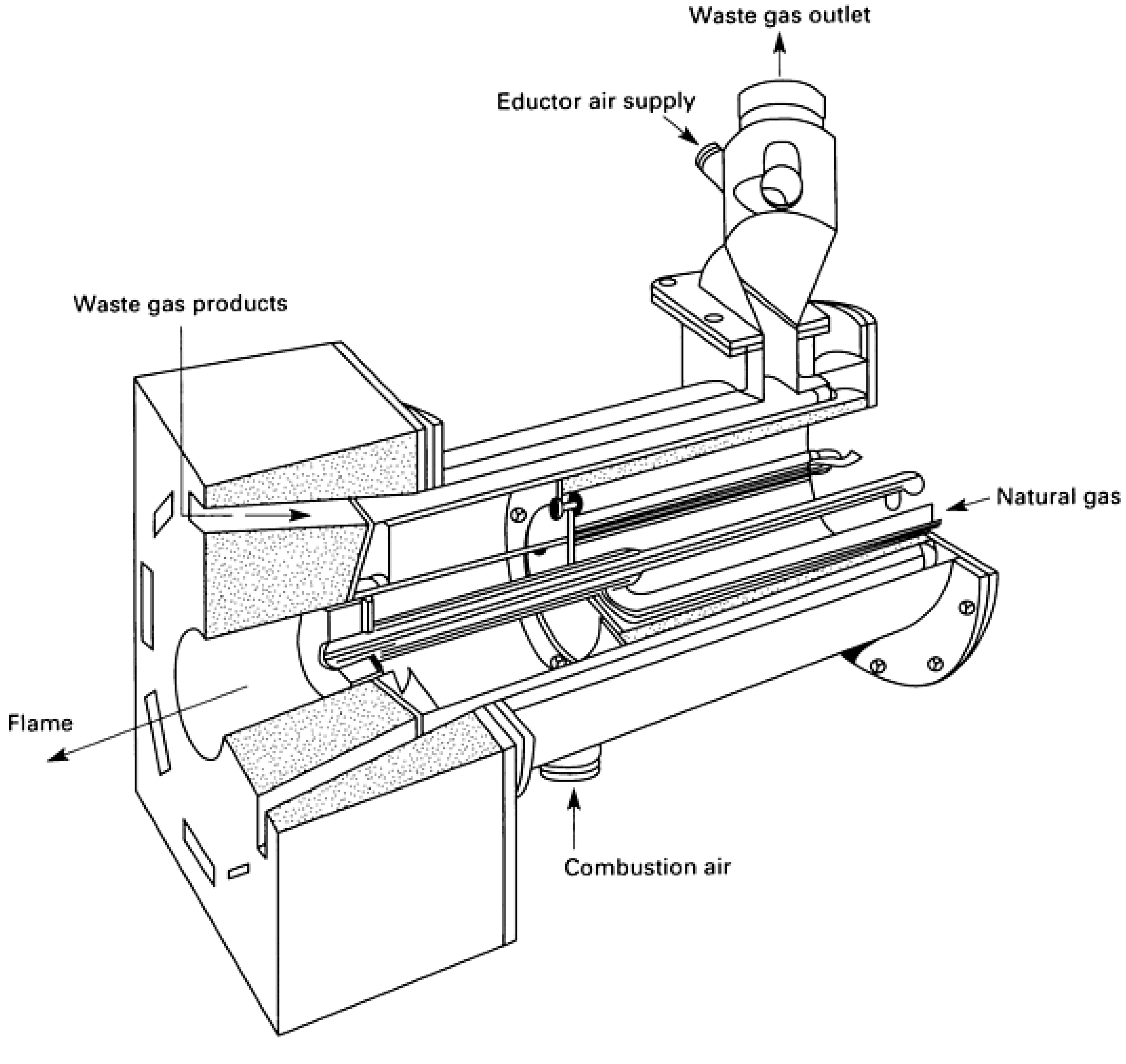


Fig. 6 Self-recuperative burner system

Self-recuperative burners are widely used in Europe and can provide fuel savings up to about 30% as compared to cold-air combustion. In a furnace with direct heating, the waste gases are drawn from the furnace through a series of ports that surround the burner quarl by means of an air ejector. The arrangement obviates the need for insulated hot air mains and

simplifies the necessary control system. Self-recuperative burners are also used successfully with radiant tube burners for indirect heating.

Regenerative burners, which operate on the same principle as the large regenerators used in steel and glass industries since the 1850s, provide a second method of preheating combustion air with hot flue gases. Regenerative burners typically operate at higher temperatures than recuperators and thus provide larger improvements in fuel savings (Fig. 4). Regenerative burners are also more reliable than recuperators when dirty fuel is used.

A regenerator basically consists of two chambers, each containing a permeable storage bed constructed of firebrick or another refractory shape. Flue gas gives up its heat to the refractory as it flows through one chamber, while combustion air flows through the other chamber, absorbing the heat stored in it during the preceding half of the "regenerative" firing cycle. After a certain length of time--about 20 min in a traditional system--the flows are switched.

Traditional regenerators often are larger than the furnaces they serve, and they also require large exhaust fans. To create a combination burner-regenerator compact enough to be mounted on a furnace, changes in bed material and cycle timing have been made. The surface-to-volume ratio of the refractory was increased 100-fold by switching to a granular refractory, which results in a large increase in heat-storage capacity per unit volume. Adoption of microprocessor-based controls shortens the switching time from 20 min to 20 s, which reduces the amount of heat that needs to be stored during each cycle. The regenerator bed is composed typically of ceramic spheres. Advantages of metals over ceramics in this application include higher thermal conductivity and density.

Regenerative burners are used on direct-fired furnaces and indirect-fired furnaces. In direct-fired units, exhaust fans draw flue products to the regenerator bed. In an indirect-fired unit, regenerative burners are placed at each end of a radiant tube (Fig. 7). While the regenerative burner at one end of the radiant tube is firing, the flapper valve, or damper, on its eductor is closed, which forces air through the hot refractory bed and into the burner for combustion. At the same time, the flapper of the other burner is open, which causes hot exhaust gases to be sucked through the refractory bed of the burner. Eductor suction at the nonfiring burner also maintains a negative pressure inside the radiant tube. Preheated-air temperatures are within 55 °C (100 °F) of waste-gas temperatures.

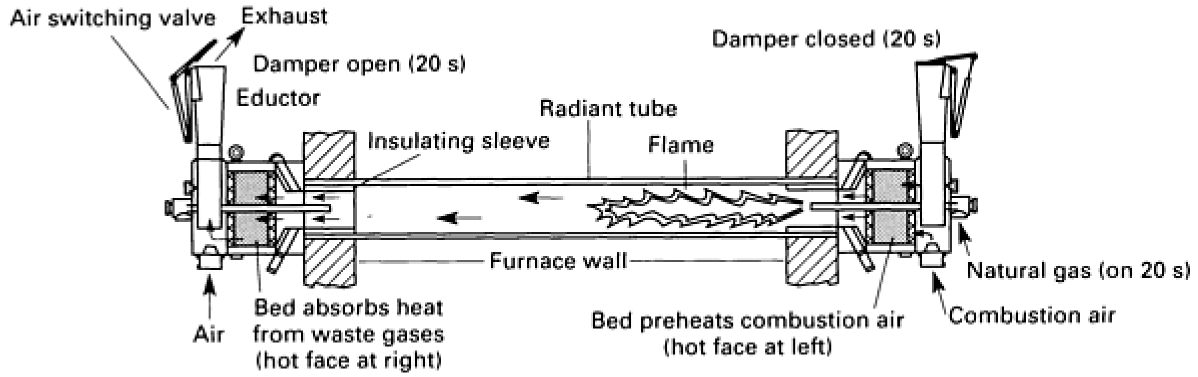


Fig. 7 Schematic of a regenerative radiant-tube burner system shows key components and principle of operation. Burner at right is firing using preheated combustion air, while burner at left reclaims heat from flue gases. Burners switch roles every 20 s. Burners are actually mounted side by side on the furnace wall, with the U-shaped radiant tube extending into the furnace.

The regenerative burner is probably the most significant advance in combustion technology in recent years. Successful heat-reclamation applications for regenerative burners are found in melting of nonferrous metals (aluminum reverberatory furnaces, for example), heat treating and forge heating (box, slot, car-bottom, and tunnel furnaces), continuous glass melters, and steel-mill pusher reheat furnaces, ladle preheaters, and continuous annealing furnaces. A specific application is described below.

Example 1: Fuel Savings with Regenerative Burners on an Annealing Furnace.

One of the first applications for regenerative radiant-tube burners, sponsored by the Gas Research Institute, was in 1984 on the annealing furnace for a continuous galvanizing line at the Inland Steel Company works in Gary, IN. The 15-zone galvanneal furnace uses 64 radiant tubes (128 regenerative burners) to heat steel strip prior to zinc coating. Annealing is performed under a protective hydrogen-nitrogen atmosphere to ensure good steel surface quality. Zone temperatures range from 815 to 980 °C (1500 to 1800 °F). The furnace originally was heated by conventional radiant-tube burners with U-shaped metallic tubes. Energy balances developed for the furnace both before and after conversion revealed that the use of regenerative burners reduced the requirement for purchased energy by more than 48%.

A microprocessor-based sequencer controls burner cycling. It serves primarily as a timer, switching fuel and air between each of the two burners of the tube at 20-s intervals (Fig. 7). Instead of modulating heat input, burners are turned on and off. Flame length is constant, which produces a uniform tube temperature from end to end.

Success of the regenerative system hinges on reliable combustion-air and gas switching valves. Under normal operating conditions, valves cycle approximately 432×10^3 times/y. In tests, these valves have survived more than 5×10^6 cycles.

Conventional radiant-tube burners create a hot spot a few feet from the burner, which is usually the point of tube burnout. Pulse firing of each regenerative burner equalizes temperatures in both tube legs. There were initial concerns that the short switching time associated with compact regenerators would induce temperature oscillations, which could cause thermal fatigue. However, because the mass of the radiant tube is large, and switching times are short, temperature fluctuations are negligible.

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Furnace Design and Operation

Although flue losses often constitute the major source of energy loss in a typical fuel-fired furnace (Fig. 1), energy efficiency is also affected by wall losses, opening losses, and conveyor system losses (that is, heating and cooling of trays, fixtures, and/or skids). The energy needed to heat a furnace to temperature can also be classified as a source of energy loss. Therefore, if intermittent operation of a batch furnace is necessary, the relative costs of idling a furnace versus furnace reheating after shutdown should be considered.

Once a furnace reaches a steady-state operating condition, the furnace losses from the furnace walls, openings, and conveyor system will remain constant provided that the operating conditions are unchanged, regardless of whether the furnace is being operated empty or with a capacity load. This constant loss reduces the relative efficiency of a furnace when it is operated at less than rated capacity. Therefore, operating below the heating rate capacity of a given furnace results in a decrease of efficiency. This effect is shown in Fig. 8 for a pusher-type furnace operating at 950 °C (1750 °F). Bringing the workpiece to temperature as quickly as possible thus can provide energy savings. Energy can also be saved by:

- Reducing the extent of opening losses
- Selecting effective materials that reduce wall and conveyor losses
- Improving heat transfer to the workpiece
- Reducing treatment temperatures and hold times, if possible

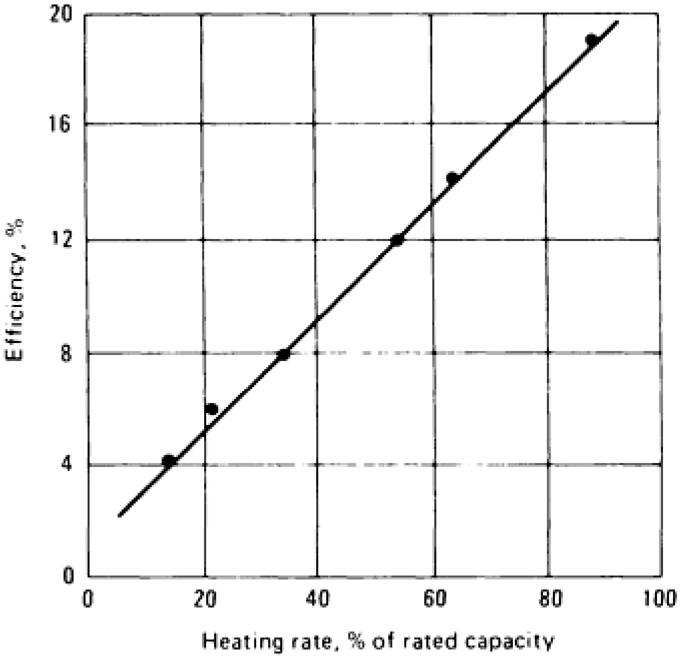

Fig. 8 Relationship between furnace efficiency and heating rate. Data are based from the metering of gas use in a pusher-type furnace operating at 950 °C (1750 °F).

Opening losses occur primarily from radiation losses, which are proportional to the area of the opening and the fourth power of temperature (T) in degrees kelvin (T^4).

Convective heat losses are also proportional to the effective area of the door opening. However, this loss can be accentuated when both doors are opened at the same time on a continuous furnace, because a tunnel effect is created. Convective losses also result around closed doors and through other openings in fuel-fired furnaces. To conserve energy, all unintentional openings should be sealed. The number of intentional openings should be reduced to the absolute minimum, and these openings should be sealed when not in use. Even when not permitting convective losses, openings in furnaces can permit infiltration of cold air, which must be heated to exit-gas temperature. Proper control of furnace pressure will help prevent these convective losses through necessary openings.

Ceramic fiber lining has replaced conventional brickwork in many batch and continuous heat treatment furnaces. Ceramic linings reduce heat loss by conduction through the walls and decrease furnace heat-up time because of their low thermal conductivity and low heat storage mass. Their low mass, reduced heat capacity, and good insulation properties are ideal for intermittent furnace operation. The low mass of ceramic linings also has structural advantages in the design of new furnaces. In some cases, the rapid thermal response of ceramic liners can be a problem.

Ceramic fiber linings are available in three basic product forms:

- Ceramic fiber blanketing
- Ceramic fiber veneer or tiles
- Sprayed-on ceramic fiber

Each of these product forms is based on the use of alumina and silica fibers containing a small amount of reducible metal oxides. Alumina contents are increased for higher operating temperatures. For temperatures above 1250 °C (2280 °F), it is necessary to use ceramic fibers with 95% alumina (such as Saffil). Saffil has a maximum recommended temperature of 1600 °C (2900 °F).

Ceramic fiber blanketing is limited to temperatures up to about 1000 °C (1830 °F) because the blanketing is susceptible to splitting from shrinkage at higher temperatures. To minimize shrinkage problems, the continuous operating

temperature of the furnace should be at least 200 °C (360 °F) below the maximum temperature rating of the fiber. Fiber blankets are also unsuitable in highly reducing atmospheres because of the disintegrating action of the atmosphere at typical temperatures.

Ceramic fiber veneer has a modular tile construction with some advantages over ceramic fiber blanketing. However, because reliable anchoring can be a concern, a safety lining of 25 to 40 mm (1 to $1\frac{1}{2}$ in.) blanket behind the veneer can be desirable. Veneer is useful in reducing atmospheres or when shrinkage from high temperatures (<1000 °C, or 1830 °F) is a concern.

Ceramic Fiber and High-Emissivity Coatings. Because veneer can have adherence or anchoring problems, sprayed-on ceramic fiber is used in veneer installation. High-emissivity coatings (for example, Pilbrico) are used to improve emissivity, which can be low (0.4 to 0.5) for some ceramic fiber products. In one application, a high emissivity coating allowed an initial 10 °C (5 °F) reduction in furnace temperature and a further 50 °C (25 °F) reduction after aging for a number of months (Ref 11).

Equipment Replacement or Modification. Proper application of refractories in reworked furnaces often can reduce or eliminate constant heat losses that may occur in water-cooled members. Water-cooled skid pipes can be replaced with alloy load supports if maximum temperature of operation permits, or with skid blocks made of high-strength, high-temperature refractories. Walking beam rails sometimes can be topped with refractory shoes rather than with noninsulating alloy shoes. Refractory materials in use include silicon nitride ceramics. Silicon nitride provides a good combination of excellent high-temperature strength along with resistance to oxidation and thermal shock.

Addition of alloy fans to existing furnaces sometimes can change a stagnant atmosphere into a high-velocity stream. This increase in ambient velocity breaks up boundary layers of furnace gases that surround the workpieces and shortens the heating time. This reduced heating time is a result of the change from heating only by radiation heat transfer to a combined radiation and convection transfer. The energy savings accrue through reduced furnace time required per cycle.

When the opportunity arises, much energy can be saved by altering the gases used in atmosphere heat treating. In some cases, an inert carrier gas can be added to the normal working gas.

Other energy-saving opportunities may be realized by improving the insulation systems in heat-treating furnaces. The energy lost through a furnace wall is a function of area, operating temperature, and composition of the insulation. The first two factors are fixed, but heat flow through and heat storage in the insulating system can be reduced by addition of insulation. Heat storage, which is the amount of heat contained in the wall, can be greatly reduced by using newly developed insulating materials, principally ceramic fibers and mineral wools. At the same time, the thickness of a wall for a given heat flow (loss) also can be changed significantly. One major heat-treating firm not only reduced energy requirements by using ceramic-fiber insulating materials, but also was able to heat treat larger rolls because of the decrease in required wall thickness, which in turn provided greater furnace work-zone width.

Energy Savings with Improved Quality Control. Energy savings can sometimes be achieved by improving heat-treating quality controls. For example, pyrometers can be used to measure surface temperature of workpieces in the furnace and thereby provide information for assessing required hold times in the furnace. This approach requires some relatively simple modeling of heat transfer within the workpiece. The potential savings accrue from knowledgeable reductions in soak times instead of relying on general specifications of soak times. Improved quality control also reduces scrap from improper treatment.

Furnace Design and Modeling. Another aspect of energy use is furnace design, which affects the transfer of heat from the burners to the workpiece. Direct-fired furnaces can provide efficient heat transfer depending on the design and disposition of the burners and flow patterns within the furnace. High-velocity burners, as mentioned earlier, are effective in improving heat transfer in direct-fired furnaces.

Improvements in furnace design depend on the particular application, and often improvements are based on experimental judgment and good furnace instrumentation. In some cases, however, modeling techniques such as those described in Ref 12 are also useful in avoiding costly furnace trials. Those techniques are summarized below.

Experimental modeling techniques utilize air, water, or perspex plastic models to study convective flow and establish the type and disposition of burners. Another method is the acid-alkali technique (Ref 13), which allows the

shape and size of diffusion flames to be observed directly in a perspex model. The use of this technique has led to burner designs that have achieved up to 30% fuel savings on glass melting furnaces (Ref 14).

Mathematical models provide a more quantitative assessment of the effects of firing conditions on furnace performance. Commonly used techniques are based on methods developed several decades ago by Hottel and coworkers (Ref 15). These methods are described by Tucker (Ref 16, 17) in more recent reviews. Modeling is also used to optimize or improve the analysis of energy use (Ref 18, 19, 20, 21, 22, 23, 24).

Energy Requirements of Different Furnace Types. As noted in the introduction of this article, energy efficiency and cost are related concerns. Some furnaces are very energy efficient, but the associated costs may not warrant their use. This is particularly true of electric furnaces, which are more efficient than gas-fired furnaces, but are often more expensive to operate because of the higher cost of electricity. An energy-cost comparison of various gas and electric furnaces is given in Fig. 9. Additional comparisons between electric and fuel-fired furnaces are discussed in the article"Types of Heat-Treating Furnaces" in this Volume.

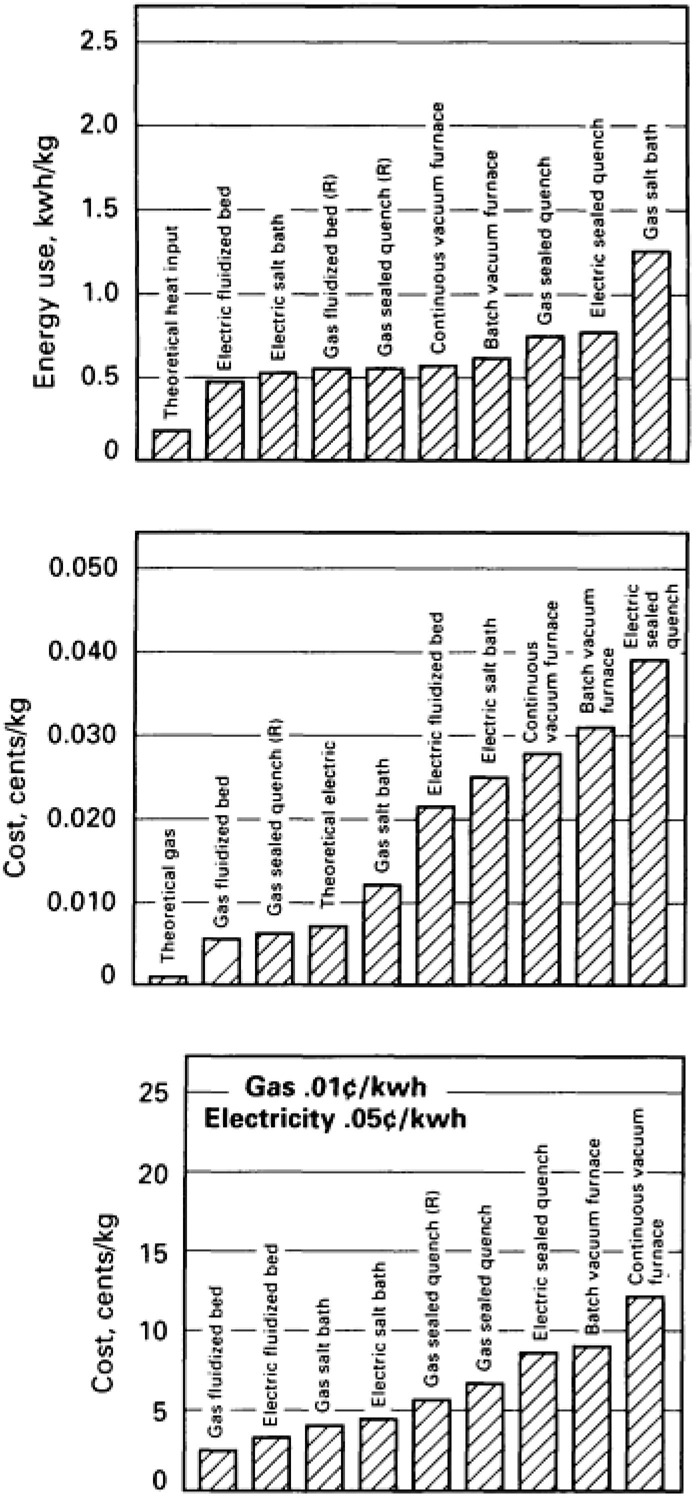

Fig. 9 Energy and cost comparisons of various furnace types with a soak temperature of about 850 °C (1560 °F). Data includes energy to heat furnace to temperature. R, recuperators fitted to burners. Source: Ref 25

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Temperature Control in Heat Treating

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Introduction

TEMPERATURE CONTROL is an integral part of heat-treating operations, which generally consist of three separate functions: material movement, the application of energy, and the supervision of process conditions. In a typical heat-treat operation, work is moved into a furnace, heated according to a time-temperature program, cooled or quenched, and finally moved out of the furnace or quench vessel. The temperature, and frequently the atmosphere, must be controlled precisely in order to achieve the desired metallurgical results.

Temperature Control Loops

Temperature instrumentation and control systems include temperature sensors, controllers, final control elements for controlling energy flow, measurement instruments, and set-point programmers. Temperature control also requires an understanding of the heat transfer mechanisms of conduction, convection, and radiation.

In recent years the separate functions of material movement, application of energy, and supervision of process conditions have been handled in the following way: programmable logic controllers (PLCs) have been used to handle material movement; analog variables (energy, temperature, pressure, flow, vacuum, percent carbon, and so on) have been controlled by single-loop controllers and set-point programmers; process supervision or data management has been done by strip chart recorders or data loggers. This separation of functions requires communication among the logic controllers, loop controllers, and data-acquisition equipment. Finally, when a supervisory computer is required to handle such functions as scheduling, parts purchasing, and statistical process control, a further layer of interfaces is required to tie the whole set of instrumentation together.

A basic control loop (Fig. 1) includes a temperature sensor, controller, and final control element. The heat process temperature is detected by a temperature sensor that generates a signal proportional to the process temperature. This actual temperature is compared to the desired temperature determined by the controller set point. Based on this comparison, the controller develops an output signal that adjusts the final control element regulating heat flow to the heat-treating process.

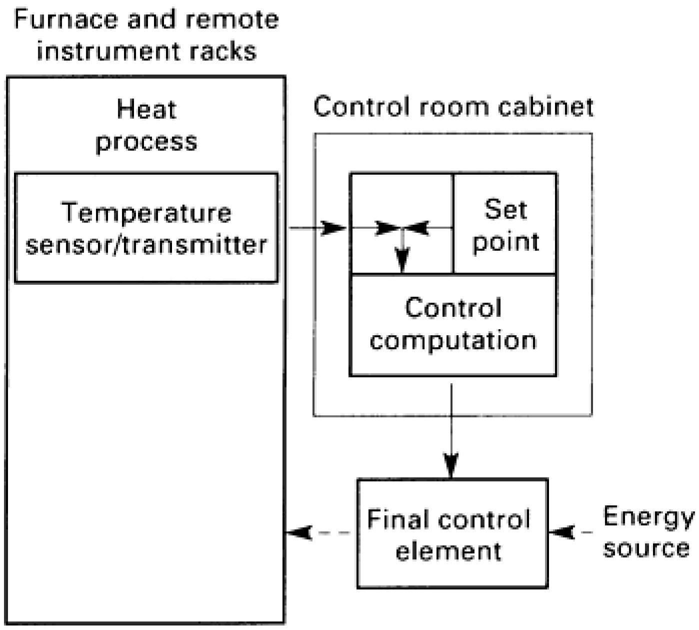

Fig. 1 Basic control loop

Sensor Signal Transmitter. The basic control loop may incorporate a temperature transmitter to amplify the temperature sensor signals. This amplification is desirable when the control instrument is remotely located from the temperature sensor. The amplification also helps to avoid interaction between two or more instruments using a common sensor. For example, the temperature signal may be transmitted to a remote central control room where it is connected to several controllers, a recorder, a data-acquisition system, or a digital computer.

Auxiliary devices used with the basic control loop include measurement instruments with set-point programming (Fig. 2). The measurement instrument monitors the same temperature sensor as that used by the controller. The set-point programmer automatically varies the controller set point to provide a temperature cycle or temperature program in accordance with an established plan.

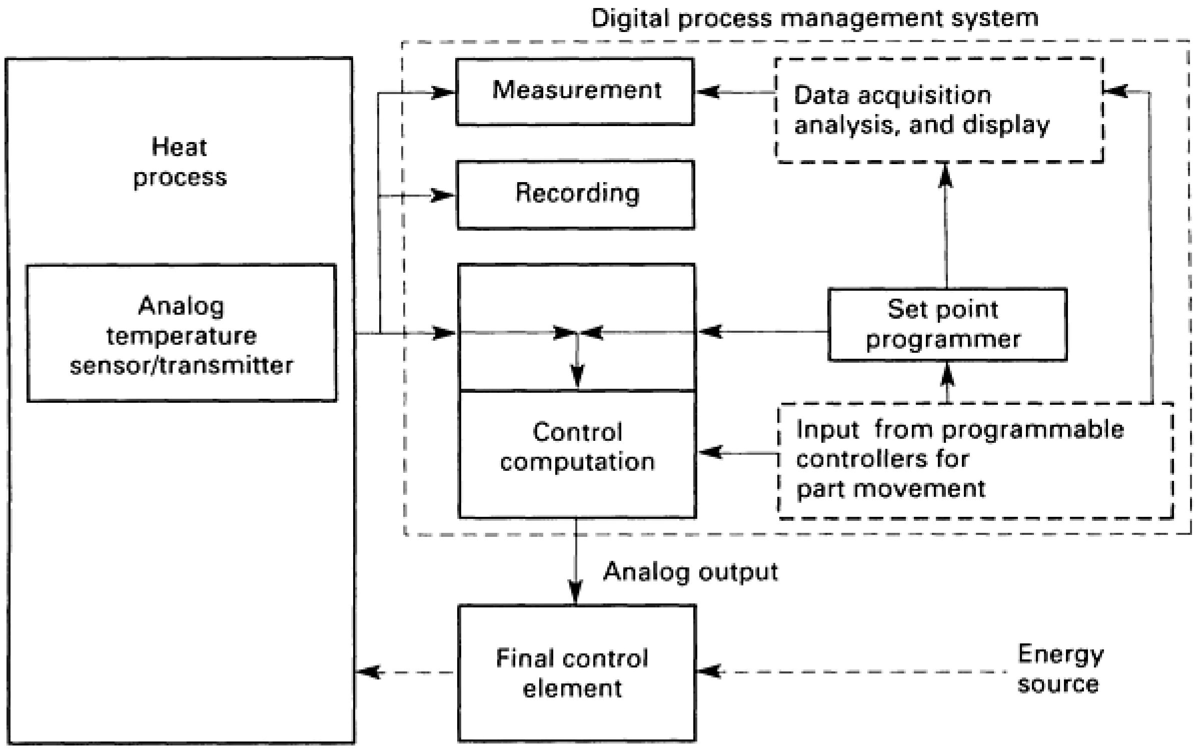

Fig. 2 Basic control loop with auxiliary devices. Functions in an integrated digital process management system are shown in the dashed blocks.

The reduced cost and more compact packaging of digital support hardware has spawned the integration of temperature control with auxiliary functions such as process documentation and workpiece flow. These process management systems can (Fig. 2) integrate the functions of temperature measurement, loop control, variable set-point control, logic (parts movement) control, data acquisition, data management, results display, and report writing, all in a package no more costly than a multipoint recorder and a few single-loop controllers.

Temperature Scales. Effective 1 January 1990, the standards groups of the world have agreed upon a new temperature scale called the International Temperature Scale of 1990 (ITS-90) (Ref 1). It differs in many respects from the last temperature scale, the International Practical Temperature Scale of 1968 (IPTS-68). Most notably, the new scale is extended down to 0.65 K; the platinum resistance thermometer is used to realize the scale up to 1234.93 K (replacing the type-S thermocouple over the upper portion of this range), and deviations between ITS-90 and IPTS-68 are less than 1 °C (2 °F) below 2400 °C (4350 °F). Additional information on the use of these temperature scales is provided in the article "Thermocouple Materials" in *Properties and Selection: Nonferrous and Special-Purpose Materials,* Volume 2 of *ASM Handbook,* formerly 10th Edition *Metals Handbook.*

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Temperature Control in Heat Treating

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Temperature Sensors

Temperature sensors are classified as either contact or noncontact, and as either electrical or nonelectrical. For example, the mercury thermometer is a contact, nonelectrical type. Because of high-temperature requirements and the trend toward electrical instrumentation, most heat-treating applications require electrical sensors. When selecting a contact sensor, certain variables should be considered, such as cost, temperature range, useful life, accuracy, size, and response speed. The selection of noncontact sensors involves similar considerations plus those related to radiation factors such as target size, surface emissivity, focal length, and sighting path interference.

Thermocouples and resistance temperature detectors (also known as resistance thermometers) are the most important contact-type electrical temperature sensors used in the metals industry. Well over 90% of the sensors used in this industry are estimated to be thermocouples. A thermocouple is rugged, inexpensive, accurate, fast in response, and covers wide temperature ranges. A resistance thermometer is more accurate and stable than a thermocouple. However, the resistance thermometer is limited to lower temperatures.

Thermocouples

Thermocouples consist of two dissimilar wires joined at one end, forming a measuring, or hot, junction. The other end, which is connected to the copper wire of the measuring instrument circuitry, is called the reference, or cold, junction. The electrical signal output in millivolts is proportional to the difference in temperature between the measuring junction (hot) and the reference junction (cold). The different types of thermocouples, classified by their metallurgical compositions, have differing output signal calibrations (see the article "Thermocouple Materials" in *Properties and Selection: Nonferrous and Special-Purpose Materials,* Volume 2 of *ASM Handbook*, formerly 10th Edition *Metals Handbook*).

The thermocouple wire combination, with or without insulators, is called a thermocouple element. A complete thermocouple assembly includes the element and a protection tube or well to protect the element from contamination and provide mechanical strength (see Fig. 3). In addition, the assembly provides mounting fittings and a terminal junction in a head assembly. Extension lead wires, which match the thermoelectric characteristics of the thermocouple elements, are used to connect these terminal junctions to the instrumentation. Figure 4 shows a simple thermocouple with lead wires and reference junction. The lower sketch of this figure shows details of a complete thermocouple assembly in a protection tube. The operating life and accuracy of a thermocouple depend on its operating temperature, time at the operating temperature, ambient atmosphere, and number of high-to-low temperature cycles.

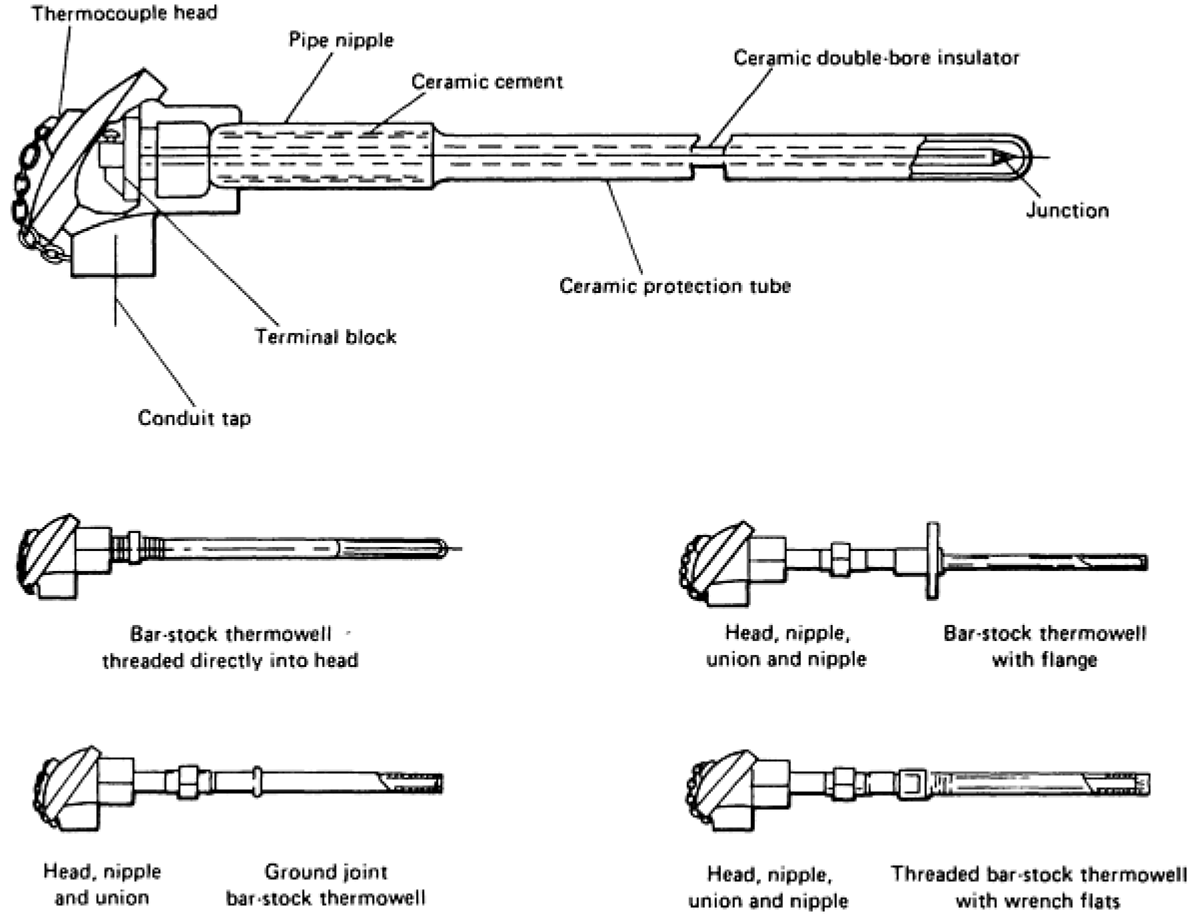

Fig. 3 Typical industrial thermocouples insulated with hard-fired ceramics

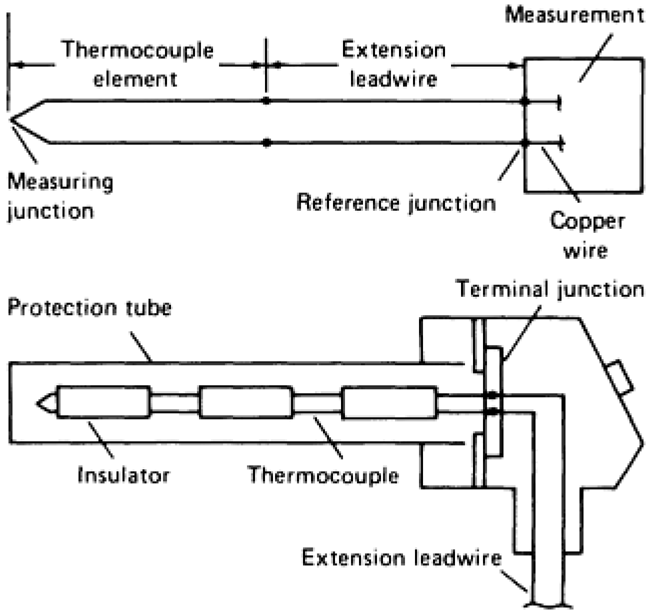

Fig. 4 Simple thermocouple (upper view); and cutaway of a thermocouple assembly (lower view)

Precautions. Heat-treating operations that rely on thermocouples require numerous precautionary measures. For example, thermocouple error due to contamination normally is characterized by a low output signal. Contamination comes from touching the wires with bare hands during assembly, dirty insulators, oils and dirt inside the protection tube, or the atmosphere used in the process. Consequently, cleanliness is important in assembling thermocouples. Insulators that become contaminated in normal service should not be reused. Even the cutting oils used to cut threads on protection tubes contain sulfur, which can cause contamination. These tubes should be thoroughly degreased before use. In high-temperature applications, the furnace atmospheres penetrate protection tubes and sheath materials. Consequently, routine replacement of the contaminated thermocouple elements is required. Frequency of replacement depends largely on operating temperature, environment, and freedom from mechanical stress.

Thermocouple Location. Location of thermocouple measuring junctions must allow exposure to the correct heat process temperature. Normally, the tip of the thermocouple (measuring junction) is placed near the work in the furnace. Thus, it is exposed to the same heating environment as the workpieces.

A common error occurs when the thermocouple assembly is not inserted far enough into the furnace. Under this condition, heat is conducted by the thermocouple assembly away from the measuring junction, toward the colder furnace wall. Consequently, the thermocouple indicates a temperature lower than the actual work temperature. One way to determine correct location is to place an adjustable flange on the thermocouple protection tube. The correct insertion depth then can be determined by adjusting the flange to achieve the maximum temperature and the minimum insertion depth, while the furnace is in operation. However, thermocouples never should be located near burners or heating elements because radiant heat may cause erroneous readings.

The speed of response of the thermocouple to process temperature changes should be as fast or faster than that of the work in the furnace. If the workpieces are small and the thermocouple is contained in a heavy protection tube, the thermocouple temperature will lag behind the actual work temperature. Consequently, workpieces will be overheated when they are initially brought up to control temperature.

Furnace temperature uniformity is important and should be checked before installing the permanent control thermocouple. If an air recirculating system is used, an average temperature in the duct work can be measured by installing three or more thermocouples across the duct width connected in parallel. (A single thermocouple in the center of the duct typically will indicate a higher temperature because this location is normally the hottest.)

However, in order for the average to be valid, the electrical resistances of the several thermocouples must be equal. A superior solution to averaging thermocouple signals is to measure each individually and average digitally. Furthermore, a true temperature profile can be detected this way. Finally, if one thermocouple signal deviates significantly from the others, failure of that element may be found. Microprocessor-based recorders and data management systems make these types of calculations easy.

Types of Thermocouples. Thermocouples most commonly used in heat processing applications are listed in Table 1. Table 2 gives temperature limits for thermocouples in oxidizing atmospheres, and Table 3 contains limits of error as a percentage of the temperature readings for these thermocouple types. (For more information on thermocouples, see the article "Thermocouple Materials" in *Properties and Selection: Nonferrous and Special-Purpose Materials,* Volume 2 of *ASM Handbook*, formerly 10th Edition *Metals Handbook*).

Table 1 Comparison of thermocouple types

Type	Usable temperature range		Advantages	Restrictions
	°C	°F		
J (iron-constantan)	-185-870	-300-1600	Comparatively inexpensive; suitable for continuous service to 870 °C (1600	Maximum upper limit in oxidizing atmosphere is 760 °C (1400 °F), due to the oxidation of

			°F) in neutral or reducing atmospheres	the iron; protection tubes should be used above 480 °C (900 °F); protection tubes should always be used in a contaminating medium
K (nickel, chromium-nickel, aluminum)	-20-1370	0-2500	Suitable for oxidizing atmospheres; in higher temperature ranges, provides a more mechanically and thermally rugged unit than platinum, rhodium-platinum, and longer life than iron-constantan	Especially vulnerable to reducing atmospheres, requiring substantial protection when used
N (nickel, chromium, silicon-nickel, silicon, magnesium)	-245-1300	-410-2370	Significantly greater stability and longer life than type K in oxidizing atmospheres and somewhat superior in reducing atmosphere	
T (copper-constantan)	-185-370	-300-700	Resists atmosphere corrosion; applicable in reducing or oxidizing atmospheres below 315 °C (600 °F); its stability makes it useful at subzero temperatures; has high conformity to published calibration data	Copper oxidizes above 315 °C (600 °F)
E (nickel,chromium-constantan)	-185-870	-300-1600	Has high thermoelectric power; both elements are highly corrosion-resistant, permitting use in oxidizing atmospheres; does not corrode at subzero temperatures	Stability is unsatisfactory in reducing atmospheres
S (platinum, 10%	-20-	0-	Usable in	Easily

rhodium-platinum) R (platinum, 13% rhodium-platinum)	1480	2700	oxidizing atmospheres; provides a higher usable range than type K; frequently more practical than noncontact pyrometers; has high conformity to published calibration data	contaminated in other than oxidizing atmospheres
B (platinum, 30% rhodium-platinum, 6% rhodium)	870-1650	1600-3000	Better stability than types S or R; increased mechanical strength; usable to higher temperatures than types S or R; reference-junction compensation is not required if junction temperature does not exceed 65 °C (150 °F)	Available in standard grade only; high temperature limit requires the use of alumina insulators and protection tubes; easily contaminated in other than oxidizing atmospheres

Table 2 Temperature limits for thermocouples in oxidizing atmospheres

Upper temperature limits are a function of wire diameter; because temperature tends to have deleterious effects on thermocouples, the larger the amount of material in thermocouple cross section, the longer it can be expected to last.

Thermocouple			**AWG (American Wire Gage)**											
			8		**14**		**16**		**20**		**24**		**30**	
Type	**Material**	**Condition**	**°C**	**°F**	**°C**	**°F**	**°C**	**°F**	**°C**	**°F**	**°C**	**°F**	**°C**	**°F**
J	Iron-constantan	Bare	650	1200	480	900	480	900	425	800	345	650	315	600
		Protected	760	1400	595	1100	595	1100	480	900	370	700	370	700
K	Nickel, chromium-nickel, aluminum	Bare	1095	2000	925	1700	925	1700	870	1600	760	1400	700	1300
		Protected	1260	2300	1095	2000	1095	2000	980	1800	870	1600	815	1500
N	Nickel, chromium, silicon-nickel, silicon, magnesium	Bare	1095	2000	925	1700	. . .	. . .	870	1600	760	1400	700	1300
		Protected	1260	2300	1095	2000	. . .	. . .	980	1800	870	1600	815	1500
T	Copper-constantan	Bare	315	600	315	600	260	500	205	400	205	400	200	400
		Protected	370	700	370	700	315	600	260	500	205	400	200	400
E	Nickel, chromium-constantan	Bare	760	1400	595	1100	595	1100	480	900	370	700	370	700
		Protected	870	1600	650	1200	650	1200	540	1000	425	800	425	800

S and R	Platinum, rhodium-platinum	Protected	. . .	. . .	. . .	. . .	. . .	. . .	1540	2800	1480	2700	1315	2400
B	Platinum, 30% rhodium-platinum, 6% rhodium	Protected	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	1705	3100	. . .	. . .

Table 3 Limits of error for thermocouples

ANSI type	**Type of thermocouple**	**Temperature range**		**Limits of error**[a]	
		°C	**°F**	**Standard**	**Special**
J	Iron and constantan	-190 to -75	-310 to -100	. . .	±2%
		-175 to 315	-100 to 600	±2 °C (±4 °F)	±1 °C (±2 °F)
		315-425	600-800	±2 °C (±4 °F)	±0.33%
		425-760	800-1400	±0.75%	±0.33%
K	Nickel, chromium and nickel, aluminum	0-275	32-530	±2 °C (±4 °F)	±1 °C (±2 °F)
		275-1260	30-2300	±0.75%	±0.38%
N	Nickel, chromium, silicon-nickel, silicon, magnesium	0-275	32-530	±2 °C (±4 °F)	±1 °C (±2 °F)
		275-1260	30-2300	±0.75%	±0.38%
T	Copper and constantan	-185 to -60	-300 to -75	. . .	±1%
		-100 to -60	-150 to -75	±2%	±1%
		-60 to 95	-75 to 200	±1 °C (±1.5 °F)	±0.5% °C (±0.75 °F)
		95-370	200-700	±0.75%	±0.38%
E	Nickel, chromium and constantan	0-315	32-600	±2 °C (±3 °F)	±1 °C (±2 °F)
		315-870	600-1600	±0.5%	±0.38%
S	Platinum, 10% rhodium and platinum	-15 to 540	0-1000	±1.5 °C (±2.5 °F)	±1 °C (±1.5 °F)

		540-1480	1000-2700	±0.25%	±0.15%
R	Platinum, 13% rhodium and platinum	-15 to 540	0-1000	±1.5 °C (±2.5 °F)	. . .
		540-1480	1000-2700	±0.25%	. . .
B	Platinum, 30% rhodium and platinum, 6% rhodium	870-1705	1600-3100	±0.5%	. . .

(a) When expressed as a percentage, the limit of error is a percentage of the temperature reading, not of the range.

Selection of a specific kind of thermocouple is based primarily on the required temperature range and cost. However, the choice also is affected by its metallurgical properties. For example, type J is superior to type K in a reducing atmosphere, and type K is superior to type J in an oxidizing atmosphere. Type K is very susceptible to sulfur contamination, such as sulfur dioxide in combustion gases. Type K should be used in a large protection tube or one with a ventilated design. If the ambient atmosphere has a low oxygen concentration, the resulting green-rot corrosion results in a low output signal. Green rot is caused by preferential oxidation of chromium at low oxygen concentrations. The type-N thermocouple was designed to overcome some of the limitations of type K (Ref 2), and repeated results suggest superior performance for bare wire (Ref 3).

The two major thermocouple design classifications are the compacted ceramic, and the protection tube or well-type, with integral element insulators.

Compacted ceramic thermocouples use a ceramic powder to insulate the thermocouple wires. These wires are compacted inside a metal sheath, providing protection from the environment. This compacted ceramic thermocouple is small in outside diameter, provides fast response and can be bent easily to suit installation requirements. It can be used at high pressures and high temperatures. Two types of compacted ceramic thermocouples, grounded and ungrounded, are shown in Fig. 5. The metal sheath has a plug of the same metal welded in place as the tip. In the grounded type, the end of the thermocouple is permitted to touch this plug, providing more rapid response. The ungrounded type is used when required by the measurement and/or control circuit electronics. Recent results suggest that the superiority of type N over type K observed in bare wire thermocouples may not be so great for compacted ceramic thermocouples (Ref 4).

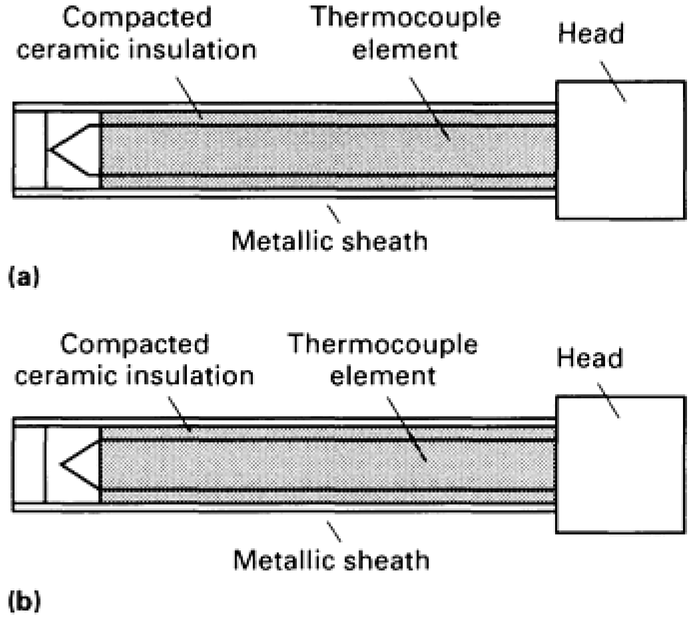

Fig. 5 Grounded and ungrounded types of compacted ceramic thermocouples. (a) Grounded. (b) Ungrounded

Protection Tubes and Wells. Thermocouple elements with insulators and compact ceramic elements are used inside protection tubes and wells (Fig. 3). The thermocouple elements with insulators are less expensive than the compacted ceramic elements and can be manufactured by users. Protective tubes and wells are used to provide mechanical support and protect the thermocouple from the process environment. Protection tubes are made from metallic or ceramic materials and are used in air or other gaseous atmospheres (Table 4). These atmospheres are near atmospheric pressure such as those used in heat-treating furnaces.

Table 4 Protection tube and thermowell materials

Material[a]	Recommended maximum temperature		Description
	°C	°F	
Metal and metal-ceramic materials			
Carbon steel	540	1000	Satisfactory in any except corrosive atmospheres
Yoloy (Ni-Cu alloy steel)	700	1300	Resistant to corrosion in both oxidizing and reducing environments; ideally suited for use in condensate return lines, salt-water and brine solutions, condenser water lines, vent and waste piping, or corrosive water lines
Cast iron	700	1300	Generally more useful than Yoloy in the chemical industry; resistant to concentrated sulfuric acid and caustic solutions; can be used to 870 °C (1600 °F) in reducing atmospheres
304 stainless steel (18Cr-8Ni)	870	1600	Resistant to oxidation and corrosion; generally used in wet-process applications such as steam lines, oil refineries, and chemical solutions; resists nitric acids well, halogen acids poorly, and the sulfuric acids moderately
316 stainless steel (18Cr-8Ni-2Mo)	870	1600	Superior to 304 stainless steel in corrosion resistance; resists pitting in phosphoric and acetic acids
446 stainless steel (28Cr, Fe)	1095	2000	Excellent corrosion resistance at high temperatures; used extensively in general-purpose alloy tubes; highly resistant to sulfur attack
Nickel	1095	2000	Resistant to attack by many chemicals at high temperatures; principally used for hot caustic and molten-salt baths; should not be used where sulfur is present
Inconel 600 (80Ni-15Cr)	1150	2100	For general high-temperature use; has greater mechanical strength than 446 stainless steel; should not be used in sulfur atmospheres
R-Monel (67Ni-30Cu)	480	900	Used where high strength and resistance to corrosion are required, such as sea water, dilute sulfuric acid, and strong caustic solutions

F-11 ($1\frac{1}{4}$ Cr-$\frac{1}{2}$ Mo)	595	1100	Generally used in power plants, on water and steam line applications; available in thermowells only
F-22 ($2\frac{1}{4}$ Cr-1Mo)	595	1100	Same as F-11, except has better oxidation resistance
LT-1 (77Cr-23Al_3O_4)	1370	2500	For high-temperature applications; intermediate between metal and ceramic tubes, has good thermal and mechanical shock resistance
Ceramic materials			
L&N Fyrestan	1540	2800	A highly refractory porcelain, normally used for primary protection and often for secondary protection. L&N Fyrestan tubes can be substituted in many applications for nickel or chromium-alloy tubes, and although not as strong as metal alloys, are fully as gas-tight. Having a softening point of 1650 °C (3000 °F), these tubes can be mounted vertically at a temperature of 1540 °C (2800 ° F). When mounted horizontally, the recommended maximum temperatures are 1510, 1455, 1370, and 1260 °C (2750, 2650, 2500, and 2300 ° F) for unsupported lengths of 75, 150, 300, and 450 mm (3, 6, 12, and 18 in.), respectively. The tubes are impervious to air to 1650 °C (3000 °F) and to dry hydrogen to 1400 °C (2550 °F). Their low rate of thermal expansion gives good thermal shock resistance
High-purity alumina	1870	3400	A highly refractory 99+% pure alumina, normally used for primary or secondary protection. Alumina tubes have excellent deformation resistance and superior resistance to reducing atmospheres and chemical reactions at temperatures as high as 1870 °C (3400 °F). (If the tube is mounted horizontally, it must be supported at temperatures above 1650 °C (3000 °F.) Its excellent resistance to oxidizing and reducing atmospheres, as well as its exceptional stability at elevated temperatures, make this material the ideal choice for protection of precious-metal thermocouples--especially type B. These tubes are highly resistant to corrosive alkaline vapors and aluminum chloride vapors, and are stable to acids, alkalis, molten metals, most glass fluxes; molten salts, and slags. The tubes are also impermeable to most gases under the conditions found in industrial furnaces
Silicon-carbide refractory	1650	3000	Highly resistant to the cutting action of flames and gases and the corrosive effects of SO_2, tubes of silicon carbide refractory can be used for primary as well as secondary protect for temperatures up to 1650 °C (3000 °F). Ceramic-bonded silicon carbide features high thermal conductivity, high thermal-shock resistance, high strength, and low permeability at differential pressures less than 50 to 75 mm (2 to 3 in.) H_2O

(a) Materials are, in general, arranged in the order of their increasing resistance to oxidation, increasing mechanical strength at elevated temperatures, and increasing limit of useful temperatures.

Wells are metallic and made of either drilled metal bar stock (one-piece construction) or from welded pipes. Most often, wells are used to protect the thermocouple in liquid or gaseous environments with pressures greater than 345 kPa (50 psi) for the drilled design. Typically, they are used in quench tanks, hydraulic systems, or steam lines.

If the insulation between the thermocouple wires in the element or extension leadwire breaks down from heat, contamination, or mechanical damage, a low output signal results. This signal indicates an erroneously low temperature. This type of error results in process operation at an excessive temperature. Valuable energy is lost, and the work can be damaged or destroyed.

Thermocouple Applications. A typical thermocouple construction includes the thermocouple wire element with insulators mounted in a protection tube. The thermocouple head provides terminals for a junction between the thermocouple element and leadwire used for connection to instrumentation.

A typical application is a car-bottom annealing furnace used up to 1100 °C (2000 °F) with an air atmosphere. An 8 gage type K or N thermocouple in a ceramic protection tube is selected because it is useful up to 1260 °C (2300 °F) in an oxidizing atmosphere and is less expensive than the noble metal types R, S, and B. A 16 gage type K or N leadwire with synthetic fiber insulation is selected because it matches the type K element up to 200 °C (400 °F), suitable for a heat-treating area, and is strong enough for pulling through a conduit. Type K or N should be used for all the furnace measurements to maintain uniformity; that is, recording and control of furnace temperatures, plus the high limit safety control and work temperatures.

The furnace temperature thermocouple element should be 8 gage for maximum life and long enough so that its tip or measuring junction can be inserted well into the furnace cavity while the head is far enough back from the furnace wall to prevent its rising above 200 °C (400 °F). A ceramic protection tube will meet the process temperature requirements and is strong enough not to sag if mounted horizontally. An adjustable flange permits changing the depth of insertion in the furnace to the optimum depth. For example, when the furnace is at operating temperature, the thermocouple may be slowly withdrawn until its temperature indicator starts to drop, showing that it is too close to the cold furnace wall. The adjustable flange may then be locked in place on the protection tube. Location of thermocouples depends on furnace design, but, in any event, the thermocoupler must be inserted to locations where representative temperatures exist.

Resistance Temperature Detectors

Resistance temperature detectors (RTDs) are contact-type sensors. Their electrical resistance is proportional to temperature. Typical detector materials are platinum, copper, and nickel. They are more stable, accurate, and interchangeable than thermocouples, but even the platinum detectors have an upper temperature limit of approximately 750 °C (1380 °F), which reduces their usage in the metals industry.

Resistance temperature detectors are normally larger in size and slower in response than thermocouples. However, the new thin-film deposited detectors minimize this advantage, which characterizes the conventional wire-wound detectors.

Resistance temperature detectors are used typically in quenching systems, low-temperature annealing furnaces, and tempering furnaces. Resistance is measured with a two-lead, three-lead, or four-lead configuration. With the two-lead configuration, the resistance measured includes that of the leads, so this effect must be small enough to be ignored or a correction must be made for it. The correction is complicated by the fact that the resistance of the leads (typically copper wires) depends on the temperature of the leads, and the leads will be going through a temperature gradient. A three-lead measurement compensates for lead resistance but not for any difference in resistance between two leads. This is the configuration used for most process control applications. The four-lead configuration eliminates all lead effects and is generally reserved for those applications requiring great accuracy. A four-lead measurement is used with the standard platinum resistance thermometers in realizing the International Temperature Scale.

Noncontact Temperature Sensors

Temperature is a measure of the ability to transfer heat. Heat may be transferred by conduction, convection (actually conduction to a fluid followed by translation), and by thermal radiation. Noncontact temperature sensors depend on the thermally generated electromagnetic radiation from a surface of a test object. Electromagnetic radiation is emitted from a heated body when electrons within the body change to a lower energy state. Both the intensity and the wavelength of the radiation depend on the temperature of the surface atoms or molecules. For a blackbody, the radiation wavelength and spectral emission power vary as a function of temperature, as shown in Fig. 6(a). Planck blackbody distributions of spectral radiance for temperatures typically encountered in the heat treating of metals are shown in Fig. 6(b).

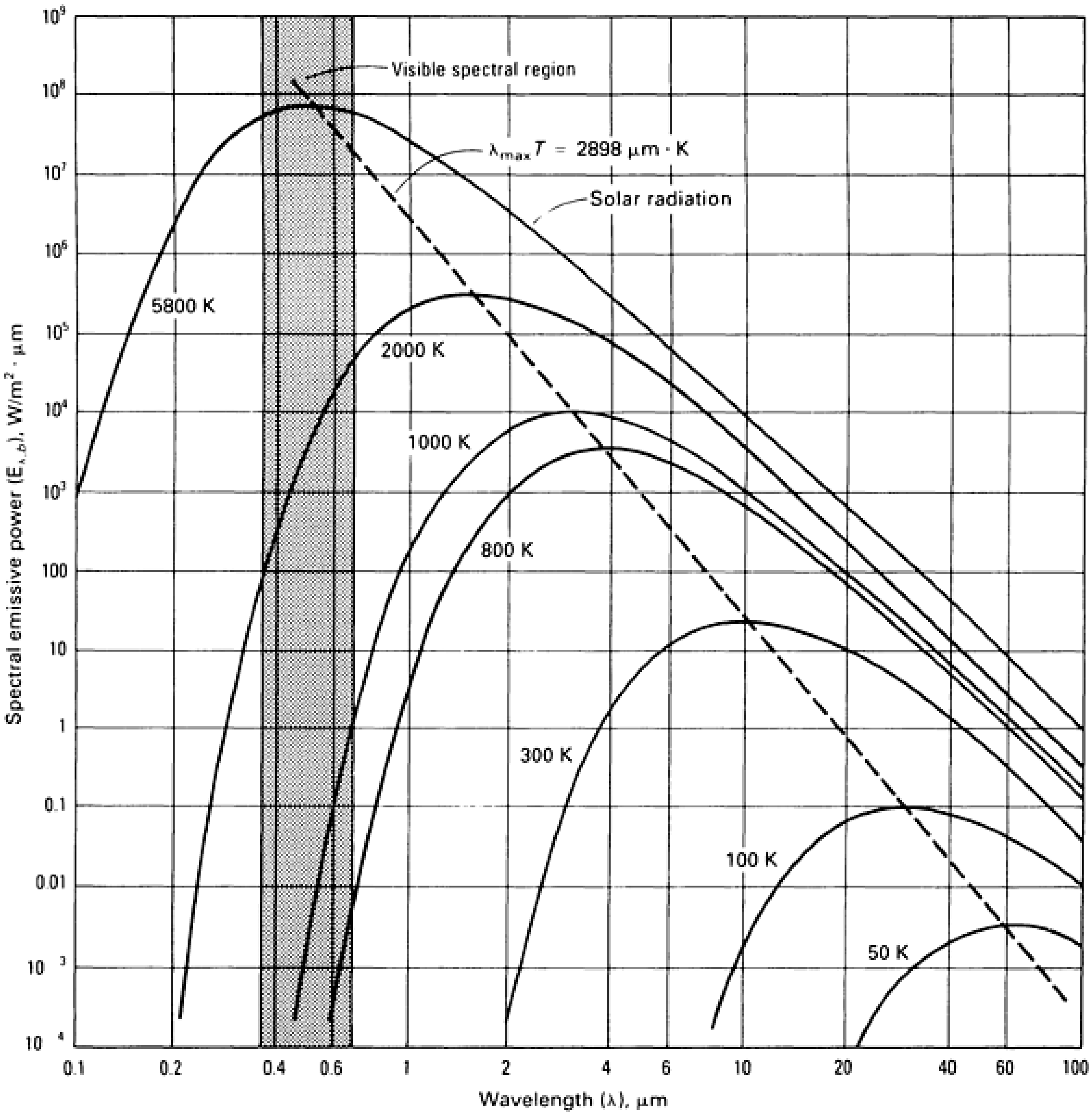

Fig. 6(a) Spectral blackbody emissive power for wavelengths in the thermal radiation spectrum (0.1 to 100 μm)

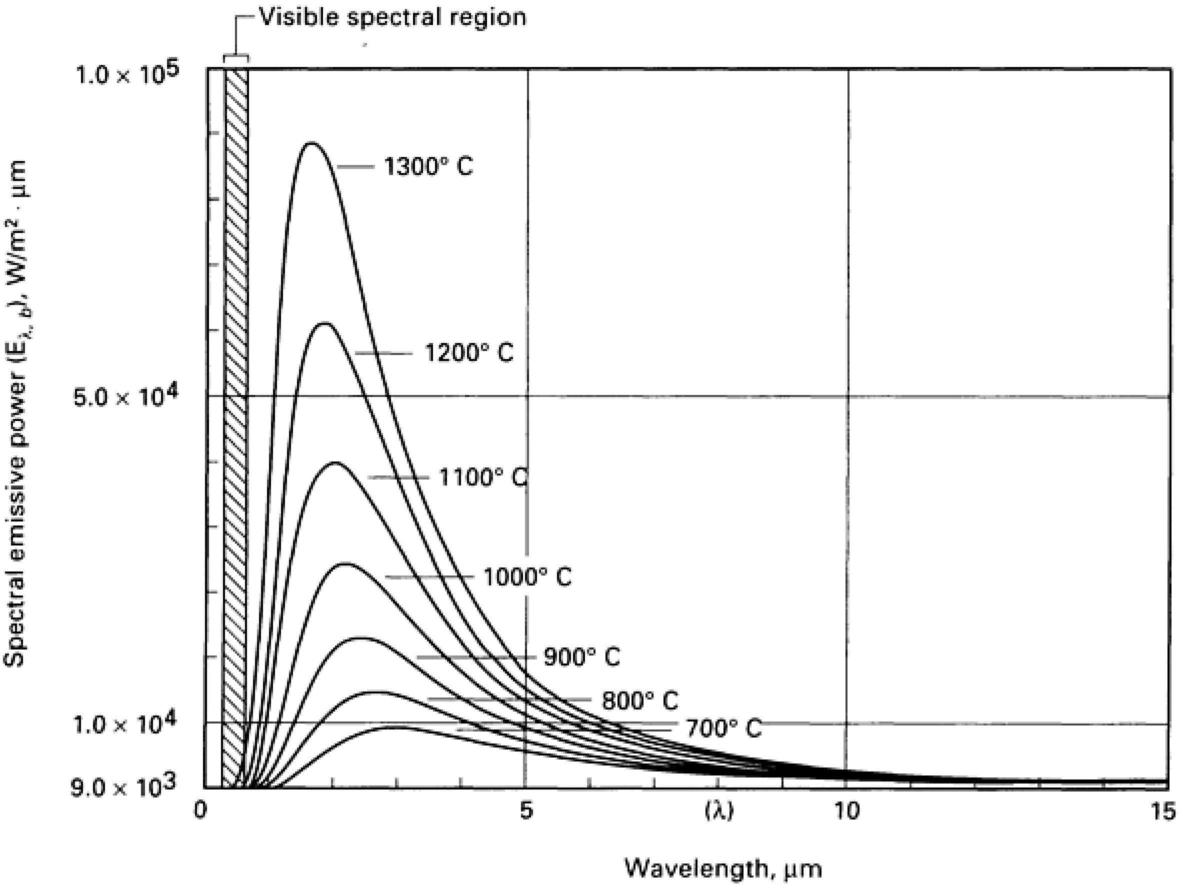

Fig. 6(b) Spectral blackbody emissive power for wavelengths in the near-infrared radiation spectrum (0.75 to 3.0 μm). Dominant wavelengths are shown for temperatures typically encountered in the heat treating of metals.

Blackbodies, the most efficient radiators and absorbers of electromagnetic radiation, have an emissivity of 1.0. All other bodies have an emissivity less than 1.0. Variations in emissivity change the power of radiation emitted at a given temperature and thus affect radiation temperature measurements.

Instruments that determine temperatures from measurements of thermal radiation are called radiation thermometers. The various types of noncontact temperature sensors include infrared imaging sensors, radiometers, and pyrometers. Radiometers and pyrometers are devices for measuring radiation, or spot or line temperatures, respectively, without the spatial resolution needed for an imaging system. Radiometers, because they usually have slow response times, are most useful for monitoring constant or slowly varying temperatures. Pyrometers are used as non-contacting thermometers for temperatures from 0 to 3000 °C (32 to 5400 °F). Newer instruments can superimpose a line trace of the temperature on the visible-light image of the surface or scene being viewed. Radiometers and pyrometers are usually rugged, low-cost devices that can be used in an industrial environment for the long-term monitoring of processes.

The tremendous advantage of radiation thermometers is that they yield accurate temperature measurements of the target without touching the test object (which is referred to here as a target because radiation thermometers must be sighted on the object of interest). Thus, radiation thermometers are preferred to contact thermometers (thermocouples, resistance thermometers, and so on) where the target is difficult to touch because it is moving, fragile, small, of small "thermal mass," hot, corrosive, or in a corrosive or protected environment. Radiation thermometers are thus a useful alternative to contact thermometers. The principal challenge is to be able to infer temperature from a signal that can depend not only upon target temperature but also upon target emittance, background emittance coupled with target reflectivity, intervening absorptance, or emittance and partial targets.

Optical Pyrometers. As the temperature of a heated target approaches 700 °C (1300 °F), it begins to emit thermal radiation in the visible portion of the spectrum (Fig. 6(a), 6(b)) as a deep red color. Further increases in temperature result

in changes in color from red, through orange, to white, with concurrent increases in brightness. Because of these variations in color and intensity, an experienced eye can make a fairly accurate prediction of temperature.

However, it would be far better to have the eye compare the temperature of the target of interest to that of a target of known temperature. This is exactly the principle of the disappearing filament optical pyrometer (Fig. 7). The hot target is viewed through a small terrestrial telescope that contains a lamp filament having brightness that can be adjusted by varying the amount of current through it. The current is adjusted until the brightness of the lamp filament equals that of the target and the filament seems to disappear into the glowing background of the target (Fig. 8). The temperature of the filament, and thus that of the target, is known from previously established calibration curves. Optical pyrometers generally are used to calibrate radiation sensors.

Fig. 7 Typical optical pyrometer

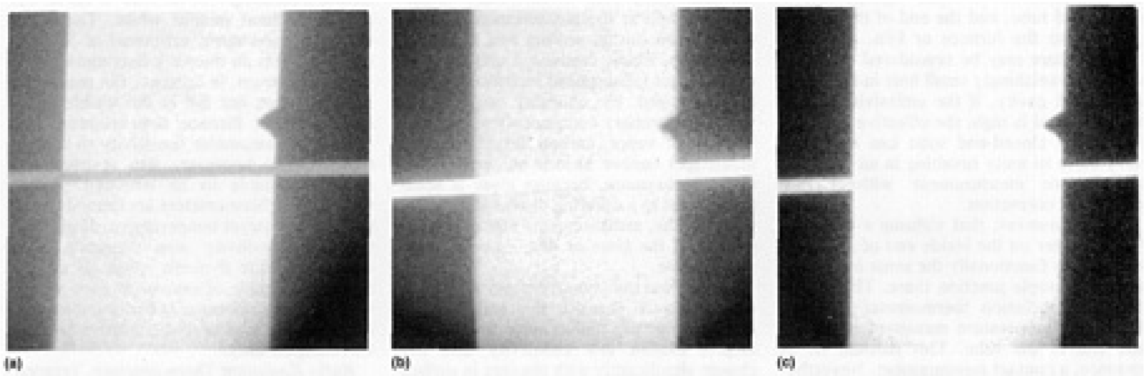

Fig. 8 Pyrometer filament (thin horizontal line) with various amounts of current paralleling radiation brightness of various temperatures. (a) Too low (cold). (b) Too high (hot). (c) Balanced (filament "disappears")

On-Line Radiation Thermometers. Radiation thermometers that do not depend on the eye consist of a detector sensitive to thermal radiation, an optical system to collect thermal radiation and concentrate it on the detector, a housing to support and protect the optics and the detector (Fig. 9), and electronics to measure the signal from the detector and compute and display the temperature. Even though selectivity can be controlled by the choice of a detector, it is often restricted further with optical filters (including windows and lenses).

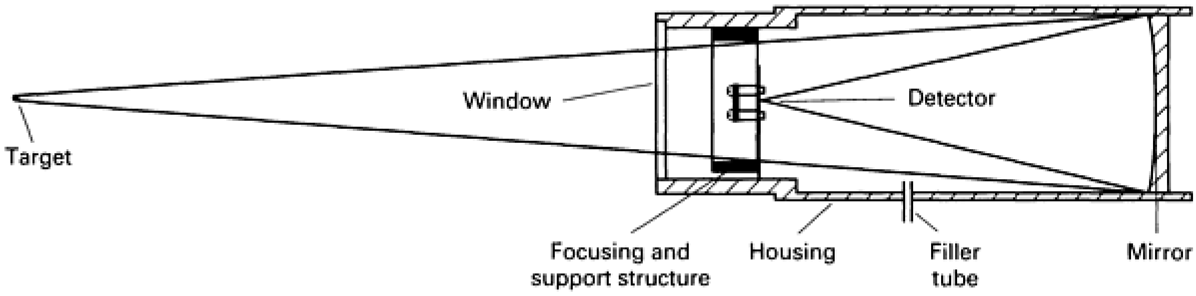

Fig. 9 Diagram of a radiation thermometer with a silicon thermopile

The detector is usually either a quantum (photon) detector, producing a quantity of electrons proportional to the number of photons impinging upon the detector, or a thermal detector, producing a signal proportional to an increase in the temperature of one part of the detector with respect to another part. An example of the former is the silicon photodiode, whereas thermopiles and pyroelectric detectors are frequently used thermal detectors. The silicon thermopile is a recent advance that provides a previously unobtainable combination of sensitivity, stability, speed, and broad spectral response (Fig. 10). Thin-film thermopiles include several layers: a radiation absorber, a metal, a second different metal, and an electrically insulating support. The signal is magnified by connecting multiple metal junctions in series. Replacing one of the metals with polycrystalline silicon can increase the signal further by almost an order of magnitude.

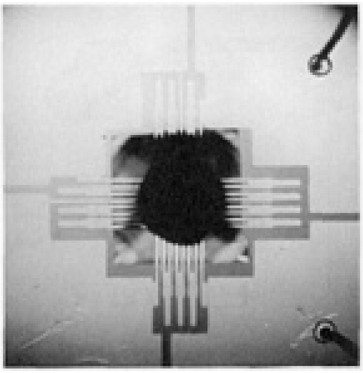

Fig. 10 Silicon thermopile with electrical connects. The circular radiation absorber at the center is 460 μm (18 mil) across.

Emissivity Errors and Calibration with Blackbody Cavities. In order for the target temperature to be inferred from the detector signal, the thermometer must be calibrated. At first glance, calibration might seem to consist of simply sighting the thermometer on a target of known temperature (as determined by a contact thermometer) and measuring the signal. However, different targets at the same temperature can emit significantly different amounts of energy because of variations in emissivity. Thus, the single measurement--detector signal--depends on two, usually independent, quantities: the temperature of the target and the emissivity of the target. Much of the following discussion is aimed at choosing thermometers and procedures that minimize uncertainties resulting from targets with uncertain or varying emissivity. These uncertainties are called emissivity errors. To eliminate emissivity errors during the calibration of radiation thermometers, so-called blackbody targets are used. Blackbody targets, which are perfect absorbers and emitters of radiation, can be approximated by a large uniformly heated cavity with a small hole for the emission of radiation (or the nearly perfect capture of incoming radiation).

Minimizing Interferences. An interference is defined as any condition that can cause a change in the amount of thermal radiation reaching the detector but that is unrelated to a change in target temperature. Unaccounted interferences lead to errors in temperature measurement. Potential interferences include variations in target emissivity, absorption or emission of radiation in the sight path between the thermometer and the target, radiation reflected by the target from hot surroundings to the thermometer, and variations in target size where the target does not always fill the field of view of the thermometer. The choice of the thermometer is often dictated by the need to reduce errors resulting from these interferences. The principal methods successful in reducing interference errors are to control the shape of the target, to purge the sight path between the target and the thermometer, and to choose the best wavelength. The use of ratio thermometers might also reduce the errors associated with interference effects.

Shaping. The most common use of target control is in the measurement of the internal temperatures of furnaces and kilns. Here the thermometer is often sighted into a closed-end tube, and the end of the tube is placed into the furnace or kiln. Although this structure may be considered fairly far from the vanishingly small hole in the large, isothermal cavity, if the emissivity of the tube material is high, the effective emissivity of the closed-end tube can approach very close to unity resulting in an accurate temperature measurement without any emissivity correction.

Note, however, that sighting a radiation thermometer on the inside end of a closed-end tube is functionally the same as placing a thermocouple junction there. That is, although a radiation thermometer is being used, the temperature measured is that of the end of the tube. This method is, in essence, a contact measurement. Nevertheless, this is often done in high-temperature metals applications where, for instance, the temperature is too high for thermocouples, or the sight tube is in an erosive or vibration environment where failure is frequent and resulting loss of a thermocouple is being prevented.

Purging can be important where the target is being obscured by absorbing or radiating gases, flames, or gas-born particles. Purging is usually accomplished with a so-called purged sight tube, where the thermometer sights at the target through an open-ended tube extending from the thermometer to a point close enough to the target that intervening interferences can be ignored. The tube is, typically, constantly purged with a nonabsorbing gas (frequently nitrogen or dry air) to keep the sight path free from the interfering material. Purging also helps to keep the lens or window of the thermometer clean. The distance through an absorbing medium may also be minimized by using fiber optics. Notice, however, that even where the sight path can be kept clean, emittance errors can destroy measurement accuracy.

Wavelength Selection. Because the temperature of the target may be determined from energy in any part of this distribution (total area, single band, band ratio, energy maximum, inflection points, and so on), one way to achieve accurate temperature measurements is to pick spectral regions where the effects of intervening interferences are minimized and target emittance is known. An illustrative (and commercially important) example is the measurement of glass temperature during sealing and annealing operations. Flame (emission) and combustion product (absorption) interferences can be minimized by choosing wavelengths where the primary components of combustion (water vapor, carbon dioxide, carbon monoxide) neither absorb nor emit radiation. Furthermore, because glass is semi-transparent to a differing degree at different wavelengths, measurements specific to the surface of the glass or deep into the glass are possible.

While glass radiation thermometry can be very accurate because the emittance of glass is generally reproducible, most metal targets exhibit low emissivity that can change significantly with changes in surface roughness or with oxidation. The effect of changing emissivity can be minimized by choosing a thermometer having a signal strongly dependent on target temperature, such as in the case of a radiation thermometer sensitive to short wavelengths (see Example 1 at the end of the section "Emissivity Values" in this article). The benefit of choosing a thermometer with short-wavelength sensitivity can be seen in the blackbody spectral distribution of Fig. 6(a) and 6(b). Notice that although the energy increases with increases in temperature at all wavelengths, it rises much faster at the shorter wavelengths. The curves become skewed to the left (shorter wavelengths) with increases in temperature. This means that the signal from a thermometer sensitive to short wavelengths only will rise much faster with increases in temperature than that for a thermometer sensitive to longer wavelengths. The short-wavelength-sensitive thermometer will be more sensitive to temperature changes. This is apparent to an observer. At 1000 °C (1830 °F), the color of a furnace enclosure viewed through a small hole is a pleasing red. At 1600 °C (2910 °F), it is a brilliant painful white. The sun's surface temperature, estimated at 5500 °C (9930 °F), has an intensity maximum in the visible spectrum. In contrast, the maximum intensity does not fall in the visible spectrum at most furnace temperatures. Restricting thermometer sensitivity to shorter wavelengths, however, also restricts the energy available to be detected. Short-wavelength thermometers are limited to relatively high target temperatures. High-temperature sensitivity also demands of a detector a wide dynamic range. If a thermometer capable of measuring over a very wide temperature range is desired, it may be necessary to choose one sensitive to long wavelengths only.

Ratio Radiation Thermometers. Temperature also can be inferred from the ratio of signals measured at two different wavelengths. Instruments making such a measurement are called two-color, dual wavelength, or ratio thermometers. Ratio thermometers are potentially useful in three areas:

- Partial targets where the target is too small to fill the field of view of the thermometer
- Occluded targets where the target is partially obscured by dust, smoke, and so on
- Targets for which emittance varies but does so equally in the two spectral regions to which the thermometer is sensitive

In all of these cases, variations (in target size, occlusion, emittance) that affect the signal equally for both wavelength regions do not affect the signal ratio or the temperature inferred. However, applying ratio thermometry should include the following considerations:

- The temperature is determined from the ratio of two signals, both of which are rising with increases in temperature. Therefore, the ratio can be less sensitive to temperature changes than either individual signal. Although the temperature sensitivity of the signal ratio can be increased by making the wavelengths farther apart, this diminishes the likelihood that the emittance will behave identically at each wavelength
- A decrease in signal will result in a lower apparent temperature for any signal wavelength thermometer. A lower apparent temperature will result from a decrease in signal at the shorter wavelength for a ratio thermometer, but a higher apparent temperature will be inferred from a relative decrease in signal at the longer wavelength. Therefore, an increase in absorptance (or decrease in emittance) can result in either negative or positive errors from a ratio thermometer
- Compared to single-wavelength thermometers, ratio thermometers are generally more complicated to construct, more fragile, and more expensive. For a more detailed analysis of ratio thermometers, see Ref 5

Emissivity Values. Emissivity is a function of several variables such as surface roughness and wavelength. The emissivity value in a given situation can be determined experimentally by measuring the signal from the target, measuring the target temperature independently, and calculating the correction to the calibration curve required to make the thermometer agree with the independent method. The independent method is usually to use a contact device (thermocouple) but may involve knowing that the target is at a fixed point such as a melting point.

Where such independent determination of target emissivity is not practical, published data may be used. However, great caution should be exercised here because the apparent emissivity of the target depends not only on the emissivity of the target material but also on the shape, roughness, and degree of oxidation of the target. Furthermore, emissivity values frequently depend on target temperature and the wavelength of the thermometer. With all of these cautions in mind, Table 5 shows values of emissivities for materials at 0.65 μm (the wavelength used by the disappearing filament optical pyrometer) (Ref 6). More detailed values are given in Ref 7. Besides emissivity values, this reference includes descriptions of how different preparation techniques and temperatures affect emissivity. Values at different wavelengths are also shown.

Table 5 Emissivity values for materials at 0.65 μm wavelengths

Material	State	Emittance
Metal		
Beryllium	Solid	0.61
	Liquid	0.61
Carbon	Unoxidized	0.85
	Graphite	0.76
	Graphite	0.95
	Powdered	. . .
Cesium	. . .	0.37

Chromium	Solid	0.34-0.45
	Liquid	0.39
Cobalt	Solid	0.36
	Liquid	0.37
Columbium	Solid	0.37-0.49
	Liquid	0.40
Copper	Solid	0.10-0.11
	Liquid	0.13-0.17
Erbium	Solid	0.55
	Liquid	0.38
Gold	Solid	0.04-0.16
	Liquid	0.07-0.22
Indium	. . .	0.30
Iron	Solid	0.35-0.37
	Liquid	0.37
Magnesium	Liquid	0.27
Manganese	Solid	0.59
	Liquid	0.59
Molybdenum	Solid	0.37-0.43
	Liquid	0.40
Nickel	Solid	0.36

	Liquid	0.37
Palladium	Solid	0.33
	Liquid	0.37
Platinum	Solid	0.30-0.33
	Liquid	0.38
Rhodium	Solid	0.24-0.29
	Liquid	0.30
Silver	Solid	0.04-0.07
	Liquid	0.07
Steel	Liquid	0.37
	Solid	0.35
Stellite	. . .	0.33
Tantalum	. . .	0.50
Tellurium	. . .	0.51
Thorium	Solid	0.36
	Liquid	0.40
Titanium	Solid	0.63
	Liquid	0.65
Tungsten	Solid	0.39-0.46
Uranium	Solid	0.54
	Liquid	0.34

Vanadium	Solid	0.35
	Liquid	0.32
Yttrium	Solid	0.35
	Liquid	0.35
Zirconium	Solid	0.32
	Liquid	0.30
Oxides		
Alumel	Solid	0.87
Aluminum	. . .	0.30
Beryllium	Solid	0.31-0.35
Cerium	. . .	0.58-0.80
Chromium	Solid	0.60-0.70
Cobalt	Solid	0.77
	Liquid	0.63
Columbium	. . .	0.71
	. . .	0.70
Chromel	Solid	0.87
Copper (Cuprous)	Solid	0.48-0.80
Carbon steel	Solid	0.80
Iron	. . .	0.63-0.98
	Liquid	0.53

	Cast	
	Oxidized	0.70
Magnesium	. . .	0.70
Manganese	Liquid	0.47
Nickel	Solid	0.85-0.96
	Liquid	0.68
Thorium	Solid	0.50-0.57
	Liquid	0.69
Tin	. . .	0.32-0.60
Titanium	Solid	0.52
	Liquid	0.51
Uranium	Solid	0.30
	Liquid	0.31
Vanadium	. . .	0.70
Yttrium	. . .	0.60
Zirconium	. . .	0.40
80 Ni 20 Cr	Oxidized	0.90
60Ni-24Fe-16Cr	Oxidized	0.83
55Fe-37.5Cr-7.5Al	Oxidized	0.78
70Fe-23Cr-5Al-2Co	Oxidized	0.75
55Cu-45Ni (Constantan)	Oxidized	0.84

Carbon steel	Oxidized	0.80
Stainless steel	Oxidized	0.85

Source: Leeds and Northrup Instruments

The relatively low emissivity values of most metals can be significantly affected by changes in surface roughness or oxidation. These variations in emissivity also affect temperature measurements by changing the power of radiation emitted at a given temperature. The errors from these uncertainties in emissivity values can be reduced by making temperature measurements at shorter wavelengths. The example below illustrates the potential effects of uncertainties in emissivity (or absorptance) in four thermometers with different spectral responses.

Example 1: Temperature Measurements from Four Radiation Thermometers with Different Spectral Sensitivities.

Figure 11 shows calibration curves--plots of signal versus temperature--for four thermometers: a thermometer sensitive to a narrow spectral region centered at 0.65 μm, a thermometer sensitive to a narrow spectral region centered at 0.9 μm, a ratio thermometer sensitive to 0.65 and 0.9 μm, and a "total radiation" thermometer sensitive to radiation at all wavelengths. The curves are normalized to be equal at 1500 °C (2730 °F). The effect of a 20% decrease in signal at 1500 °C (2730 °F) is also shown.

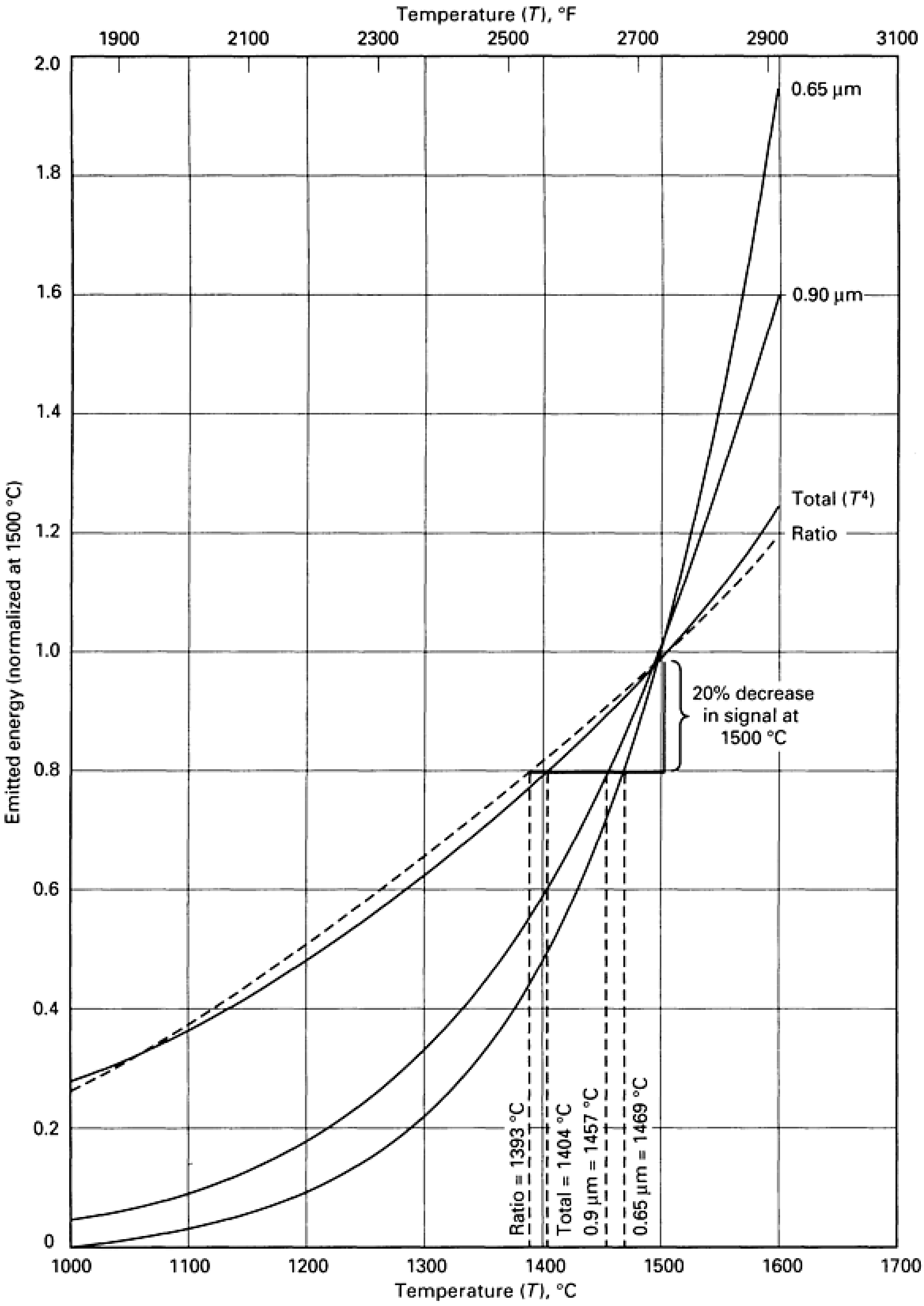

Fig. 11 Calibration curves of four thermometers with various spectral sensitivities

First, looking at the general shape of the four curves, it can be seen that the 0.65 μm curve rises most rapidly, which can also be inferred from the blackbody curves (Fig. 11), where it is seen that energy at short wavelengths increases most rapidly with increases in temperature; the 0.9 μm curve rises less rapidly than the 0.65 μm curve for the same reason; the

total radiation curve shows a weaker temperature dependence than the short-wavelength curves because most of the energy contributing to this curve comes from wavelengths longer than 0.65 or 0.9 μm, where temperature dependence is weaker; the ratio curve shows weak temperature dependence simply because it is the result of the two other curves (0.65 and 0.9 μm), which have very similar temperature dependences. (The apparent similarity between the ratio curve and the total radiation curve is coincidental and results from the specific choices of wavelengths and temperatures for this example.)

The effect of a 20% decrease in signal (or signal ratio for the ratio thermometer) from a 1500 °C (2730 °F) target should now be considered. Very simply, the results from thermometers with steeper calibration curves are affected less. The 0.65 μm and 0.9 μm thermometers show errors of 31 and 43 °C (56 and 77 °F), respectively, and the less-temperature-sensitive total and ratio thermometers exhibit errors of 96 and 107 °C (173 and 193 °F), respectively, for identical changes in signal. Such a signal change could result from an uncompensated 20% decrease in target emittance (at the shorter wavelength for the ratio thermometer), a 20% increase in absorptance (again at the shorter wavelength for the ratio thermometer), or some combination of the two. (In general, the performance of a properly chosen ratio thermometer is better than that indicated here because many interferences have a nearly equal effect in both wavelength regions.)

To summarize, using shorter wavelengths results in smaller errors from uncertainties in emissivity or absorptance. Selecting short wavelengths to minimize emissivity error is even more useful for bare metals in the open because the emissivities of most metals decrease with increases in wavelength. Exceptions to this rule are when choosing a shorter wavelength results in signals that are too small to be measured accurately, and when the target is surrounded by a hotter environment. In this latter case, energy reflected by the target from the hot environment to the thermometer will be richer in short-wavelength energy and may cause a larger positive error for a short-wavelength thermometer. This situation, an example of which is a soaking pit, cannot generally be solved with a single thermometer.

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Measurement and Control Instruments

The various measurement and control loop configurations must function properly to achieve optimum operation of the system. Although the necessity of this coordination is obvious, one or more elements of the system are commonly neglected. For example, if the temperature sensor, which may be only 1% of the instrumentation cost, is out of calibration or not properly located, the performance of the complete system is degraded. Poor input into even the most sophisticated temperature measurement and control systems will produce poor output.

Measurement Instruments and Accuracy. The accuracy of the measurement depends greatly on the accuracy of the temperature sensor and the connecting circuitry. The accuracy of the measurement instrument is defined in its specifications under referenced conditions for its power supply, ambient conditions (temperature and humidity), electrical noise rejection, and maximum source impedance. Transmitters, which are used in some sensors to amplify and condition the temperature signal, have similar qualifications on their accuracy specifications.

Temperature measurement instruments incorporate reference junction compensation in their circuitry for thermocouple measurements and emissivity compensation for noncontact radiation sensors. Reference junction compensation automatically adjusts the measurement depending on the temperature at the junction between the thermocouple wire and the copper wire of the measuring circuit of the instrument. Radiation-type temperature measurements require an emissivity compensator. This compensator makes a calibration adjustment by comparing measurement of the same target with an optical pyrometer or calibrated thermocouple. The emissivity compensator is adjusted to make the radiation pyrometer measurement indication agree with the reference calibration instrument.

In the measurement area, the problem is always to make the sensor as sensitive as possible to the variable being measured and as insensitive as possible to changes in all other variables. Consequently, there will be more use of multiple sensors to compensate for systematic errors given by single sensors. For example, in a reheat furnace, the thermal radiation signal received from a target can be a combination of radiation emitted by the target plus radiation emitted by the furnace walls and reflected by the target. Using a second radiation thermometer to measure this wall contribution can yield superior results in such applications (Ref 8).

Single-Loop Control. A temperature controller should provide just enough energy to satisfy process requirements, even though operating conditions vary. Variations include changes in process load, fuel characteristics, and ambient temperature. Thus, controller requirements are more stringent when process requirements are demanding and especially when operating conditions vary significantly.

In operation, the controller set point that represents the desired temperature is compared with the process or actual temperature. The stability of the controller and its sensitivity to the difference between desired and actual temperatures are critical. Based on this comparison, the controller regulates the energy flow to the process.

The two basic types of control are the two-position, or on-off, type and the proportioning, or modulating, type. These two basic types exist in many variations.

On-off types of controllers are inexpensive, simple to operate, and easy to maintain. On-off types, however, use energy inefficiently and increase the cost of heater and brickwork maintenance, particularly when controlling high-temperature processes in which heat transfer lags are long. The process temperature cycles above and below the controller set point as the controller turns the heat input on and off. During start-up, the heat remains on until the temperature reaches the controller set point and then turns off. Consequently, the thermal inertia of the process, equipment, and work load, causes an overshoot beyond the set point, and energy is wasted.

After the temperature has stabilized in a characteristic on-off cycle, energy is still wasted because of the effects of heat transfer. Assuming that the temperature cycles are equally distributed above and below the controller set point, the average actual temperature will equal the set-point temperature. However, heat transfer losses or wasted energy, which result from losses above the set point, exceed the savings that result from temperatures below the set point. Thus, a net loss is produced, even though the average actual temperature is equal to the set point. These losses increase as operating temperature increases.

The magnitude of the temperature cycle, that is, the magnitude of the deviation from the set point, is directly related to the heat transfer characteristics and measuring lags of a particular process. Therefore, if the temperature measurement responds rapidly to changes in heat input, departure from the set point will be small. Conversely, when response is slow, substantial temperature deviations will result.

The effect of process demand on two-position (on-off) control is illustrated in Fig. 12. The curve in Fig. 12(a) shows that temperature cycles evenly above and below the set point. In other words, the heater on and off times are equal. Shown in Fig. 12(b) is the response for a higher process demand, such as more heat required to maintain a given temperature. In this case, the on time is greater. In the curve in Fig. 12(c) the temperature cycles are at a lower average value. The average value is higher than the set point. The curve in Fig. 12(d) shows the effects reversed for a lower process demand, which again brings the average to very near the set point. The relationship between heat supply, the controlled variable, and the set point at about one-half load conditions also is shown in Fig. 12(e).

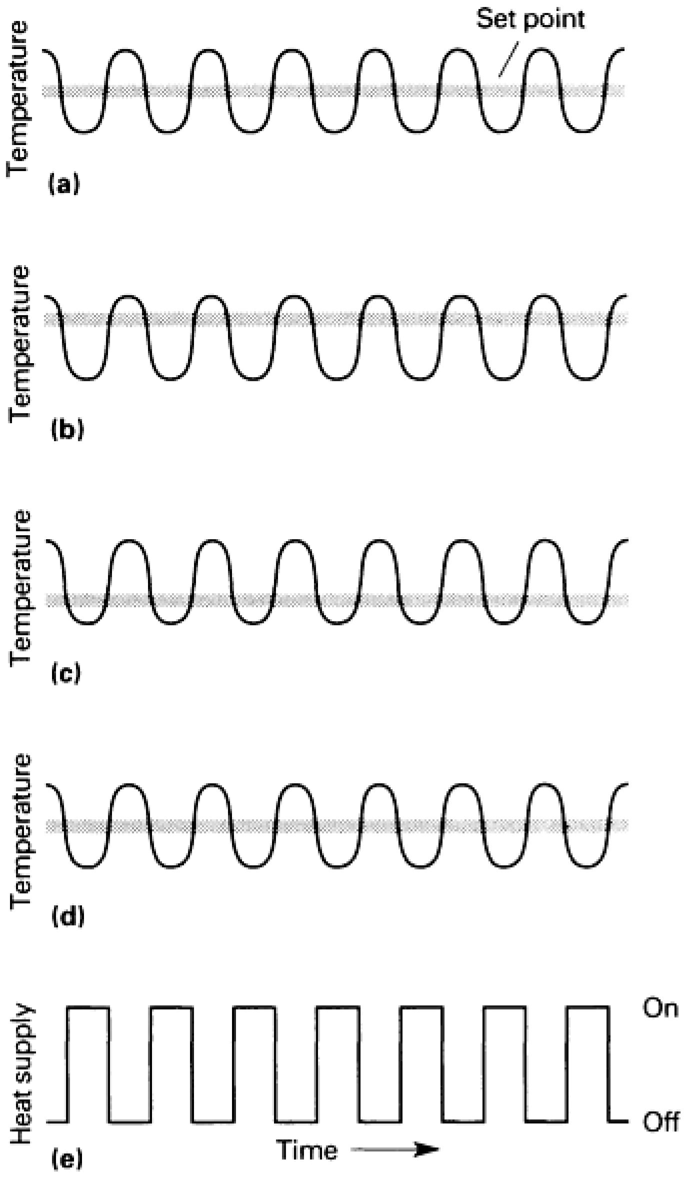

Fig. 12 Effect of process demand on two-position (on-off) control

Cyclic process temperatures cause cyclic process pressures in enclosed gas atmosphere furnaces and ovens. This condition can cause breathing, or inspiration of ambient air, resulting in additional energy losses.

In summary, on-off controllers have the advantage of low cost and simple installation. However, they should be considered only for relatively noncritical processes.

Proportioning or Modulating Controllers. When process temperatures are critical, or when large quantities of energy are consumed, proportioning control should be considered. Compared to on-off controllers, proportioning or modulating controllers are more expensive and sophisticated. They are less expensive to operate, however, because they use energy more efficiently. The process temperature is consistently maintained at the controller set-point temperature because the controller adjusts the heat input to match the heat demand of the process. Any changes in the process demand temperature will be matched by corresponding changes of the heat input to offset the temperature changes and maintain the desired temperature. Proportioning controllers can be designed to minimize or eliminate set-point overshoot, which is caused by the thermal inertia of the furnace and work load when the process is initially brought from ambient to operating temperature. Normally the process heat head, if not controlled, causes the temperature to overshoot.

The process-control response characteristics vary significantly for various processes. They even can vary for the same process when different operating conditions exist. For example, a furnace might be idled at 120 °C (250 °F) and operated at 1095 °C (2000 °F). The proportioning controller, in response to the error signal comparison (set-point temperature versus actual temperature), performs a computation to solve the control equation. This computation includes proportional, integral, and derivative terms; thus, the controller is referred to as a PID, or three-mode, controller. The proportional term is proportional band or gain, and its units are percent proportional band or gain. The integral term is reset, and its units are repeats per minute. The derivative term is rate, and its units are minutes. These tuning adjustments (proportional band, reset, and rate) match the controller response to the process dynamics. Proportional band relates to the size of the error signal. Reset relates to the error signal size plus the length of time it has existed. Rate relates to the error signal speed of change. Consequently, the controller, when properly tuned in response to these error-signal characteristics, continuously adjusts the energy input to the process to maintain the desired controller set-point temperature. A properly tuned proportional controller will reduce energy losses significantly by closely maintaining the desired temperature.

Proportional controllers, which are classified according to their outputs, include current-adjusting type (CAT), position-adjusting type (PAT), and duration-adjusting type (DAT). The CAT may be used with an electric power regulator, such as a silicon-controlled rectifier (SCR), to control electrically heated processes. It also can be used with an electropneumatic converter to regulate an air-operated valve. The PAT may be used with an electric motor drive unit to regulate a lever-operated valve. The DAT may be used with an electrical contactor, electric motor drive unit-valve combination, or solenoid-operated valve.

Typical applications include the use of a CAT controller to regulate an SCR. The SCR, in turn, regulates electrical power to heater elements in a furnace. A PAT controller typically is used with electric-motor drive to operate a valve on a gas-fired furnace. The DAT controller is used with an electric contactor to regulate electric power to heater elements. Electric contactors are less expensive than SCRs and are adequate for slow-response, high-temperature furnaces. DAT control also is used to operate gas valves on radiant tube-fired furnaces to achieve uniform heating throughout the tube.

The process temperature, even with PID control, tends to overshoot the control set point during start-up. This action is because of the system's thermal inertia. If the temperature sensor is of heavy construction, its slow response speed will compound this condition. A feature called Approach Action may be specified in the controller to minimize this problem, if the controller is properly tuned. This function also can be achieved with a feature called reset limiting.

Energy Flow Regulators. The final element of the control loop responds to the controller output by regulating the energy flow. It may consist of one or more components such as valves, dampers, power regulators, heater elements, converters, or actuators. Some desirable characteristics include fast response speed, linear response, high sensitivity, adequate power, and reliability. The final element should have a linear response over its full range; that is, a change in the final element should produce a corresponding change in temperature. The sizing of the valves, power regulators, and heaters should match the process requirements to optimize control performance. The final element may provide feedback devices, such as slidewires and limit switches, for use in the control system. The final element also may be designed to drive to a limit or to lock in its last position, in the event of a power failure.

Some final elements used with electric controllers are:

- An electric motor-valve combination used to regulate flow of steam or hot water
- An electric motor-valve-burner combination used to regulate fuel combustion
- Pneumatic valves used to regulate fuel; an electropneumatic converter used to convert the output signal from the controller
- Electrical resistance-type heating elements used with contactors, saturable core reactors, silicon-controlled rectifiers, and triacs

Design of the final element in any energy-efficient control system is extremely critical because it regulates the energy flow. For example, butterfly valves are frequently selected instead of proportioning valves because the butterfly valves cost less. However, their flow characteristics are nonlinear, which makes control over the entire range more difficult. In butterfly valves, a large flow change occurs near the closed valve position, and a small change occurs near the open position.

Data Acquisition. Traditionally, the day-to-day control of thermal processes has been enhanced by comparing present results with previous results and watching trends within a current run (batch or continuous) using traces printed by strip chart recorders. Besides this control aid, increasing emphasis is being placed by customers and quality control managers on statistical results and even on proof that a specific run, or even a specific piece, has experienced the right time-temperature treatment. To help manage this increasing data and results requirement, a class of powerful, microprocessor-based recorders has been developed. These instruments (Fig. 13) provide not only usual strip chart multipoint display of temperature as a function of time, they also calculate results (for example, averages of several thermocouple readings), print in a data logging format, indicate the occurrence of discrete events, and provide a variety of alarm functions.

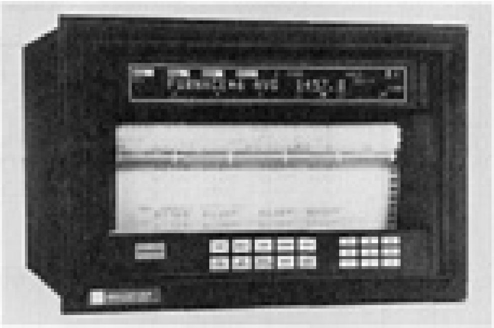

Fig. 13 A microprocessor-based recorder with control, analysis, and alarm function capabilities

Process Management Systems. As described earlier in the section "Auxiliary Devices," computer technology has allowed the development of small process management systems that integrate all the functions required to manage a heat-treat system. Process management systems provide a common database for all functions and allow the integration of analog loop control, discrete logic control, data acquisition, data management, statistical calculations, and reporting. Communications and interconnection are also by means of soft wiring, that is, by configuration and programming instead of physical hard wiring.

A further advantage is that while all system information is available at a central management station (consisting of a computer, keyboard and CRT screen, control, and data acquisition), other functions can be located in local processing units close to the process. This minimizes wiring costs on installation (or future upgrades in the installation) and maximizes reliability; even if communication to the central management station is severed, the local processing unit will continue to function following whatever predetermined course of action it has been configured to do in that situation. The capabilities of a process management system are described in more detail in Ref 9.

Distributed Control Systems (DCSs). When a process control requirement reaches a certain size, the capabilities of a DCS are needed. The main capabilities that a DCS might hold over a minicomputer process management system are size (the number and types of analog and discrete inputs and outputs the system can handle), speed, redundancy (reliability), ease of configuration, graphics available, or complexity of calculations or control algorithms. In general, if there are only a few control loops with little action required between loop (analog) and logic (discrete) control, and if recorders will suffice for the data acquisition, a hardwired interconnection system should be considered. When the number of control loops has grown from 10 to 100, when integral control of loop and logic functions or calculations are required, and when downloading of many different process recipes is required, a minicomputer process management system, at least, will probably be chosen. A DCS is appropriate for even larger processes, the integration of many processes, or where special reliability capabilities are required. One special capability of some present DCSs is full redundancy with doubly redundant fiber-optic communication networks among the components of the system. These fiber-optic links allow the system to be distributed over several miles of a large plant.

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Characteristics of Process, Product, and Production

A control system regulates the energy input to the process to achieve desired heating and cooling rates and maintains soak temperatures by matching heat input to heat losses. If these heat losses were always constant, a preset heat supply could keep temperature in balance indefinitely.

In practice, this never happens. Furnaces must be started up, idled, and operated at varying production rates and temperatures.

To handle such changes efficiently, control systems must constantly readjust heat input so that the work temperature is maintained despite changing operating conditions.

Two principal characteristics of the instrumentation and the process equipment influence the selection of a control system, lag and thermal inertia.

In a heat-treating furnace, refractory, muffles, or retorts through which the heat must flow represent heat barriers. The greater their number, the greater the heat transfer resistance or lag, with the result that there is a longer delay between the heat input change and a change in product temperature. After this mass is heated--refractory, muffles, retorts--thermal inertia is a consideration.

The thermal inertia of a process is its capacity to continue a temperature change in the same direction after the heat supply is altered, before it begins to move in the opposite direction. The time it takes to turn a process around determines the extent of its thermal inertia. A furnace with a large, heavy muffle has a high heat storage capacity. Heat heads build up rapidly during heat input periods, and the momentum from the latent heat continues to push product temperature up after the heat is turned off. The converse is also true: Product temperature continues to drop after the heat is turned on. In short, the furnace is sluggish, and the temperature swings are wide and slow.

In addition to the resistance to heat transfer and the thermal inertia of the product and process equipment, there are five characteristics of the product to be considered in the selection of a temperature control system. The first characteristic of the product is its state. This is important in deciding the degree of acceptable temperature tolerances. For example, a solid product such as steel or a ceramic may have a temperature tolerance of ±3, 6, 8 °C (±5, 10, 15 °F), or even more.

The second characteristic concerns the material of the product, that is, whether it is ferrous or nonferrous. Most nonferrous and high-alloy steel products have temperature tolerances of ±3 or 6 °C (±5 or 10 °F). On the other hand, low-carbon steel and other ferrous metals may have a temperature tolerance of ±8 to 14 °C (± 15 to 25 °F).

The third characteristic--assuming the furnace is properly designed for the job--is the mass and shape of the product. This determines the responsibility the control system must assume for uniform heat penetration. The mass and shape of a large roll of steel influences the selection of not only the furnace design but also the control system required to maintain uniform heat from top to bottom and side to side.

The fourth characteristic of the product is its critical temperature. As the temperature of the product approaches its critical temperature, the more accurate and responsive must be the control system.

The fifth and last characteristic of the product is the quality of the product after heating. In heat treating, for example, the effect of furnace atmosphere varies with temperature. Oxidation and carburizing occur faster at higher temperatures. For parts of uniform quality, temperature must be held uniformly throughout the furnace load.

Furnace Atmospheres for Heat Treating

Revised by Paul Johnson, National-Standard Company

Introduction

CONTROL OF FURNACE ATMOSPHERES has become increasingly critical to successful heat treating with more precise metallurgical specifications. The prevention of surface oxidation or scaling when metals are exposed to elevated temperatures remains an important task of the furnace atmosphere. In a more sophisticated view, the atmosphere within the furnace chamber is a full-fledged partner in achieving the chemical reactions that occur during heat treating.

Properly applied and controlled, furnace atmospheres provide the source of elements in some heat-treating processes, surface cleansing of parts being treated in other processes, and a protective environment to guard against adverse effects of air when metals are exposed to elevated temperatures in still other processes.

Practical Flow Formula

Control of the flow of gases through a furnace chamber is important to ensure that sufficient atmosphere gas is being admitted to the furnace to seal the mechanical leaks against air infiltration or that a vestibule is being purged rapidly enough. In common practice, a chamber is considered essentially purged after five volume changes.

The simple way to adjust atmosphere flow to a furnace is through a meter that can be read directly. In some instances, however, atmosphere distribution among various inlets is required even though total atmosphere flow is metered. Flow rate is a function of the volume of a furnace chamber and time. A practical flow formula that is sufficiently accurate to deal with furnace atmosphere flows is as follows:

$$Q = 1651.25 \times A \times C \times \sqrt{h/d} \qquad \textbf{(Eq 1)}$$

where Q is flow rate, in ft^3/h; A is area of orifice, in $in.^2$; C is coefficient of discharge; h is differential pressure, and d is specific gravity of the gas.

For a thin-plate orifice in this equation, $C = 0.61$; for spuds with a tapered entrance, $C = 0.95$; and for spuds used in reverse (tapered outlet), $C = 0.9$.

Fundamentals of Gases

Gas molecules are somewhat widely separated, and they move about unceasingly in the space in which they are contained. Gases differ from liquids in two respects; gases are highly compressible and they fill any closed vessel in which they are placed. Gases resemble liquids in that both are capable of:

- Flowing
- Exerting pressure upon surfaces they contact
- Exhibiting flow velocity that can be measured through an orifice

Although there is no clear distinction between gases and vapors, the term vapor usually is applied to a gas that is near its liquefying temperature. Steam and carbon dioxide usually are called vapors because they are easy to liquefy. Air, hydrogen, and nitrogen ordinarily are called gases.

Gas Pressure. The characteristic of compressibility of gases leads to a very simple relationship between the pressure of a gas and its volume. The relationship is known as Boyle's law: The volume of a confined body of gas varies inversely as the absolute pressure, provided the temperature remains unchanged.

The pressure of confined gases can be measured by U-shaped manometer tubes containing mercury or other liquids. The gas whose pressure is to be measured is connected to one side of the manometer, and the other leg of the tube remains open. Pressure exerted by the gas will force the liquid up the leg open to the atmosphere. The difference in height of the liquid in the two columns multiplied by the density of the liquid indicates how much the gas pressure exceeds atmospheric pressure. This pressure is known as gage pressure, to distinguish it from absolute pressure, which includes the pressure of the atmosphere.

Diffusion. When two or more closed vessels, originally containing different gases, are joined so that each gas has access to all containers, and assuming no chemical reaction takes place, molecular motion causes each gas to penetrate the entire volume of all containers. By this diffusion, the mixture eventually becomes homogeneous. Each gas expands into the total available volume as though the other gas were not present. According to Boyle's law, the absolute pressure of each gas is reduced to a lower value called its partial pressure. The pressure of the resulting mixture of gases will be equal to the sum of the partial pressures of the constituent gases. This phenomena is expressed as Dalton's law: A mixture of several gases that do not react chemically exerts a pressure equal to the sum of the pressures that the several gases would exert separately if each were allowed to occupy the entire space alone at the given temperature.

Avogadro's law states: At the same temperature and pressure, equal volumes of different gases contain equal numbers of molecules. When this law is applied to a particular quantity of a gas, the quantity is known as a mole (abbreviated mol), or gram-molecule, or gram-molecular weight. The mole of a substance is a mass in grams numerically equal to the sum of the atomic weights of the atoms in a molecule of that substance. The number of molecules in a mole of gas is known as Avogadro's number. A mole of any gas contains 6.02×10^{23} molecules, and at 0 °C (32 °F) and standard atmospheric pressure of 760 mm (100 kPa) mercury, or sea level pressure, occupies 22.4 L (0.79 ft^3) of space.

Density. The density of a gas is the amount of mass contained in a unit volume, and the density is influenced by pressure and temperature. The density and pressure increase in the same proportion, and gases expand when heated and contract when cooled. The density of air has been determined with great care. One liter (0.038 ft^3) of air at standard temperature and pressure weighs 1.293 g (0.04561 oz), or an air density of 1.3 kg/m^3 (0.081 lb/ft^3). The specific gravity of a gas is normally expressed with reference to air as standard (Table 1).

Table 1 Properties of common gases and vapors

Gas	Chemical symbol	Approximate molecular weight	Density[(a)]		Specific gravity[(b)]
			kg/m^3	lb/ft^3	
Air	. . .	28.97[(c)]	1.293	0.0807	1.000
Ammonia	NH_3	17.03	0.760	0.0474	0.588
Argon	Ar	39.95	0.178	0.0111	1.380
Carbon dioxide	CO_2	44.02	1.965	0.1228	1.520
Carbon monoxide	CO	28.01	1.250	0.0780	0.967
Helium	He	4.00	0.179	0.0112	0.138
Hydrogen	H_2	2.02	0.090	0.0056	0.070
Methane	CH_4	16.04	0.716	0.0447	0.552
Nitrogen	N_2	28.01	1.250	0.0780	0.968
Oxygen	O_2	32.00	1.429	0.0892	1.105

Propane	C_3H_8	44.09	1.968	0.1229	1.522
Sulfur dioxide	SO_2	64.06	2.860	0.1785	2.212

(a) Standard temperature and pressure: 0 °C (32 °F) and 760 mm Hg.

(b) Relative density compared to air.

(c) Because air is a mixture, it does not have a true molecular weight. This is the average molecular weight of its constituents.

Viscosity. Molecular friction, or viscosity, is present in gases as well as in liquids, although the wide spacing of the molecules results in appreciably lower viscosity in gases. This friction retards the motion of gases through such channels as tubes and ducts. The coefficients of viscosity for gases and liquids are expressed in poise or centipoise. A rise in temperature causes a rise in the viscosity of gases and a lowering of liquid viscosity.

Temperature Effect. Charles's law states: The volume of a fixed mass of gas and its pressure vary directly with the absolute temperature.

Using the effect of temperature, a general gas law can be written in the form of a mathematical equation, as follows:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \qquad \textbf{(Eq 2)}$$

where P is absolute pressure, V is volume of a fixed mass, T is absolute temperature, and subscripts 1 and 2 are two different sets of conditions of pressure, volume, and temperature.

When a furnace atmosphere is required to contribute an element or elements during heat treating, these fundamental gas laws become important. Many forms of control are used to develop carbon potential, or the potential of an element, within an atmosphere. Differing amounts of an element can be utilized in the heat-treating chemical reaction, with a constant potential reflected. A quantitative measure of an element is developed by an understanding of the chemical formula involved in the reaction and the partial pressures of the formula gases used to produce the element.

Principal Gases and Vapors

Air is an important gas in furnace atmospheres because it comprises the atmosphere in a furnace in which no protective atmosphere is used, and because it is a major constituent in many prepared atmospheres. The chemical makeup of air is approximately 79% nitrogen and 21% oxygen, with trace amounts of carbon dioxide. As an atmosphere, air behaves like an oxygen atmosphere because oxygen is the most reactive constituent in air.

Oxygen reacts with most metals to form oxides. In addition, oxygen reacts with carbon that is dissolved in steel to lower the carbon content of its surface.

Nitrogen. Molecular nitrogen is passive to ferrite and is entirely satisfactory for use as an atmosphere in the annealing of low-carbon steels; however, it must be completely dry to be used as a protective atmosphere for high-carbon steels because small amounts of water vapor in the nitrogen will cause decarburization. Molecular nitrogen is reactive with many stainless steels and cannot be used in their heat treatment. Atomic nitrogen (created by the temperatures of normal heat treating) is not a protective atmosphere because it combines with iron to form finely divided nitrides that impart hardness to the surface.

Carbon Dioxide and Carbon Monoxide. These two gases are important in atmospheres used in processing steel. At austenitizing temperatures, carbon dioxide reacts with surface carbon in a steel surface to produce carbon monoxide:

$$(C) + CO_2 \text{ € } 2CO \qquad \textbf{(Eq 3)}$$

in which (C) represents carbon dissolved in austenite. This reaction continues until there is no carbon dioxide available or until the steel surface is completely free of carbon--at which point, if there is a continuing supply of carbon dioxide, iron and ferrous oxide will be oxidized by the following reactions:

$$Fe + CO_2 \text{ € } FeO + CO \qquad \textbf{(Eq 4)}$$

$$3FeO + CO_2 \text{ € } Fe_3O_4 + CO \qquad \textbf{(Eq 5)}$$

Ferrous oxide (FeO) is the stable oxide formed above 555 °C (1030 °F), whereas the magnetic oxide (Fe_3O_4) is formed below 555 °C (1030 °F) as shown in Fig. 1.

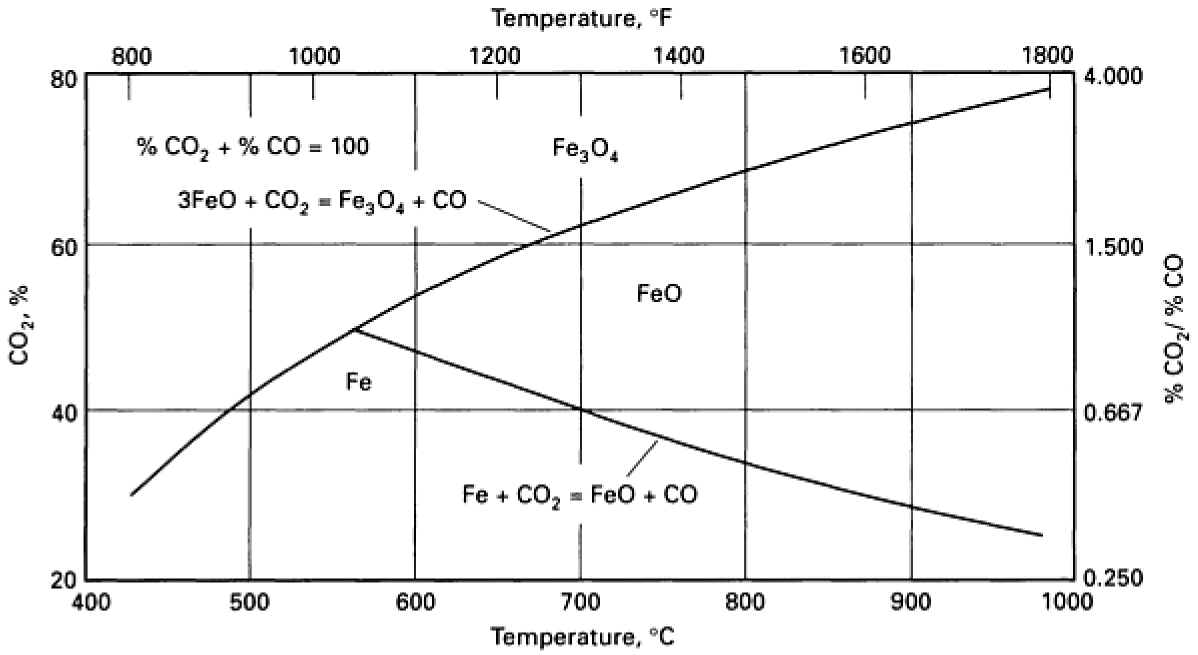


Fig. 1 Equilibrium curves for the formation of scale (FeO and Fe_3O_4) when heating iron in a CO-CO_2 atmosphere at different temperatures

The above reactions will proceed until equilibrium is established. These reactions progress at a rate depending on time, temperature, and pressure of the system. The equilibrium conditions for carbon steels of various carbon concentrations heated in a CO-CO_2 atmosphere are shown in Fig. 2.

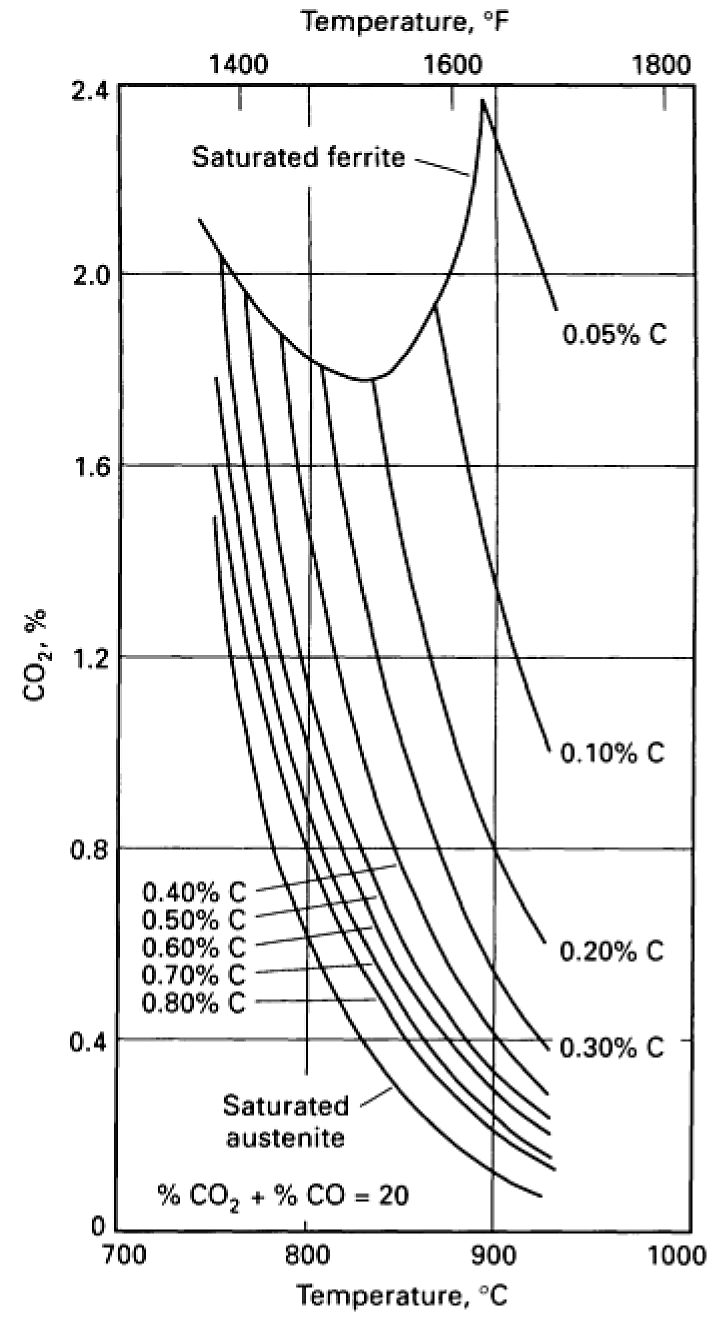


Fig. 2 Temperature and percentage of carbon dioxide for equilibrium conditions with carbon steels of various carbon contents

Hydrogen reduces iron oxide to iron. Under certain conditions, hydrogen can act to decarburize steel. The decarburizing effect of hydrogen on steel depends on furnace temperature, moisture content (of the gas and furnace), time at temperature, and carbon content of the steel. The decarburizing effect of hydrogen at 705 °C (1300 °F) or below is negligible, but it increases markedly above this temperature. Water vapor increases the decarburizing effect because it dissociates, thus providing a supply of nascent hydrogen and oxygen. Hydrogen reacts with carbon in steel to form methane:

$$(C) + 4H \rightleftharpoons CH_4 \quad \textbf{(Eq 6)}$$

Oxygen reacts with carbon in steel to form carbon monoxide as follows:

$$(C) + O \text{ € } CO \qquad \textbf{(Eq 7)}$$

Even a low-dew-point hydrogen atmosphere has some decarburizing effect, particularly on high-carbon steels because of the ability of the gas, even when it is not in the nascent condition, to react with carbon:

$$(C) + 2H_2 \text{ € } CH_4 \qquad \textbf{(Eq 8)}$$

Obviously, the decarburizing potential of hydrogen in either form is markedly influenced by the carbon content of the steel and may be expected to increase directly with the increase of carbon content.

Water vapor is oxidizing to iron:

$$Fe + H_2O \text{ € } FeO + H_2 \qquad \textbf{(Eq 9)}$$

and combines with carbon in steel to form carbon monoxide and hydrogen:

$$(C) + H_2O \text{ € } CO + H_2 \qquad \textbf{(Eq 10)}$$

It is reactive to steel surfaces at very low temperatures and low partial pressures. It is a principal cause of blueing during cooling cycles.

The effect of water vapor on the oxidation of iron at various temperatures is indicated by the equilibrium curves shown in Fig. 3.

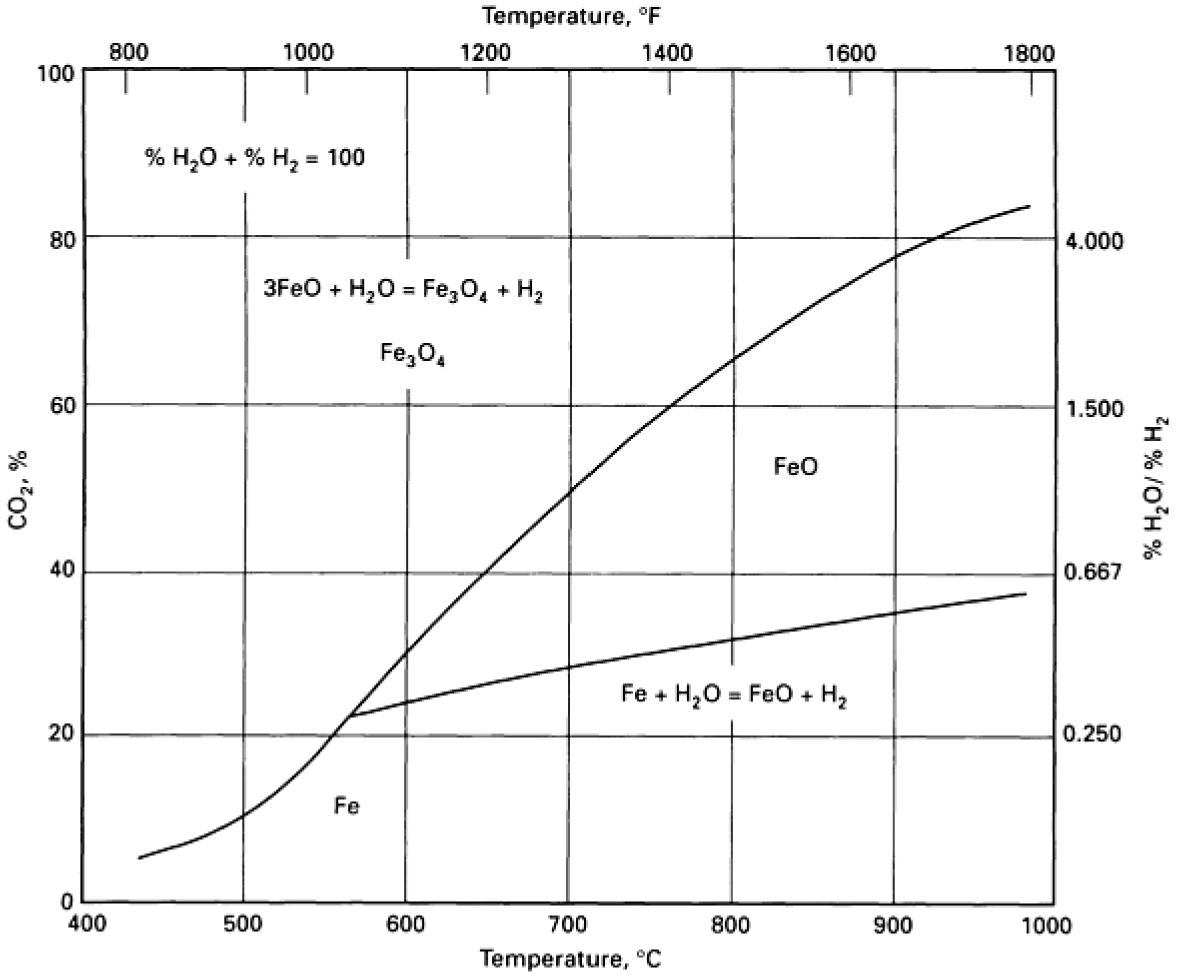


Fig. 3 Equilibrium curves for the formation of scale (FeO and Fe_3O_4) when heating iron in a H_2-H_2O atmosphere at different temperatures

Hydrocarbons. The most common hydrocarbon gases added to or found in furnace atmospheres are methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}). These gases impart a carburizing tendency to a furnace atmosphere. The chemical activity in reacting with the surface of hot steel depends on their thermal decomposition and their tendency to form nascent carbon at the steel surface, and on the temperature of the furnace chamber and work load. Thermal decomposition results in formation of soot in amounts proportional to the number of carbon atoms in the hydrocarbons; therefore, butane and propane are more likely to cause soot in the furnace chamber than are ethane and methane.

Inert Gases. The inert gases of argon and helium are frequently used during the thermal processing of reactive metals and alloys of these metals. Argon, approximately half the cost of helium, is generally favored. Because helium sources are limited, the price of helium is more dependent on end-use location than is argon.

Air contains approximately 0.93% argon by volume. Argon is recovered by liquefying air followed by the fractionation of liquid air. Helium is recovered by similar cryogenic methods from natural gas deposits found in the western United States. A limited number of deposits in the United States and Mexico contain 1 to 8% helium. Because of the low density of helium (0.179×10^{-3} g/cm^3, or 6.47×10^{-6} lb/in.^{3}, at 20 °C, or 70 °F), much of the helium released into the atmosphere is permanently lost beyond the atmosphere of the earth. As a result of this loss, the future supply of helium is threatened.

Protective atmospheres of inert gases are particularly useful during thermal processing of metals and alloys that cannot tolerate the usual constituents of other protective atmospheres. Two applications of inert gases are as protective atmospheres during the bright hardening of stainless steels, and the heat treatment of titanium alloys. Oxygen and water vapor must be avoided during the bright hardening of stainless steels. Oxygen content of less than 0.01% and dew points

below -50 °C (-60 °F) are essential. Titanium alloy heat treatments require atmospheres free of hydrogen, oxygen, and carbon-bearing gases.

Caution: Careful consideration should be given to the residual entrapment of inert gases and nitrogen. When human entry into vessels and chambers is a function of operation or maintenance, special precautions are recommended. Although these gases are not toxic, asphyxiation can occur in entrapped areas. Being odorless and colorless, inert gases and nitrogen are not readily recognized as dangerous.

Helium and nitrogen can be trapped in overhead chambers of bottom-loaded furnaces, and argon and nitrogen can be trapped in vertical top-loaded furnaces. Agitation and flushing with air is recommended before entry. Other appropriate safety procedures may also be beneficial.

Furnace Atmosphere Gas Reactions

Flue gases in a direct-fired furnace are the effluent products created by combustion of hydrocarbon fuel. The composition of these gases inside a furnace contains a mixture of some, or all, of the following principal components: carbon dioxide, carbon monoxide, hydrogen, oxygen, nitrogen, and water vapor.

When burners are adjusted to operate with an excess of combustion air, the products of incompletely burned fuel, carbon monoxide, and hydrogen, are minimized, but measurable amounts of residual oxygen remain. Conversely, burners operating with a combustion-air deficiency consume all of the available oxygen before complete burning of the fuel. In this case, resultant oxygen is minimized, and measurable quantities of unburned carbon monoxide and hydrogen remain. Under all conditions, substantial quantities of water vapor are produced by the combustion.

Other major factors that may materially affect the overall flue-gas furnace atmosphere are burner efficiency, tightness of the furnace and size of the door openings. The openings contribute to the rate of possible air infiltration and the amount of oxygen present. Moreover, furnaces that are equipped with multiple burners may be operating with various air-fuel ratios that can produce a mixed atmosphere of unpredictable composition.

When flue gases contain excess oxygen along with water vapor and carbon dioxide, the oxidizing potential promotes rapid formation of loose scale on steel. Air-deficient burner operation produces much less oxygen and greater amounts of carbon monoxide and hydrogen, which are reducing constituents that can cause steel surface decarburization. Carbon dioxide and water vapor, in this instance, promote formation of a tight oxide that is not easily removed. In both instances, the amount of scale formation is a function of furnace temperature and the amount of time material is held at temperature.

Although a direct-fired furnace cannot be expected to provide a completely neutral atmosphere, specially designed direct-fired furnaces with closely controlled burner systems and specific time/temperature process cycles are capable of cost-efficient heat treating and heat processing for a variety of applications with fully acceptable results.

Carbon Dioxide Plus Hydrogen. Hydrogen will react with either carbon dioxide or oxygen to form water vapor. Water vapor has a high oxidizing potential or decarburizing potential for steel and must be controlled in a furnace atmosphere.

Water Gas Reaction. The reactions listed below by which steel or iron is oxidized at elevated temperatures are irreversible and cannot be controlled:

$$2Fe + O_2 \rightarrow 2FeO \qquad \textbf{(Eq 11)}$$

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3 \qquad \textbf{(Eq 12)}$$

$$3Fe + 2O_2 \rightarrow Fe_3O_4 \qquad \textbf{(Eq 13)}$$

Other oxidizing gas-metal reactions, however, are reversible and can be controlled, and hence may be employed to advantage. In the reactions:

$$Fe + H_2O \rightleftharpoons FeO + H_2 \qquad \textbf{(Eq 14)}$$

$$Fe + CO_2 \text{ € } FeO + CO \quad \textbf{(Eq 15)}$$

water vapor and carbon dioxide are oxidizing gases, and hydrogen and carbon monoxide are reducing gases. Ultimately, the quantity of reducing gas or oxidizing gas formed may become great enough for one to cancel the effects of the other. By proper control of these reactions, a neutral, reducing, or oxidizing effect may be produced.

The opposing reactions may be controlled according to the water gas reaction, which is as follows:

$$CO + H_2O \text{ € } CO_2 + H_2 \quad \textbf{(Eq 16)}$$

The gases that enter into the water gas reaction react with the surface of steel to cause oxidation or reduction, depending on the equilibrium condition corresponding to the temperature and composition of the system.

At 830 °C (1525 °F), the oxidizing potentials of carbon dioxide and water vapor are equal, and the reducing potentials of carbon monoxide and hydrogen are equal. At this temperature, therefore, the equilibrium constant of the water gas reaction has a value of unity. Above 830 °C (1525 °F), carbon dioxide is a stronger oxidizing agent than water vapor, and hydrogen is a stronger reducing agent than carbon monoxide. Below 830 °C (1525 °F), the reverse is true. Consider the reactions:

$$C + CO_2 \rightarrow 2CO \quad \textbf{(Eq 17)}$$

$$CO + H_2O \text{ € } CO_2 + H_2 \quad \textbf{(Eq 18)}$$

$$C + H_2O \text{ € } CO + H_2 \quad \textbf{(Eq 19)}$$

and their equilibrium constants, which are, respectively:

$$K_1 = \frac{[CO_2]}{[CO]^2} \quad \textbf{(Eq 20)}$$

$$K_2 = \frac{[CO][H_2O]}{[CO_2][H_2]} \quad \textbf{(Eq 21)}$$

$$K_3 = \frac{[H_2O]}{[CO][H_2]} \quad \textbf{(Eq 22)}$$

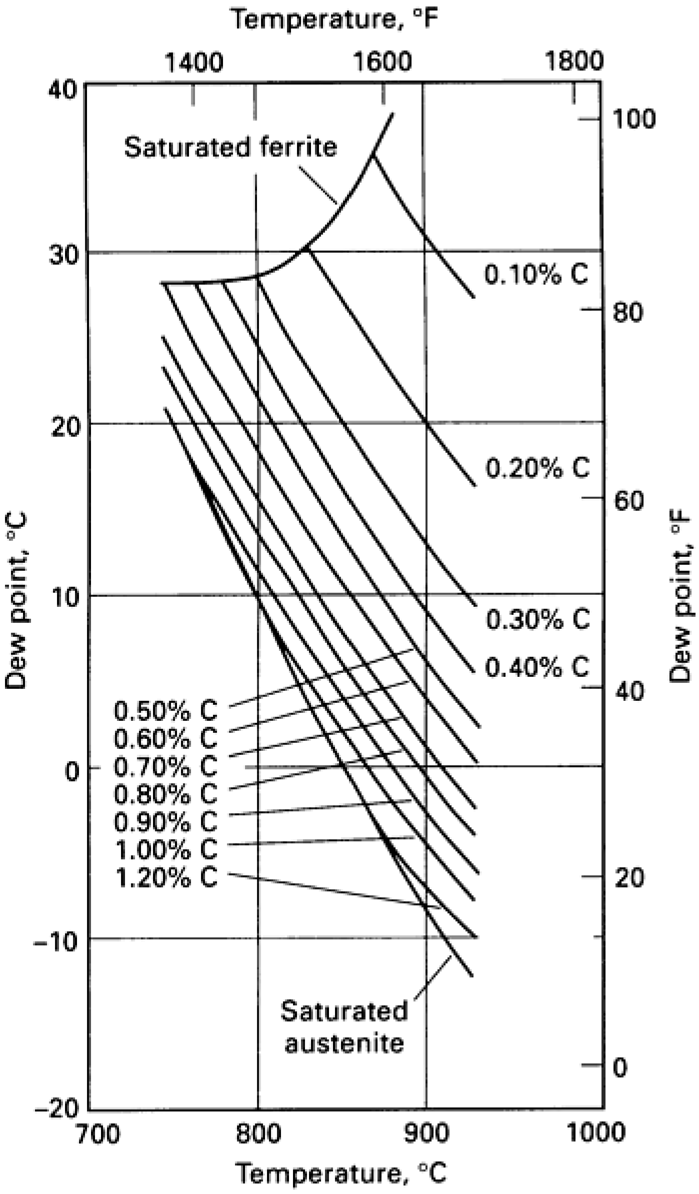
Calculations for the data in Table 2 were developed, assuming that the hydrogen content of the system remains constant at 40% and the CO + CO_2 content remains constant at 20%. Figure 4 shows the equilibrium conditions for steels with carbon concentrations from 0.10 to 1.20%.

Table 2 Variation of equilibrium constants, composition, and dew point of an H_2-H_2O-CO-CO_2 system

The hydrogen content is assumed to remain constant at 40% and the CO + CO_2 content is assumed to remain constant at 20%.

Temperature		Equilibrium constants			Composition, %		Dew point	
°C	°F	K_1	K_2	K_3	CO_2	H_2O	°C	°F
650	1200	3.770	0.51	1.922	4.5	4.5	+32	+90
705	1300	0.942	0.66	0.695	2.6	3.4	+24	+75

760	1400	0.348	0.83	0.363	1.2	2.0	+18	+65
815	1500	0.125	1.02	0.127	0.5	1.02	+7	+45
870	1600	0.050	1.22	0.061	0.2	0.49	-3	+27
925	1700	0.022	1.44	0.003	0.1	0.25	-12	+10



$$\% H_2 = 40$$

$$\% CO_2 + \% CO = 20$$

$$\% H_2O = K \times \% H_2 \times \frac{\% CO_2}{\% CO}$$

$$\text{Dew point} = T - 459.6$$

$$\% H_2O = 10^{8.0615 - \frac{407}{T}}$$

Fig. 4 Dew point for equilibrium conditions with carbon steel of various carbon concentrations

Ammonia Vapor. Ammonia dissociates in the endothermic reaction:

$$2NH_3 \rightarrow N_2 + 3H_2 \qquad \textbf{(Eq 23)}$$

with the dissociated ammonia containing 75% hydrogen and 25% nitrogen. Dissociation occurs when ammonia vapor is heated and passed over the proper catalyst. Dissociated ammonia then is cooled and often passed through a purifying molecular-sieve absorption system to remove undissociated ammonia and water vapor.

Ammonia vapor also may be used as an additive to suitable carbon-bearing carrier atmospheres for carbonitriding, or it may be used directly for nitriding processes. In these instances, partial ammonia dissociation occurs inside the furnace, allowing nitrogen to react with heated steel surfaces to form hard nitrides.

Lithium Vapor. Lithium vapor reacts with water vapor in the furnace atmosphere to form lithium oxide and hydrogen:

$$2Li + H_2O \rightarrow Li_2O + H_2 \qquad \textbf{(Eq 24)}$$

Lithium vapor also combines with any free oxygen present in the furnace atmosphere to form lithium oxide:

$$4Li + O_2 \rightarrow 2Li_2O \qquad \textbf{(Eq 25)}$$

The lithium oxide formed by these reactions oxidizes some of the carbon monoxide present in the atmosphere, causing the release of a certain amount of lithium:

$$2Li_2O + CO \rightarrow Li_2CO_3 + 2Li \qquad \textbf{(Eq 26)}$$

The lithium liberated can then pick up more oxygen.

The practical application of this vapor as a furnace atmosphere has been in forging furnaces as a protection against scaling of the surface of steel heated to forging temperature.

Sulfurous Gases. Sulfurous gases in a furnace atmosphere are basically deleterious and are to be avoided. These gases result from the presence of sulfur compounds in industrial fuels, furnace refractories, and cutting oils on work being processed.

Sulfur compounds occur as hydrogen sulfide (H_2S); sulfur dioxide (SO_2), or sulfur trioxide (SO_3); mercaptans; thiophene (C_4H_4S); and metallic sulfates. When sulfur is present in reducing atmospheres, it is generally found as hydrogen sulfide from the following reaction:

$$SO_2 + 3H_2 \rightleftharpoons H_2S + 2H_2O \qquad \textbf{(Eq 27)}$$

$$C_4H_4S + 6O_2 \rightarrow 4CO_2 + 2H_2O + SO_2 \qquad \textbf{(Eq 28)}$$

$$2SO_2 + 3Fe + 2Ni \rightarrow Fe_2O_3 + NiS + NiO + FeS \qquad \textbf{(Eq 29)}$$

When sulfur is present in atmospheres in which high-nickel steels are heated, both nickel sulfide and nickel oxide are formed, and an alligator surface results. In addition to damaging parts being treated, this effect accelerates the failure of high-nickel, high-chromium, heat-resistant alloy furnace parts, trays, and fixtures. In general, the presence of sulfur in a furnace atmosphere accelerates the rate of scaling, and this rate increases as temperature increases.

Classifications of Prepared Atmospheres

Most prepared atmospheres are commonly referred to in the field by their generic names, or, in some instances, by trade names. The American Gas Association has classified the commercially important prepared atmospheres into six groups on the basis of method of preparation or on the original constituents employed. These groups are designated and defined as follows:

- *Class 100, exothermic base:* Formed by partial or complete combustion of a gas-air mixture; water vapor may be removed to produce a desired dew point
- *Class 200, prepared nitrogen base:* An exothermic base with carbon dioxide and water vapor removed
- *Class 300, endothermic base:* Formed by partial reaction of a mixture of fuel gas and air in an externally heated catalyst-filled chamber
- *Class 400, charcoal base:* Formed by passing air through a bed of incandescent charcoal
- *Class 500, exothermic-endothermic base:* Formed by complete combustion of a mixture of fuel gas and air, removing water vapor, and re-forming the carbon dioxide to carbon monoxide by means of reaction with fuel gas in an externally heated catalyst-filled chamber
- *Class 600, ammonia base:* This can consist of raw ammonia, dissociated ammonia, or partially or completely combusted dissociated ammonia with dew point regulated

These broad areas of classification are subclassified and numerically designated to indicate variations in the method by which they are prepared. This subclassification is differentiated by replacing the two zeros of the six basic designators by one of the following two-digit numbers that indicate some special preparation of the furnace atmosphere:

- *01:* Use of a lean air-gas mixture
- *02:* Use of a rich air-gas mixture
- *03 and 04:* Preparation of the gas was completed within the furnace itself without the use of a separate machine or generator
- *05 and 06:* Original base gas was subsequently passed through incandescent charcoal before admission to the work chamber
- *07 and 08:* Addition of a raw hydrocarbon fuel gas to the base gas before admission to the work chamber
- *09 and 10:* Addition of a raw hydrocarbon fuel gas and raw dry anhydrous ammonia to the base gas before admission to the work chamber
- *11 and 12:* Addition of a combusted mixture of chlorine, hydrocarbon fuel gas, and air to the base gas before admission to the work chamber
- *13 and 14:* Base gas has had all sulfur or all sulfur and odors removed before admission to the work chamber
- *15, 16, 17, and 18:* Addition of lithium vapor to the base gas before admission to the work chamber
- *19 and 20:* Preparation of the gas was completed within the furnace itself with the addition of lithium vapor
- *21 and 22:* Some additional special treatment was given to the base gas before admission to the work chamber
- *23 and 24:* Addition of steam and air in conjunction with a catalyst within the generator to convert CO to CO_2, which is then removed
- *25 and 26:* Addition of steam in conjunction with a catalyst within the generator to convert CH_4 to H_2 and CO_2, which is then removed

This classification system provides for a large number of possibilities. In practice, only a few of the possible atmosphere classifications are industrially important. Table 3 lists significant furnace atmospheres and typical applications.

Table 3 Classification and application of principal furnace atmospheres

Class	Description	Common application	Nominal composition, vol%				
			N_2	CO	CO_2	H_2	CH_4
101	Lean exothermic	Oxide coating of steel	86.8	1.5	10.5	1.2	. . .
102	Rich exothermic	Bright annealing; copper brazing; sintering	71.5	10.5	5.0	12.5	0.5
201	Lean prepared nitrogen	Neutral heating	97.1	1.7	. . .	1.2	. . .
202	Rich prepared nitrogen	Annealing, brazing stainless steel	75.3	11.0	. . .	13.2	0.5
301	Lean endothermic	Clean hardening	45.1	19.6	0.4	34.6	0.3
302	Rich endothermic	Gas carburizing	39.8	20.7	. . .	38.7	0.8
402	Charcoal	Carburizing	64.1	34.7	. . .	1.2	. . .
501	Lean exothermic-endothermic	Clean hardening	63.0	17.0	. . .	20.0	. . .
502	Rich exothermic-endothermic	Gas carburizing	60.0	19.0	. . .	21.0	. . .
601	Dissociated ammonia	Brazing, sintering	25.0	. . .	. . .	75.0	. . .
621	Lean combusted ammonia	Neutral heating	99.0	. . .	. . .	1.0	. . .
622	Rich combusted ammonia	Sintering stainless powders	80.0	. . .	. . .	20.0	. . .

Furnace Atmosphere Hazards

Furnace atmospheres constitute one of the major safety hazards involved in heat treating. Generally, these hazards fall into three groups: fire, explosion, and toxicity.

Fire. When an atmosphere contains more than 4% of combustible gases, it is classified as flammable. Included in this percentage is a practical safety margin that should never be ignored. *Caution: The combustible gases H_2, CO, CH_4, and other hydrocarbon fuel gases should never be admitted to a furnace chamber at temperatures below 760 °C (1400 °F) without proper inert gas purging (per NFPA standard 86C).*

Explosion. At some point, mixtures of air and combustible gas will explode when ignited. When a furnace chamber is properly gassed with the chamber temperature at or above 760 °C (1400 °F), it is likely that combustible gases will burn before creating an explosion hazard. An adjacent cold chamber or vestibule can then be flared as the atmosphere flows from the furnace to the vestibule until it is free of oxygen from the air. The vestibule can then be closed. The positive flow of atmosphere through the furnace and adjoining cold chamber or vestibule can then be burned. An ignited effluent from an atmosphere furnace is an immediate visual sign that a safe condition prevails.

Toxicity. *Caution: Many of the gases making up furnace atmospheres are toxic.* Burning them at the furnace exits reduces their chemistry to the products of combustion. These products should then be vented outside the building to avoid

dilution of the available oxygen supply within the building. *Caution: Ventilation of the building containing atmosphere generators and atmosphere heat-treating furnaces is a major safety consideration*.

Furnace Atmosphere Hazards (Ref 1, 2, 3, 4, 5, 6, 7). Furnace atmospheres (endo, exo, dissociated ammonia, dissociated alcohols, and nitrogen based) normally consist of a mixture of gases, which may be flammable, toxic, asphyxiant, or a combination of these. Explosion, fire, and poisoning are potential hazards. National Fire Protection Association standard 86C covers various safety considerations pertaining to continuous conveyor belt furnaces used in the thermal processing industry.

Four intrinsic dangers are associated with producing and using the common atmosphere gases. A mixture of atmosphere gas and air can accumulate in a confined area and explode. Relatively small quantities of atmosphere gas can unexpectedly burn or flash out of control. Personnel may be poisoned by carbon monoxide, ammonia, or methanol. Simple asphyxiation is possible when asphyxiants are present in high concentrations.

Table 4 describes the characteristics of the common sintering atmosphere constituent gases. Most of the major constituents are flammable; four are toxic; and four are simple asphyxiants. Carbon monoxide, ammonia, and methanol are both flammable and toxic. The percentage by volume of the flammable ingredients ranges from 75% hydrogen in dissociated ammonia atmosphere to only a few percent in purified exothermic and nitrogen-based atmospheres.

Table 4 Potential hazards and functions of heat treating atmosphere-constituent gases

Gas	Potential hazard			Atmosphere function
	Flammable	Toxic	Simple asphyxiant	
Nitrogen	. . .	. . .	Yes	Inert
Hydrogen	Yes	. . .	Yes	Strongly reducing
Carbon monoxide	Yes	Yes	. . .	Carburizing and mildly reducing
Carbon dioxide	. . .	Yes	Yes	Oxidizing and decarburizing
Natural gas	Yes	. . .	Yes	Strongly carburizing and deoxidizing
Ammonia	Yes	Yes	. . .	Strongly nitriding
Methanol	Yes	Yes	. . .	Carbon monoxide and hydrogen generating

Dangers are present even when heat treating with atmospheres that contain relatively small percentages of hazardous ingredients because the gases may accumulate or concentrate. Under typical operating conditions, however, the active ingredients in nitrogen systems are diluted below the level that is flammable, even if all the nitrogen is replaced by air. Explosion, burning, poisoning, and asphyxiation hazards are thus reduced, but not eliminated.

The explosive ranges of typical atmosphere constituents are:

Atmosphere constituents	Concentration in air, %
Hydrogen	4.0-74
Carbon monoxide	12.5-74
Methane	5.3-14
Ammonia	15.0-28
Methanol	6.7-36

Any mixtures between the high and low limits of flammability will burn when ignited, and, under certain conditions, detonate or explode. The destructive power of the pressure wave from an ignited flammable mixture depends on the amount of gas and the heat of combustion of the fuel gas, the combustion mode (deflagration or detonation), and the configuration of the confinement space. The energy released is either absorbed by the surroundings or destroys them.

The explosive potential of the large volumes of flammable gases used in sintering furnaces poses an important safety consideration. To ensure the safety of sintering and heat treating, the equipment and systems that handle gases must be designed, operated, and maintained to prevent accumulation of explosive mixtures. Dangerous accumulations that cannot be readily detected by personnel can occur. Properly designed safety systems, maintained and operated by well-trained and competent personnel, substantially reduce explosion hazards.

Generally, sufficient volumes of atmosphere gas flowing through the furnace leave the charge and discharge doors, mix with air, and burn uniformly and completely. However, several conditions may exist that prevent the atmosphere gas from burning off properly. Sometimes, a combustible mixture of air and gas may form in the furnace throats or vestibules. It may burn rapidly and forcefully exhaust, or flash, flames and hot gases through the furnace door. Unprotected personnel in the vicinity may be burned. Eyes are particularly sensitive to damage.

Although flashes of this type are more common than explosions, they are potentially less destructive. Nonetheless, personnel who approach these areas without safety glasses, protective face shields, gloves, and flameproof clothing risk serious flash burns. If safe methods are established and used for cleaning jam-ups, inspecting the furnace interior, and removing products from the furnace, this hazard is substantially reduced.

Protective guards and shields used for routine operation are no substitute for the required protection of personnel working in the vicinity of the furnace doors. However, the possibility of flashback under nonflammable, nitrogen-rich atmospheres is remote.

Ammonia, carbon monoxide, and methanol, which are highly toxic, are used routinely in the sintering and heat-treating industries. Liquid ammonia produces dissociated ammonia or ammonia vapor for nitriding, and carbon monoxide is a constituent of exothermic, endothermic, and dissociated methanol gases. Methanol is used to produce dissociated methanol, which consists of hydrogen and carbon monoxide. Concentrations of less than $\frac{1}{2}$% ammonia or carbon monoxide in air are considered fatal in less than $\frac{1}{2}$h of exposure. The physiological effects of various concentrations of these gases are given in Tables 5 and 6.

Table 5 Physiological effects of ammonia

Concentration,	Physiological effects

ppm	
20	First perceptible odor
40	Slight eye irritation in a few individuals
100	Noticeable irritation of eyes and nasal passages after a few minutes of exposure
400	Severe irritation of the throat, nasal passages, and upper respiratory tract
700	Severe eye irritation; no permanent effect if the exposure is limited to less than $\frac{1}{2}$ h
1700	Serious coughing, bronchial spasms; less than $\frac{1}{2}$ hr of exposure may be fatal
5000	Serious edema, strangulation, asphyxia; almost immediately fatal

Table 6 Physiological effects of carbon monoxide

Concentration, ppm	**Physiological effects**
100	Allowable for an exposure of several hours
400	Can be inhaled for 1 h without appreciable effect
600	Causes a barely appreciable effect after 1 h of exposure
1000	Causes unpleasant symptoms, but not dangerous after 1 h
1500	Dangerous for exposure of 1 h
4000	Fatal for exposure of less than 1 h

Threshold limit values, published by the American Conference of Governmental and Industrial Hygienists, lists carbon monoxide, carbon dioxide, ammonia, and methanol as commonly used toxic chemicals. Concentrations as small as 35 ppm of ammonia, 400 ppm of carbon monoxide, and 250 ppm of methanol are harmful; therefore, only short exposures are allowed.

Protection from poisoning by raw ammonia or methanol vapor or from contact with liquid ammonia or methanol is provided partly by the design of the storage and delivery system. Suppliers are excellent sources of detailed safety information on ammonia and methanol systems and ammonia dissociators.

Carbon monoxide is not quite as toxic as ammonia; however, because is is odorless, it poses a greater safety hazard. Lethal concentrations can collect in isolated areas and remain undiscovered until personnel are overcome by the fumes.

According to Ref 2, ". . . in concentrations far short of the asphyxiation level, carbon monoxide is still dangerous, especially if exposure is prolonged. Carbon monoxide (poisoning) can be a contributing factor to death that ultimately results from other causes, such as fatal accidents, and is a health as well as safety problem." Carbon monoxide interferes with the ability to breathe, and, as a result, the ability of the body to utilize oxygen. It is over 200 times more attractive than oxygen to the blood hemoglobin that delivers oxygen throughout the body. A relatively small amount of carbon monoxide, therefore, depletes the body of a large amount of oxygen.

To ensure personnel safety, piping between the generator and the furnace must be leaktight, and all gas that enters the furnace must be either burned off or properly vented. The highly toxic nature of carbon monoxide requires use under carefully controlled conditions. The safest and most convenient disposition of carbon monoxide is to ensure complete mixing of the furnace atmosphere effluent with air to combustible proportions and subsequent ignition of the mixture. Products of combustion are far less toxic but should still be properly vented.

In some applications, carbon monoxide cannot be burned directly because it has been diluted in inert gas to a level that is nonflammable when mixed with air. Special precautions must be taken to vent and dilute it to below toxic limits. To ensure the continued effectiveness of the venting, carbon monoxide levels near the furnace setup must be monitored continuously. Consequently, apparatus using or emitting gas containing carbon monoxide that will not burn when mixed with air should not be operated unless the user is willing to accept the added liability. Additionally, special gas-monitoring and disbursing equipment should be installed.

Personnel should also be familiar with the early symptoms of carbon monoxide poisoning and trained in appropriate first aid. Early symptoms include slight dizziness, weakness, or headache. In the later stages of poisoning, the victim's lips and skin turn a characteristic cherry red.

Finally, the danger of asphyxiation is not intrinsic to the gases used in the heat treating industry, but is a concern. Asphyxiation can be caused by a harmless gas (for example, one that has no significant physiological effect) if it is present in high concentrations in the air. Normal oxygen content in air is about 21 vol%. Minimum oxygen content should be 18 vol% under normal atmospheric pressure.

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Exothermic-Based Atmospheres

Exothermic gases (class 100) have been used extensively for many years as lower-cost prepared furnace atmospheres. Exothermic atmospheres are divided into two basic classes: rich and lean. Rich exothermic atmospheres (class 102) have moderate reducing capabilities of 10 to 21% combined carbon monoxide and hydrogen, and lean exothermic atmospheres (class 101), usually with 1 to 4% combined carbon monoxide and hydrogen, have minimal reducing qualities.

Rich Exothermic Atmospheres

The principal uses of rich exothermic furnace atmospheres include clean heat treating of certain ferrous and nonferrous applications. Among these are annealing and tempering of steel, brazing of copper and silver, and sintering of powdered metals.

Reducing properties of rich exothermic atmospheres may be varied to make them suitable for specific processes. Figure 5 indicates the usual operating range of the gas generator and reflects changes (by dry volumetric measurement) in the following constituents of the product gas at any particular setting: carbon dioxide, carbon monoxide, hydrogen, and unburned methane. The remainder of the mixture is nitrogen. Because these atmospheres have a carbon potential below 0.10%, steel heat treating is generally limited to processes for low-carbon steels to minimize decarburizing, or processes where decarburization is unimportant. Water vapor is present in substantial quantities and may be removed partially by initial cooling and refrigerant drying to an equivalent 5 °C (40 °F) dew point. This procedure may be followed by further dehydration with an adsorbent desiccant dryer for final few points of -40 to -50 °C (-40 to -60 °F), as applications require.

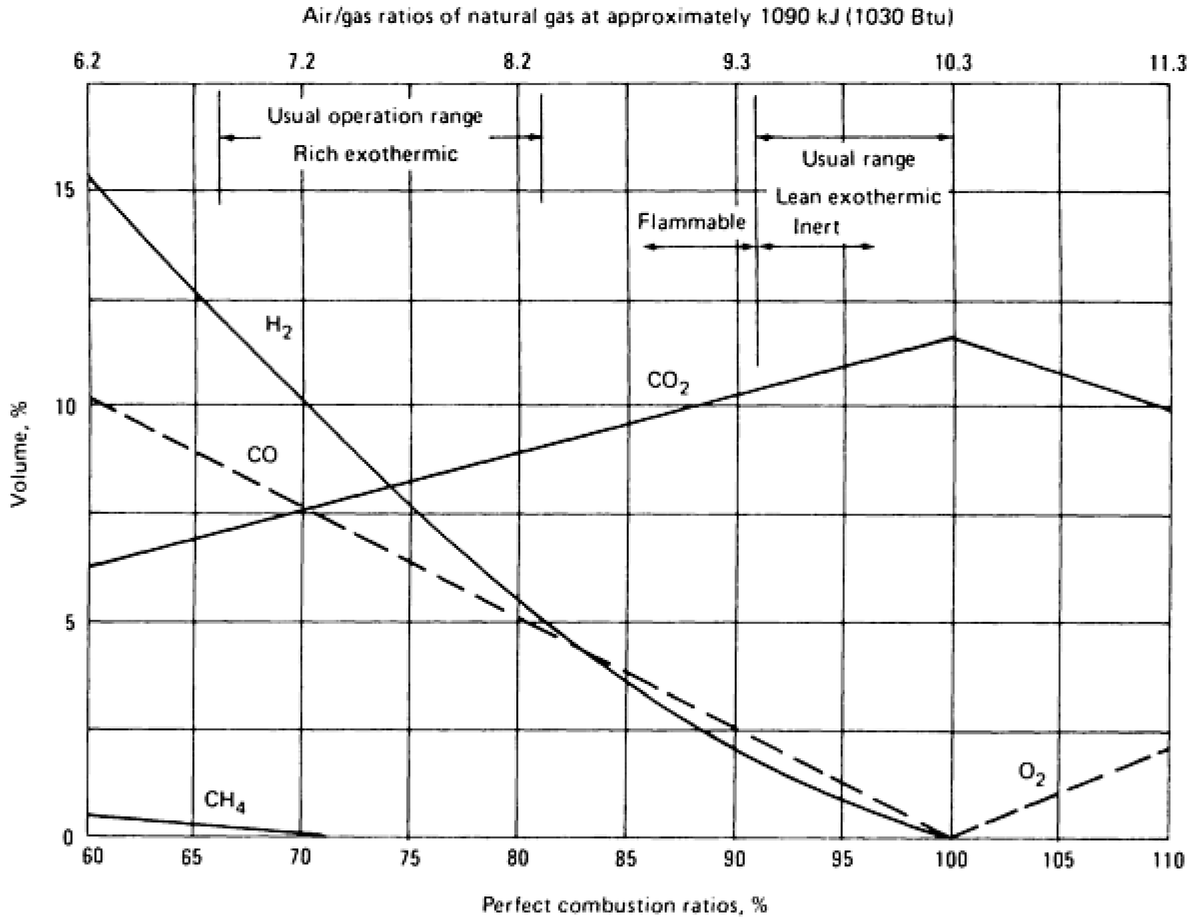

Fig. 5 Exothermic atmosphere composition versus air-to-fuel ratio (natural gas)

Gas Production. Rich exothermic gas is produced by combustion of a hydrocarbon fuel such as natural gas or propane with the air-to-fuel ratio closely controlled. This air-gas mixture is burned in a confined combustion space to maintain a reaction temperature of at least 980 °C (1800 °F) for sufficient time to permit the combustion reaction to reach equilibrium. Heat is obtained directly from combustion. The resultant gas is then cooled to remove part of the water vapor formed by burning and to permit convenient transportation and metering. In this process, the simplified theoretical reaction of methane with air is:

$$\begin{aligned} CH_4 + 1.25O_2 + 4.75N_2 &\rightarrow 0.375CO_2 \\ &+ 0.625CO + 0.88H_2 + 4.75N_2 \\ &+ 1.12H_2O + \text{heat} \end{aligned} \qquad \textbf{(Eq 30)}$$

where 1 volume of fuel and 6 volumes of air yield 6.63 volumes of product gas mixture, with water vapor removed. In practice, exothermic gas generators are seldom operated with an air-to-gas ratio lower than about 6.6 to 1, to prevent formation of soot as a result of incomplete reaction. Trace percentages of unreacted methane also exist in the product gas.

The basic rich exothermic gas generator (Fig. 6) has a refractory-lined combustion chamber, which in some designs may be partially filled with a catalyst. The chamber incorporates a burner with a combustion-control system especially designed to provide a constant supply of air and fuel gas with a closely maintained preselected ratio. The combustion chamber is followed by a water-cooled heat exchanger for primary gas cooling and partial water vapor condensation. At this point, product atmosphere is saturated with moisture at approximately 8 °C (15 °F) above the temperature of the cooling water.

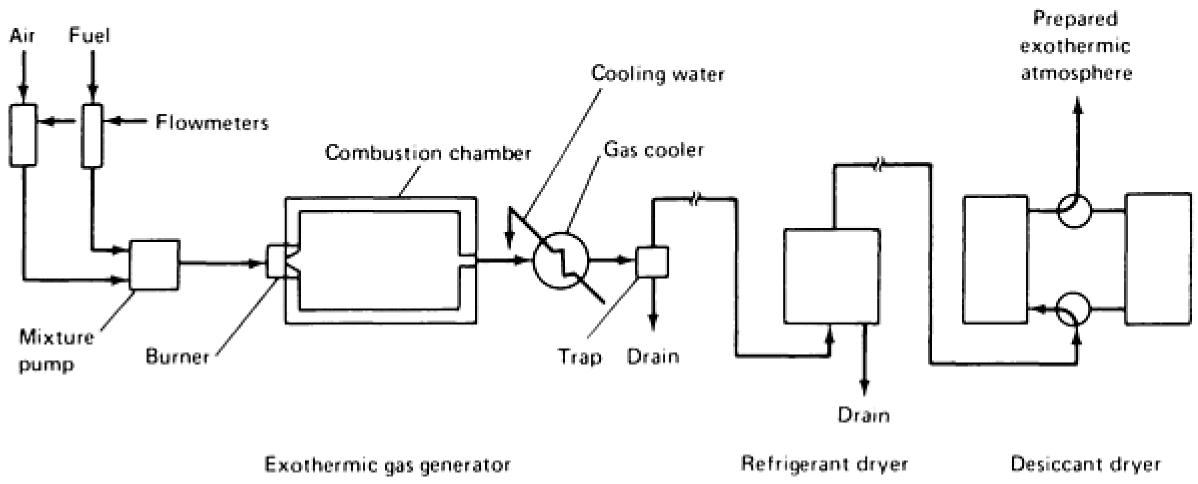

Fig. 6 Flow diagram of an exothermic gas generator system

Operation is uncomplicated and continuous, incorporating input air and fuel-gas flow meters with manual or automatic control of process flow and ratio. Safety devices include sequenced burner ignition, automatic flame monitoring, pressure switches, and manual-reset fuel-safety valves. Periodic operational monitoring consists of observing pressures and flow rates and taking occasional product gas samples for analysis of desired composition. Available continuous gas analyzers, either indicator-reading or recording, usually are calibrated to indicate the content of combustibles. Some analyzers may be adapted for automatic radio control.

Operating Economics. The following are requirements needed to produce 28 m^3 (1000 ft^3) of rich exothermic atmosphere:

Requirement	Value
Natural gas, m^3 (ft^3)	4.4 (155)
Electric energy consumption, MJ (kW · h)	1.4 (0.4)
Cooling water, L (gal)	1135 (300)
Electric energy consumption for refrigerant dryer, MJ (kW · h)	1.8 (0.5)
Electric energy consumption for desiccant dryer, MJ (kW · h)	5.4 (1.5)

Safety Considerations. *Caution: Rich exothermic atmospheres contain sufficient carbon monoxide and hydrogen to be considered flammable gases when mixed in proper proportions with air. In handling or use as a furnace atmosphere, they should be treated with the same precautions exercised with any combustible gas.* Established furnace-operating practices should be observed carefully, particularly with respect to proper purging procedures and prevention of air infiltration. Most generators are equipped with electrically programmed ignition sequencing and are monitored with additional safety devices. These devices should be periodically tested to ensure fail-safe operation. Because these atmospheres contain measurable amounts of carbon monoxide, extreme care should be taken to prevent leaking into the surrounding atmosphere. Proper venting, burnoff, and ventilation facilities should be employed. Furnace safety is discussed in this article in the section "Classifications of Prepared Atmospheres."

Lean Exothermic Atmospheres

Lean exothermic atmospheres generally have limited use in most heat-treating applications, particularly for ferrous materials, except when these atmospheres are used as intentional surface oxidizing agents or for specialized low-temperature operations. Lean atmospheres are used to some extent for processes such as copper annealing and are employed more widely when the primary processing aim is to exclude oxygen or to provide purging and blanket gas.

Figure 5 indicates the usual operating range of the gas generator and reflects changes (by dry volumetric measurements) in the product gas at any particular setting with respect to carbon dioxide, carbon monoxide, and hydrogen. The balance of the mixture is nitrogen. Reducing capabilities are limited. Water vapor that is present in substantial quantities may be removed partially by initial cooling and refrigerant drying to an equivalent 5 °C (40 °F) dew point. This process may be followed by further dehydration with an adsorbent desiccant dryer for final dew points in the range of -40 to -50 °C (-40 to -60 °F), as applications require.

Gas Production. Lean exothermic gas is produced by combustion of a hydrocarbon fuel such as natural gas, propane, or light fuel oil with the air-to-fuel ratio closely controlled. This air-fuel mixture is burned in a confined combustion space for sufficient time to permit the reaction to reach equilibrium. The resultant gas is then cooled to partially condense water vapor formed by burning and to permit convenient transport and metering. In this process, the simplified theoretical reaction of methane fuel with air is:

$$CH_4 + 1.9O_2 + 7.6N_2 \rightarrow 0.9CO_2 + 0.1CO + 0.1H_2 + 7.6N_2 + 1.9H_2O + \text{heat} \quad \textbf{(Eq 31)}$$

where 1 volume of fuel and 9.5 volumes of air yield 8.7 volumes of product gas mixture, with water vapor removed. In practice, exothermic gas generators are seldom operated with an air-to-gas ratio higher than that required to produce a minimum of 1% total carbon monoxide and hydrogen, to avoid unwanted quantities of residual oxygen. One exception involves certain purge and blanket applications where small amounts of oxygen can be tolerated and the presence of combustible materials is not desired. In this case, the air-to-gas ratio is further increased to operate with a slight amount of excess air, thus maintaining 1 to 2% oxygen in the product gas. The basic lean exothermic gas generator is shown in Fig. 6.

Operating Economics. The following are requirements needed to produce 28 m^3 (1000 ft^3) of lean exothermic atmosphere:

Requirement	**Value**
Natural gas, m^3 (ft^3)	3.3 (120)
Electric energy consumption, MJ (kW · h)	1.4 (0.4)

Cooling water, L (gal)	1590 (420)
Electric energy consumption for refrigerant dryer, MJ (kW · h)	1.8 (0.5)
Electric energy consumption for desiccant dryer, MJ (kW · h)	5.4 (1.5)

Safety Considerations. Lean exothermic gas generators that are operated at less than 4% total combustibles are considered non-flammable and may be handled and used in the same manner as other types of inert gases. *Caution: These atmospheres, however, usually contain measurable amounts of carbon monoxide, and extreme care should be taken to avoid leakage. Proper venting and ventilation facilities should be employed. Moreover, when lean exothermic gas is used for purging and blanket applications, the chamber or vessel will lack oxygen. If it becomes necessary to enter these spaces for any reason, the chamber should be purged thoroughly with air or an air mask and a lifeline should be employed, with someone outside holding the lifeline.*

Most generators are equipped with electrically programmed ignition sequencing and are monitored with additional safety devices that should be tested periodically to ensure fail-safe operation. Furnace safety is discussed in another article in this Volume.

Endothermic-Based Atmospheres

Endothermic-based atmospheres are produced in generators that use air and a hydrocarbon gas as fuel. These two gases are mixed in a controlled ratio, slightly compressed, and then passed into a chamber that is filled with a nickel-bearing catalyst. This chamber has been heated externally to approximately 1040 °C (1900 °F). The gases react in this chamber to form endothermic gas. Endothermic atmospheres thus produced must be cooled rapidly to ensure the integrity of their chemical compositions. Figure 7 is a schematic diagram of an endothermic gas generator.

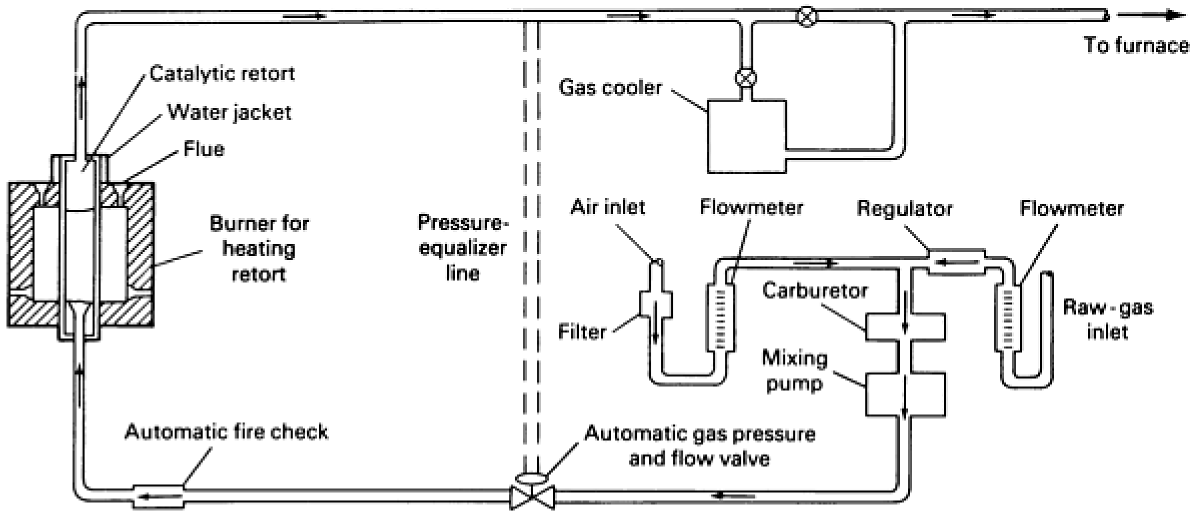

Fig. 7 Flow diagram of an endothermic gas generator system

Endothermic gas produced from natural gas, which is primarily methane, has a typical analysis as follows: 40.4% hydrogen, 39.0% nitrogen, 19.8% carbon monoxide, 0.5% methane, 0.2% water vapor, and 0.1% carbon dioxide. Although natural gas is commonly employed, endothermic generators satisfactorily crack propane, butane, or other hydrocarbon gases. The product endothermic gas chemical composition will vary when alternate hydrocarbon gases are used. When propane is used as the hydrocarbon gas, a typical analysis shows 45.3% nitrogen, 31.1% hydrogen, 23.4% carbon monoxide, 0.2% methane, <1% water vapor, and virtually no carbon dioxide.

Common Applications. Endothermic atmospheres can be used in virtually all furnace processes that require strong reducing conditions. The most common use is as carrier gases in gas carburizing and carbonitriding applications. Because of the wide range of carbon equivalencies possible, however, endothermic atmospheres also are used for bright hardening of steel, for carbon restoration in forgings and bar stock, and for sintering of powder compacts that require reducing atmospheres. It is generally necessary to couple the generator with the process to ensure that the carbon equivalent being produced in the generator is appropriate for the process. However, in gas-carburizing applications, the addition of a hydrocarbon gas to the furnace will raise the carbon equivalency of the furnace gas, thus allowing a more neutral carrier gas to be produced at the generator.

Generation of Endothermic Atmospheres. In generating endothermic-based atmospheres, hydrocarbon gas and air are metered in proportions that ensure that only sufficient oxygen is admitted to form carbon monoxide and hydrogen, without any excess for the formation of carbon dioxide or water vapor. After being compressed to about 7 to 14 kPa (1 or 2 psig), the air-gas mixture is passed through a fire-check valve to the heated catalyst, which is contained in a pressure-tight retort. The retort is externally heated, usually by natural gas.

For a completely reacted gas of consistent analysis, the temperature inside the catalyst bed should be approximately 980 to 1040 °C (1800 to 1900 °F). Furthermore, the ratio of the diameter of the retort to its length must be correct for any given capacity.

After passage over the catalyst, the reaction is frozen by quickly chilling the gases to below 315 °C (600 °F) in a water jacket surrounding the top of the retort, thus preventing the reaction from reversing and forming carbon and carbon dioxide from carbon monoxide:

$$2CO \rightarrow C + CO_2 \qquad \textbf{(Eq 32)}$$

The reaction in the direction indicated predominates at temperatures of 705 to 480 °C (1300 to 900 °F). The soot-free reacted gas can be further cooled in the gas cooler for metering and distribution.

Because natural gas is composed chiefly of methane (CH_4), the overall chemical reaction taking place in the endothermic generator using natural gas as its fuel can be expressed as follows:

$$2CH_4 + O_2 \rightarrow 2CO + 4H_2 \qquad \textbf{(Eq 33)}$$

neglecting 3.8 volumes of nitrogen (before and after) for each 2 volumes of methane.

The reaction takes place in two stages. In the first stage, some of the methane burns with air and generates heat. In the second stage, the surplus methane reacts with the carbon dioxide and water vapor produced in the first stage, and this later reaction is definitely endothermic. Therefore, a high temperature and a clean and sufficient catalyst bed are required to obtain a completely reacted gas and to minimize carbon dioxide, excess methane, or excess water vapor.

A completely reacted gas is, in practical operations, one in which the methane content does not exceed about 0.4 to 0.8%. If the temperature is not high enough and the gas is not completely reacted, the reaction will produce soot. Once the catalyst accumulates soot, it becomes ineffective, and the gas composition will drift, resulting in more methane and higher percentages of carbon dioxide and water vapor in the products. When this occurs, the generating process cannot be controlled to maintain a definite carbon potential. Furthermore, unreacted methane will break down in the heat-treating furnace to produce soot.

Clean, active catalyst is extremely important for accurate control of carbon potential. The catalyst most commonly used is of the porous refractory-base type, impregnated with nickel oxide.

The presence of hydrogen sulfide (H_2S) in natural gas will seriously affect an endothermic generator. Hydrogen sulfide will cause the generator to produce high concentrations of CO_2, CH_4, and water vapor, and become unresponsive to control adjustments of the air-to-gas ratio. This causes the endothermic atmosphere being produced to have a low carbon equivalent. Specifically, any H_2S concentration over 30 ppm in natural gas of 0.6 specific gravity will have a noticeable effect on the resultant product gas.

Most endothermic generators are controlled by monitoring the dew point of the product gas. The dew point is controlled by either manual or automatic adjustment of the ratio of air and gas going into the generator. The relationship between carbon dioxide and dew point in endothermic gas is presented in Fig. 8. In broad terms, a dew point of 16 to -12 °C (60 to 10 °F) will create a product gas in equilibrium with steel containing 0.20 to 1.5% C at normal hardening or carburizing temperatures. Figure 9 shows the relationship between dew point and carbon content in plain carbon steels at temperatures from 815 to 925 °C (1500 to 1700 °F). Producing endothermic gas of -7 °C (20 °F) dew point or higher will ensure gas that is clean enough for continuous operation without weekend shutdowns for burnout. In some instances, the percentage of carbon dioxide or the ratio of carbon monoxide to carbon dioxide or the oxygen probe is used as the controlling method of the generator.

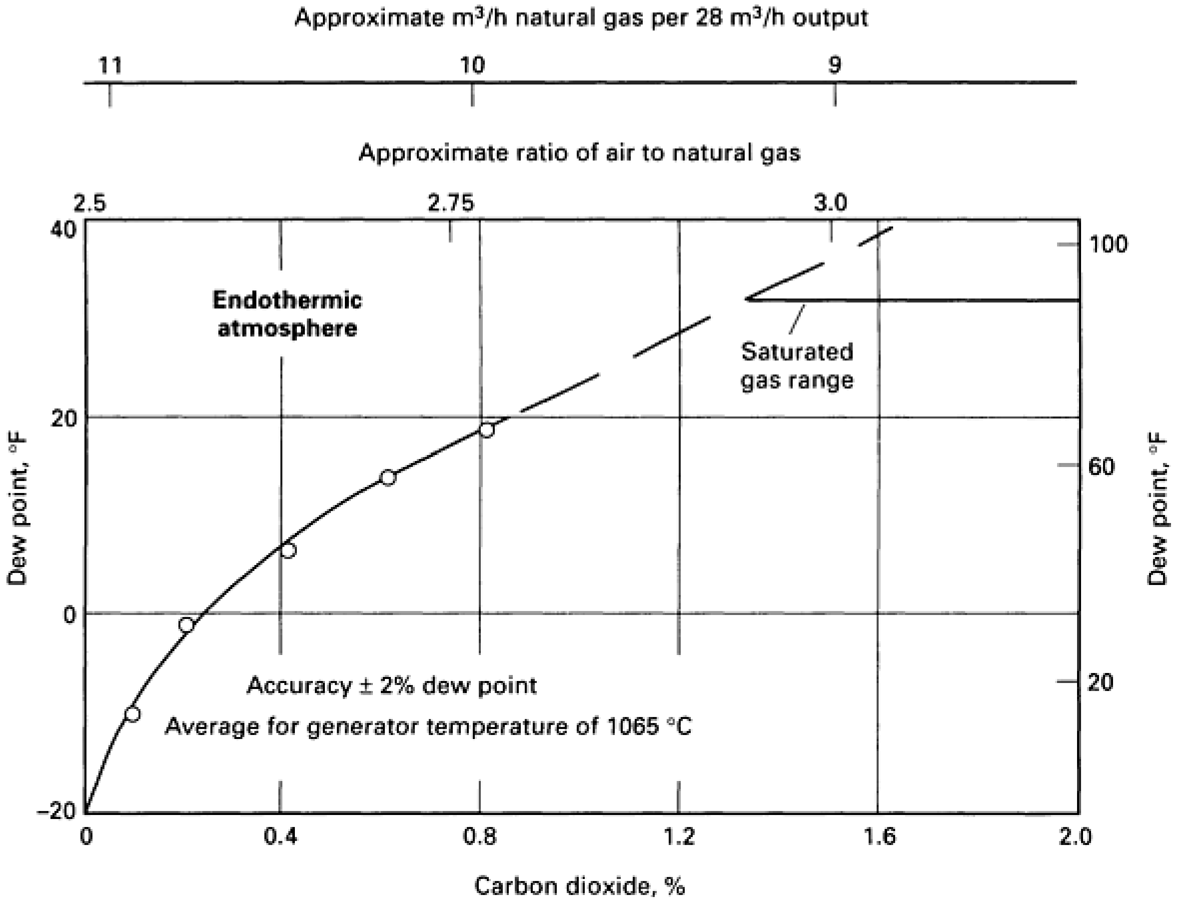

Fig. 8 Relation between dew point and carbon dioxide content in the generation of an endothermic-based atmosphere

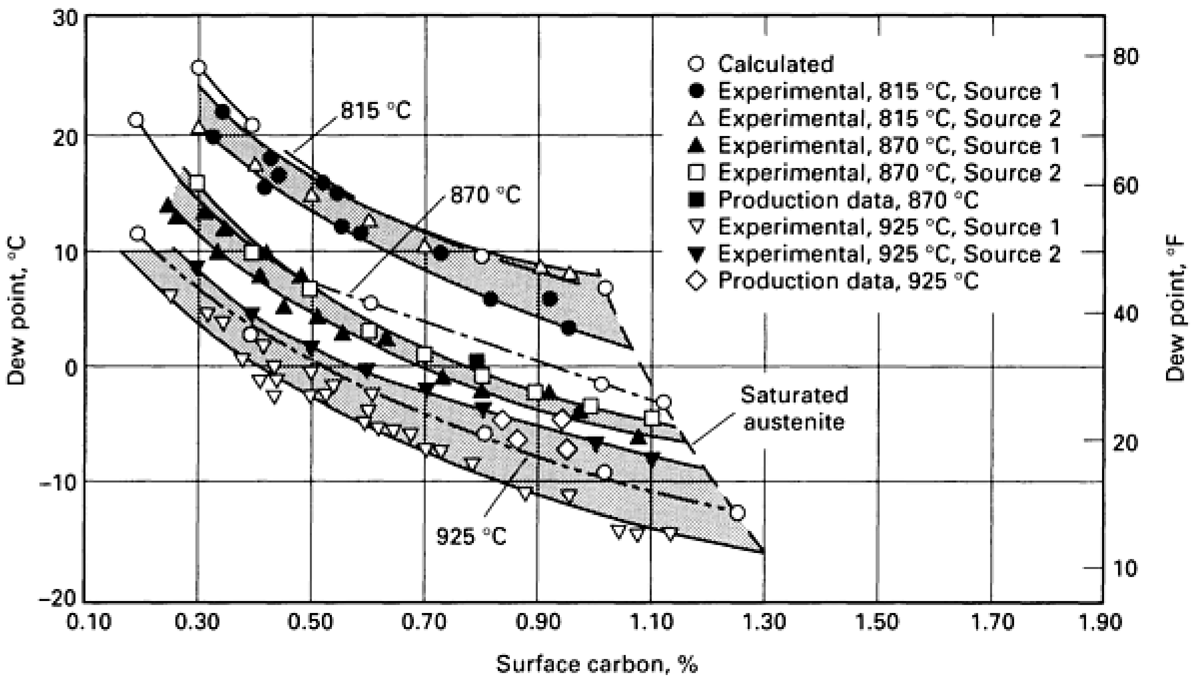

Fig. 9 Equilibrium between carbon steels and endothermic-based atmospheres

Endothermic Generator Maintenance. The maintenance requirement schedules for gas-fired endothermic-based atmosphere generators are:

Weekly and/or monthly

- Burn out carbon in generator
- Clean air filter
- Check calibration of control instruments
- Inspect thermocouples
- Service controller sample system

Annually, or as prescribed in operating instructions

- Test all safety controls
- Inspect catalyst in retort and fill to proper level or replace
- Inspect and clean burners
- Check compressor blades and bearings in mixer pump and lubricate if necessary
- Check motor bearings on mixer pump
- Clean gas lines to furnaces if necessary

Safety Precautions. *Caution: Because endothermic gas is highly toxic and highly flammable and because it forms explosive mixtures rapidly, a safety program is imperative.* The exact program will depend on the equipment being used, local ordinances, normal operating procedures, types of emergency equipment available, plant layout, and capabilities of personnel. The best safety equipment available cannot substitute for properly trained personnel.

Several areas of concern must be addressed in safety procedures and training. First, because an endothermic generator is in itself a furnace, often a gas-fired furnace, all the safety precautions normally applied to any furnace must be applied to

the generator. No attempt should be made to produce endothermic gas if the generator is not at temperature. The fire-check valve, which is installed in all generators, must be in operating condition or the danger exists of the explosive gas in the mixer being ignited. Care must be taken to prevent the volume of air in the mixture from increasing to a point at which the mixture becomes exothermic and hence explosive. Further, the cooling process must be maintained to prevent overheating of the supply system. *Caution: Overheating would allow a reversible reaction in the gas and create an explosive mixture*.

Prepared Nitrogen-Based Atmospheres

Prepared nitrogen-based atmospheres are exothermic atmospheres (produced by combustion of a mixture of air and fuel gas) from which almost all of the carbon dioxide and water vapor has been removed. The combination of very low dew point, approximately -40 °C (-40 °F), and the virtual absence of carbon dioxide accounts for the marked difference between the properties and applications of prepared nitrogen-based atmospheres as compared with those designated exothermic base.

The above definition conforms with the classification system used by the American Gas Association (AGA). Accordingly, the term prepared nitrogen-based atmospheres is not appropriate for furnace atmospheres consisting of a mixture of commercial nitrogen and other gases, nor for ammonia-based atmospheres, although both have a nitrogen base.

The high concentrations of carbon dioxide and water vapor in the products of combustion can be reduced to desirable low levels by either of two distinctly different systems. One system involves coadsorption of both gases on a molecular-sieve desiccant. The other system is a somewhat complicated miniature chemical plant that employs pumps and several heat exchangers. The carbon dioxide is absorbed by a water solution of monoethanolamine (MEA), and the water vapor is reduced by a refrigerator condenser, followed by desiccant drying.

Classification. Regardless of the method of generation, prepared nitrogen-based atmospheres are of two major types, either lean or rich. The relative richness of carbon monoxide and hydrogen in a typical rich atmosphere (class 202) is compared with a typical lean atmosphere (class 201) in Table 3.

Significantly important subtypes, which are carried in the AGA classification system as classes 223 and 224, involve the removal of almost all the carbon monoxide so that the generated atmospheres consist almost exclusively of nitrogen and hydrogen.

The methods of generator control to attain each of these two major types are described in the "Advantages and Disadvantages" and the "Typical Applications" sections of the "Prepared Nitrogen-Based Atmospheres" portion of this article.

Advantages and Disadvantages. The principal advantage of prepared nitrogen-based atmospheres is their applicability to a variety of heat-treating operations for low-carbon, medium-carbon, and high-carbon steels and for some other metals. Because of their low dew point and the virtual absence of carbon dioxide, these atmospheres (in the absence of oxygen-bearing contaminants introduced as a result of furnace operations) are neither oxidizing nor decarburizing, in contrast to the exothermic-based atmospheres. In addition, the nominal cost per unit volume of atmosphere produced are lower than for several other protective atmospheres except for the exothermic-based atmospheres.

Modified nitrogen-based atmospheres, classes 223 and 224, have the additional advantage of being nonsooting even at low furnace temperatures.

The main disadvantages of these atmospheres lie in the high initial cost of equipment, the large space requirements, and the need for more exacting maintenance and control of the generators. Further, as with any generator-based atmosphere system, extra inspection and testing of the material in process are required when generator conditions develop that force a shutdown.

Typical Applications. These atmospheres can be used in virtually all furnace applications that do not require highly reducing conditions. Because they are not decarburizing, they can be used in annealing, normalizing, and hardening of medium- and high-carbon steels. The low carbon monoxide contents of lean gases render them equally suitable for the thermal treatment of low-carbon steels. However, their usefulness in the heat treating of steels is predicated on their very low dew point, which can be maintained only if furnace design and operation prevent furnace atmosphere contamination

with air or any other oxygen-bearing chemical compound. Consequently, in actual practice, one of the more common uses is for the annealing of steel coils in airtight bell-type furnaces. For this application, ratios of about nine parts of air to one part of natural gas are employed to produce a dry, nondecarburizing, nonexplosive atmosphere containing about 4.0% combustibles. When these atmospheres are modified to eliminate the carbon monoxide (class 223), an additional advantage in annealing is that they do not produce soot during the period of slow cooling to relatively low temperatures.

Nitrogen-based atmospheres enriched with methane or other hydrocarbons are occasionally used as carrier gases in annealing, gas carburizing, and carbon restoration, but endothermic and other protective atmospheres generally are preferred because of their higher carbon potentials and better control capability.

Lean atmospheres (with a maximum of 4.0% combustibles) are also used for purging explosive gases from furnaces and for blanketing the in-process material during furnace idle periods. Although lean exothermic atmospheres are sometimes used for these purposes, the nonoxidizing, nondecarburizing nature of the nitrogen-based atmosphere is often advantageous. The rich atmospheres are not approved for use as purge gases because of the high contents of combustibles. The lean atmosphere is also used for these purposes in numerous applications within the chemical-processing industry.

Another common use of the lean atmosphere is with large semicontinuous and continuous annealing furnaces. In many instances, a lean nitrogen-based atmosphere is blended with an endothermic atmosphere to maintain adequate furnace pressure at lower overall cost. With this blend and appropriate adjustments, the higher carbon potential of the endothermic atmosphere can be maintained. With large semicontinuous furnaces, class 201 gas is often used to purge the furnace vestibules economically. The lean gas is almost always used with either type of furnace, and a part of the gas is stored under high pressure for purging the furnace when an unexpected shutdown occurs, for example, during an electrical power failure. Rich gas is avoided because it is not approved for purging for the reasons described above.

Rich nitrogen-based atmospheres may be used for the annealing or brazing of steel or copper alloys and for sintering of iron powder compacts.

Generation. In both common systems of generating prepared nitrogen-based atmospheres, molecular-sieve or MEA scrubbing, the starting gas is produced by burning an appropriate mixture of air and a hydrocarbon fuel gas, which most frequently is natural gas. Combustion is accomplished within one or more refractory lined chambers. Sufficient air is provided under pressure to partially burn the fuel, and in no situation is enough air supplied to carry the burning to so-called complete combustion. Because the ratio of air to fuel for complete combustion varies widely depending on the analysis of the fuel, the ratios cited are only approximate, and for ease in communication, are related to the analysis of natural gas that is commonly distributed in the midwestern areas of the United States.

The products of combustion consist of nitrogen, water vapor, carbon dioxide, carbon monoxide, and hydrogen, with almost undetectable amounts of free oxygen. Figure 10 indicates the approximate pattern in which percentages of carbon monoxide and hydrogen vary in the final atmosphere versus the air-to-gas ratio of the feed mixture.

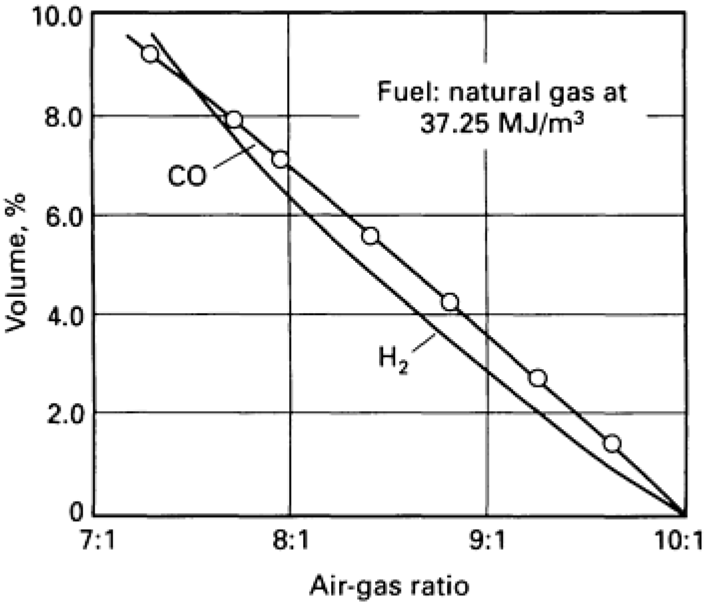

Fig. 10 CO and H_2 versus air-to-gas ratio. Approximate carbon monoxide and hydrogen contents of the generated atmosphere versus the air-to-gas ratio of the feed mixture

To maintain precise control of the air-to-gas ratio for the combustion process, it is common practice to use automatic analyzer/recorder/controller equipment. For simplicity, the various designs for control of air-to-gas ratios are not displayed in the flow diagrams of Fig. 11 and 12.

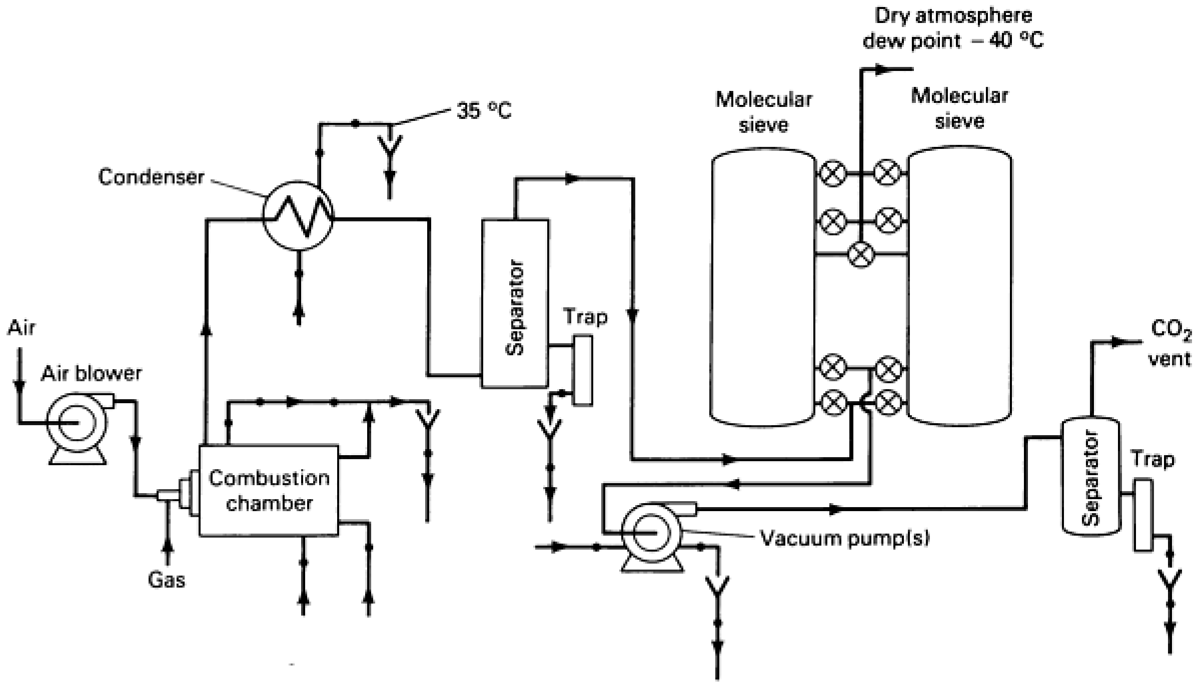

Fig. 11 Flow diagram of nitrogen-based atmosphere generator incorporating molecular-sieve removal of carbon dioxide and water vapor (and using negative-pressure regeneration of the sieves). Gas lines are indicated by solid straight lines; water lines are shown as solid lines with closed circles. Autocontrolled valves are shown as the larger circles located between the molecular sieves.

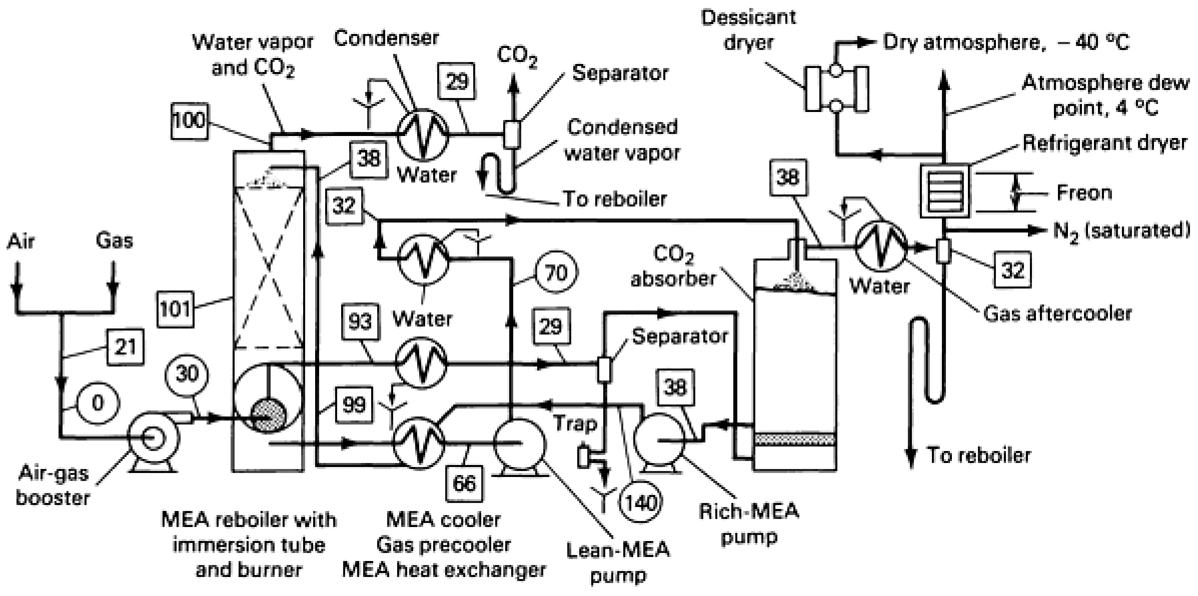

Fig. 12 Flow diagram of nitrogen-based atmosphere generator incorporating a monoethanolamine (MEA) scrubbing system. Temperature (°C) is indicated in boxes; pressure (kPa) appears in circles.

In both systems of generation, products of combustion are first passed through a water-cooled heat exchanger and then through a separator that condenses and discards most of the water of combustion. At this point, the two major systems of generation differ in the methods used for reducing the remaining water vapor and carbon dioxide to very low levels.

Molecular-Sieve Systems. A flow diagram of a typical molecular-sieve system is shown in Fig. 11. The flow diagram for a specific generator may differ significantly depending on the design of components, although overall results are the same.

After products of combustion have passed through the heat exchanger and separator, they are piped to one tower of a dual-tower system, in which both towers are filled with molecular-sieve material. While process gas is passing through the tower that is on the line, molecular-sieve material in the other tower is being reactivated. Switching between towers is controlled by a timer that automatically triggers control valves that direct the flow. In some systems, the time for a complete cycle of a tower from on the line through reactivation is about 10 min.

As the gas passes through the molecularsieve material, both carbon dioxide and water vapor are adsorbed to the extent that typically the dew point of the discharge gas is -40 °C (-40 °F) or lower, and the carbon dioxide content is below 0.15%.

Molecular-sieve systems may function either at low or high operating pressures. In a low-pressure system, reactivation is accomplished by a strong vacuum and purging with some of the discharge gas of the tower that is on the line. Discharge pressure of this system is about 3 kPa (0.5 psig). In a high-pressure system, operating pressure is about 585 kPa (85 psig). Reactivation consists of depressurizing to atmospheric pressure plus purging with some of the discharge gas from the tower that is on the line.

With either type of molecular-sieve generator, heat of combustion is transferred to the water used to cool the combustion chamber. This heated water is sometimes used in other plant processes.

Because of the comparative simplicity and relative absence of operating problems, the molecular-sieve system is often preferred over the monoethanolamine system. Nevertheless, in many installations, the maintenance problems incurred with vacuum pumps are often as troublesome as the total variety of problems encountered in monoethanolamine systems.

Monoethanolamine Systems. Figure 12 presents a flow diagram of a typical monoethanolamine system. The flow diagram for a specific generator may differ significantly depending on design of the components, although overall results are the same.

The combustion process is much the same as previously described except that the combustion chambers are contained in a unit identified as the reboiler-stripper. Heat of combustion is used to boil a recirculating solution of monoethanolamine. Most of the water of combustion in the gas is removed by heat exchangers and separators as described earlier. Gases are then piped to the bottom of the absorber tower, where they pass upward through a counter flow of cooled monoethanolamine solution from the reboiler-stripper, which is introduced at the top of the absorber. Intimate contact between the gas and monoethanolamine is attained with Raschig rings packed in the absorber tower. The upper portion of the reboiler-stripper shown in Fig. 12 is also packed with Raschig rings.

Because cool monoethanolamine, which is basically a water solution containing 12 to 18% monoethanolamine, absorbs carbon dioxide, the CO_2 content of the gases leaving the absorber tower is typically below 0.015%.

The monoethanolamine from the absorber is pumped through a monoethanolamine heat exchanger to the top of the reboiler-stripper. In the reboiler, the heat of combustion from the retort strips the CO_2 from the monoethanolamine. CO_2 and steam from the top of the reboiler-stripper pass through a water-cooled condenser to condense the steam before the CO_2 is vented (Fig. 12).

To reduce the moisture in the gas stream from the top of the absorber, the stream is passed through water-cooled and refrigerant-cooled heat exchangers and then through a dual-chambered desiccant drying system. While one chamber is on the line, the other is being reactivated. Reactivation is accomplished by a separately valved recirculating gas circuit. The volume and pressure of the circuit is maintained by feeding the circuit with a small portion of the discharge gas from the chamber that is on the line. Before being passed through the chamber to be reactivated, the recirculated gas is heated to about 230 °C (450 °F) either electrically or by way of a gas-heated retort. After having passed through the desiccant material in the chamber being reactivated, the water vapor that is picked up by the recirculated gas stream from the desiccant is partially condensed by way of water-cooled heat exchanger. At this point in the closed circuit, a separate gas pump is employed to ensure adequate volume and rate of flow in the recirculated gas stream.

Water vapor of the finished atmosphere is typically lower than 0.02%, or a dew point of less than -40 °C (-40 °F). Accordingly, the prepared nitrogen-based atmosphere is virtually free of carbon dioxide and water vapor, with carbon monoxide and hydrogen contents determined by the air-to-gas ratio fed to the combustion process.

Precautions. In the monoethanolamine process, it is essential that the air-to-gas ratio be maintained on the reducing side to avoid free oxygen in the prepared atmosphere and oxidation of the monoethanolamine. When oxidized, monoethanolamine is much more corrosive than a normal inhibited solution. Antifoaming agents are sometimes necessary in the monoethanolamine to avoid operating problems. Because of the very low surface tension and corrosiveness of monoethanolamine solutions, special care should be given to maintenance of monoethanolamine pumps to avoid leakage through pump-shaft seals.

Generator Maintenance. Rigid adherence to a cookbook recipe for maintenance of any mechanical, electrical, chemical, or electronic system is frequently neither efficient nor effective. A better method is accurate observation of prescribed system performance and adequate records of observations. The following schedules suggest minimum observation and maintenance for each of the two major systems. An adequate schedule of appropriate lubrication of all normal moving components is presumed, as well as a daily review of operator records by the immediate supervisor to detect trends and any need for corrective actions.

The following is a typical generator maintenance schedule for molecular-sieve systems:

Twice per 8-h operating shift

- Observe and record variables such as temperatures, pressures, flow rates, and liquid levels
- Observe and record details of abnormalities such as improper functioning of traps, safety switches, and excessive pump noises or leakage. Where appropriate, consult supervisor regarding the need for immediate corrective actions
- Drain designated nonautomatic traps

Monthly, or as prescribed by standard operating procedures

- Clean or replace all filters and strainers as required
- Lubricate all plug-type valves with appropriate lubricants
- Check operation of fuel safety shutoff valve and all pressure switches
- Clean all traps, unless safety considerations override
- Check the lens of the safety flame detector and clean as required

Complete annual overhaul of the system

- Cleaning heat exchangers, for which chemical cleaning is preferred over mechanical cleaning
- Cleaning, repair, or replacement of all valves, including the safety shutoff valve and the pressure-control relief valve; pressure switches; manometers; sensing lines; traps; and flame scanner and relay
- Replacement of burner block and holder
- Rebuilding of vacuum pumps and compressor as required
- Checking accuracy of all meters, pressure controllers, and pressure switches

Do not overheat the molecular-sieve desiccant. In general, maintenance schedules for monoethanolamine generator systems coincide with those for the molecular-sieve systems except for the following major differences:

- Control amount of foaming in the absorber tower. Use antifoaming agent in monoethanolamine solution as required
- Check monoethanolamine concentration monthly and include additions when required, along with additions of the recommended corrosion inhibitor (typically sodium metavanadate)
- The refrigerator system (for the refrigerant-cooled heat exchanger) should be checked and serviced monthly, also
- Annual servicing should include a check of corrosion characteristics of the monoethanolamine solution. If solution needs to be replaced, the monoethanolamine circuit should be cleaned and boiled out with an appropriate caustic solution
- Although the foregoing statements concerning vacuum pumps and molecularsieve desiccants are not applicable here, a drying tower should not be used beyond its design cycle, contamination should be avoided, and the activated alumina desiccant should not be overheated

Safety Precautions. In general, safety precautions outlined for exothermic-based atmospheres apply equally to prepared nitrogen-based atmosphere generators and usage. Safety precautions as outlined for endothermic-based atmosphere generators and usage are also applicable.

Atmospheres with less than 4% combustibles are underwriter approved for purging, and are approved for furnace operating temperatures below 760 °C (1400 °F) without the requirement that the furnace system be designed for automatic purging in case of electrical power failure or the absence of adequate furnace-atmosphere pressures.

Operating Economics. The following list indicates representative utility requirements for 28 m^3 of atmosphere under so-called standard temperature-pressure conditions (1000 ft^3 under standard temperature-pressure conditions, which is uniformly abbreviated in the English system of units as 1000 scf) for class 201 lean prepared nitrogen-based atmosphere. The following table compares the requirements for a typical molecular-sieve system with a typical monoethanolamine system, with both systems using an air-to-gas ratio of about 9.5 to 1.

Requirement	Molecular sieve	Monoethanolamine

Natural gas, m^3 (scf)	3.77 (133)	3.77 (133)
Electric energy consumption, MJ (kW · h)	28 (7.8)	14.5 (4.0)
Cooling water, L (gal)	2780 (735)	2500 (660)

Commercial Nitrogen-Based Atmospheres

Industrial gas nitrogen-based atmospheres have found technical acceptance in most metalworking applications. The shift of many heat-treating operations to nitrogen atmospheres on some or all of the furnaces accelerated in the late 1970s as a result of shifting economics of hydrocarbon fuel supplies.

Commercial nitrogen-based atmosphere systems employed by the metalworking and heat-treating industry use gases and equipment that are common among all applications. In most instances, the major atmosphere component is industrial gas nitrogen, which is supplied to the furnace from a system consisting of a storage tank, vaporizer, and a station controlling pressure and flow rate. The nitrogen serves as a pure, dry, inert gas that provides an efficient purging and blanketing function within the heat-treating furnace. The nitrogen stream is often enriched with a reactive component, and the resulting composition and flow rate are determined by the specific furnace design, temperature, and material being heat treated. Although there is similarity in the components of commercial nitrogen-based atmosphere systems, the flexibility of controlling atmosphere composition and flow rate independently over a wide range provides very different end-use characteristics.

Types of Commercial Nitrogen-Based Atmospheres. Therefore, the classification of commercial nitrogen-based atmosphere systems is appropriately made according to three major categories of atmosphere function--protection, reactivity, and carbon control--rather than by gas or equipment components.

Protective Atmospheres. The atmosphere systems required for these applications must prevent oxidation or decarburization of the metal surface during heat treatment. Such detrimental reactions normally would occur because of residual oxygen or water vapor present in the furnace as a result of air leaks or inadequate purging. Typical applications include batch and continuous annealing of most ferrous and nonferrous metals. Atmosphere systems employed may be pure nitrogen or nitrogen blended with small quantities (usually less than 5%) of a reactive gas such as hydrogen, methane, propane, or methanol vapor. Reactive gases reduce gaseous oxides present in the furnace atmosphere or reduce surface metal oxides. These systems are best employed to prevent oxidation of relatively clean metal surfaces rather than to remove gross oxidation of hot-worked or forged materials.

Reactive Atmospheres. These atmosphere systems require a concentration of reactive gases greater than 5% to reduce metal oxides or to transfer a small amount of carbon to ferrous materials. The reactive components are generally hydrogen and carbon monoxide. The concentrations depend on the amount of oxide to be removed and the level of reaction products, water vapor, and carbon dioxide, that are formed in the furnace atmosphere. Typical applications include brazing, powder-metal sintering, and powder-metal reduction.

Carbon-Controlled Atmospheres. The main function of these nitrogen-based atmosphere systems is to react with steel in a controlled manner so that significant amounts of carbon can be added to or removed from the steel surface. Significant change in the surface chemistry of the steel occurs in these heat-treating applications. These atmosphere systems are characterized by high concentrations of reactive gases in nitrogen and by the requirement that the rate and amount of carbon transfer must be controlled by the atmosphere composition. Typical atmosphere components may include 10 to 50% hydrogen (H_2), 5 to 20% carbon monoxide (CO), and trace amounts (up to 3%) of carbon dioxide (CO_2) and water vapor (H_2O). The most common applications using a carbon-controlled atmosphere include carburizing and carbonitriding of machined parts, neutral hardening, electrical-lamination decarburization annealing, powder-metal sintering, and carbon restoration of hot-worked or forged materials.

Table 7 describes heat-treating applications that are presently using nitrogen-based atmosphere systems. The major components of the generated atmosphere most commonly used for each application are compared to the nitrogen-based alternatives that are presently in use.

Table 7 Comparison of generated atmosphere systems versus commercial nitrogen-based systems

Type of atmosphere	Application	Generated atmosphere				Nitrogen-based atmosphere				
		Designation	Nominal composition, %			Designation	Nominal composition, %			
			N_2	H_2	CO		N_2	H_2	CO	CH_4
Protective	Annealing	Exothermic	70-100	0-16	0-11	Nitrogen-hydrogen	90-100	0-10	. . .	. . .
						Nitrogen-methanol	91-100	0-6	0-3	. . .
		Dissociated ammonia	25	75	. . .	Nitrogen-hydrogen	60-90	10-40	. . .	. . .
Reactive	Brazing	Exothermic	70-80	10-16	8-11	Nitrogen-hydrogen	95	5	. . .	. . .
		Dissociated ammonia	25	75	. . .					
	Sintering	Endothermic	40	40	20	Nitrogen-hydrogen	95	5	. . .	. . .
		Dissociated ammonia	25	75	. . .	Nitrogen-methanol	85	10	5	. . .
Carbon controlled	Hardening	Endothermic	40	40	20	Nitrogen-methane	97	1	1	1
	Carburizing	Endothermic	40	40	20	Nitrogen-methanol	40	40	20	. . .
	Decarburizing	Exothermic	85	5	3	Nitrogen-	90	10	. . .	. . .

Advantages of Commercial Nitrogen-Based Atmospheres. A nitrogen-based atmosphere system provides a technically viable substitute for generated atmospheres in most heat-treating applications. Although the desired results are often the same with either a commercial nitrogen-based system or a conventional atmosphere generator, there are some significant differences in equipment, operation, and function among these systems that should be understood before making the conversion from a generator to commercial nitrogen.

A generated atmosphere provides a fixed composition of output, which is determined by the input ratio of air to hydrocarbon, the scrubbing and purification process equipment of the generator, and the relative condition of the equipment and catalysts. The commercial nitrogen-based system generally starts with elemental components stored in

separate vessels, blends the desired atmosphere composition, and introduces it into the furnace. The resulting composition can be varied at different times during the cycle and at different locations within the furnace.

Most components of commercial nitrogen-based atmosphere systems are produced either by cryogenic processes or by chemical refining. As a result, the impurity levels are low, usually less than 20 ppm total impurity for liquid nitrogen, as an example. Further, because there are no by-products of air-fuel mixtures, the resulting atmosphere blend often has a dew point of less than -60 °C (-80 °F) and oxygen or carbon dioxide impurity levels of less than 10 ppm.

The reducing or carburizing potential of an atmosphere is determined by several reactions and their associated equilibrium constants. Included among these are:

$FeO + H2$ € $Fe + H_2O$ **(Eq 34)**

$Fe + 2CO$ € $FeC + CO_2$ **(Eq 35)**

$Fe + CO + H_2$ € $FeC + H_2O$ **(Eq 36)**

Because commercial nitrogen-based blends significantly reduce the amount of water vapor and carbon dioxide in the furnace atmosphere, the level of the reactive gases can also be reduced while maintaining acceptable thermodynamic potentials in the above ratios. The net result is that generated atmospheres that contain as much as 60% combustible products are often replaced with nitrogen blends containing less than 10% hydrogen and carbon monoxide. Many heat-treating atmosphere applications can be converted from combustible to noncombustible compositions in conjunction with the switch to a commercial nitrogen-based system.

Because elemental components are available, commercial nitrogen-based heat-treating practice may start with a pure nitrogen purge to eliminate oxygen from the surface. During the heat-treating cycle, a very reactive blend may be used to bright anneal heavily oxidized parts, during cooling, a less reactive protective atmosphere, and finally a pure nitrogen purge to eliminate combustibles before opening the furnace.

Because the composition of a nitrogen atmosphere may be varied with time, it may also be controlled according to the functions of different zones of the heat-treating furnace. For example, in a three-zone powder-metal sintering furnace, a pure nitrogen purge curtain may be used on both ends to reduce air infiltration. The presintering zone may be supplied with a reducing atmosphere with controlled ratio of H_2 and H_2O. Dew-point control supplies sufficient water vapor for efficient breakdown and removal of vaporized lubricants from the powder compact. The sintering zone may use a nitrogen-hydrogen-carbon monoxide blend to provide a highly reducing atmosphere with a slight carbon potential to provide the required sintered strength and metal composition. In the cooling section, it may be necessary to add only a nitrogen protective atmosphere to bring the parts back to room temperature in a clean, nonoxidized condition. In a single-zone sintering furnace, this same ability can be used to expand the range of processes that can be utilized.

The ability to control composition also allows flexibility of the overall flow rate during the heat-treating cycle. The most common advantage of this characteristic is the use of a high flow rate during charging of furnaces equipped with doors. When the door is opened, a microswitch initiates a purge flow of nitrogen to reduce air infiltration into the furnace. After the door is closed, the atmosphere flow rate returns to a level required to maintain adequate pressure in the closed furnace and to perform the required gas-metal surface reactions.

In commercial nitrogen-based applications where the hydrogen content of the atmosphere is significantly reduced from the generated atmosphere composition, it is often possible to achieve a flow rate reduction because of atmosphere density. The most frequent examples of this occur in protective atmosphere applications in which endothermic gas (40% H_2) (Fig. 13a) or dissociated ammonia (75% H_2) (Fig. 13b) is replaced with a nitrogen-hydrogen blend of less than 10% H_2. In these instances, the atmosphere density changes from a specific gravity of 0.295 for dissociated ammonia to 0.595 for endothermic, or to 0.90 for the nitrogen-hydrogen blend. This increase in atmosphere density is responsible for increased furnace pressurization and more efficient purging of impurities from the furnace. Experience shows that an average 10 to 20% flow rate reduction may be achieved relative to the flow rates of generated atmosphere with lower densities.

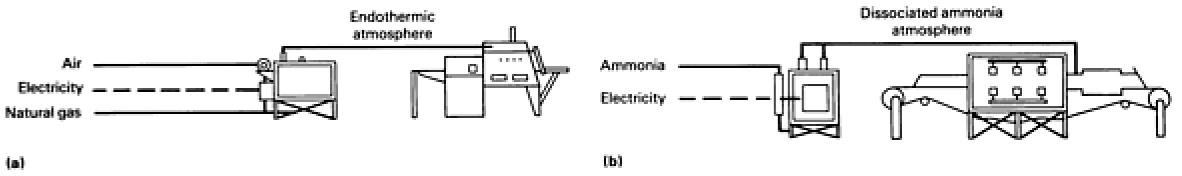

Fig. 13 Generated protective atmosphere processes. (a) Endothermic atmosphere. (b) Dissociated ammonia atmosphere

Components of Commercial Nitrogen-Based Atmosphere System. The basic components of an industrial gas atmosphere system are illustrated in Fig. 14. Figure 14(a) shows a nitrogen-hydrogen protective atmosphere system used for annealing, brazing, and sintering. Figure 14(b) is a nitrogen-methanol system typical of those used for carburizing. In both instances, there are three basic parts to the commercial-nitrogen system: the storage vessels containing the elemental atmosphere components, the blend panel used to control the flow rate of each constituent gas, and the piping and wiring required for safe operation compatible with the furnace design.

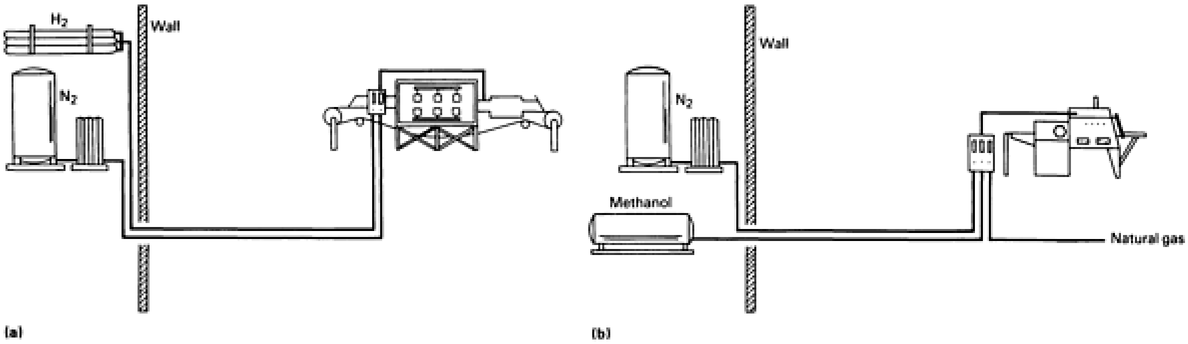

Fig. 14 Industrial-gas nitrogen-based atmosphere processes. (a) Protective atmosphere using H_2 and N_2. (b) Carbon-controlled atmosphere using methanol and natural gas

Nitrogen is the main component of most commercial nitrogen-based systems. Because nitrogen is noncorrosive, special materials of construction are not required, except that they must be suitable for the temperatures of liquid nitrogen. Tanks may be spherical or cylindrical in shape. Figure 15 illustrates a typical liquid nitrogen tank. Sizes range from 2270 to 37,850 L (600 to 10,000 gal).

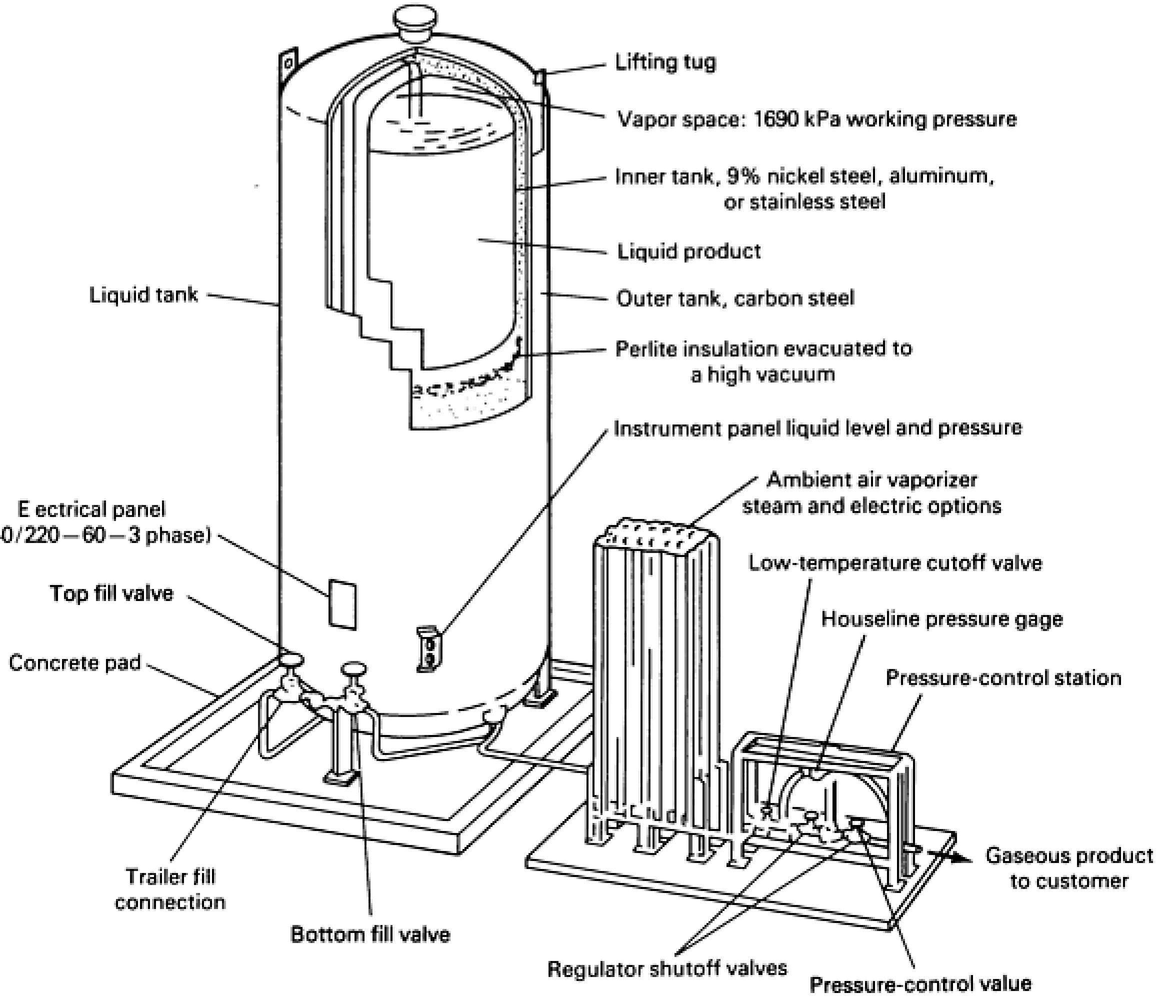

Fig. 15 Typical liquid nitrogen storage facility

Hydrogen is used as a reactive reducing gas for many heat-treating atmosphere applications. In commercial nitrogen-based systems, it is normally blended as a gas with nitrogen to form an atmosphere composition of 90% nitrogen, 10% hydrogen.

Liquid hydrogen is normally stored in tanks from which it is vaporized and used as a gas. Hydrogen may also be delivered and stored as a gas. Tube trailers are available in capacities to 3570 m^3 (126,000 scf) of hydrogen with up to 16,960 kPa (2460 psig) pressure. Modules are available in 3- to 18-tube configurations with capacities to 4250 m^3 (150,000 scf) of hydrogen.

In commercial nitrogen-based atmospheres, methanol is used as a source of hydrogen and carbon monoxide for reactive and carbon-controlled atmosphere systems. Methanol is delivered to the furnace as either a liquid or a vapor. When it is exposed to furnace temperatures greater than 760 °C (1400 °F), the methanol dissociates according to the following reaction:

$$CH_3OH \rightarrow 2H_2 + CO \qquad \textbf{(Eq 37)}$$

Methanol is classified by the U.S. Department of Transportation (DOT) as a flammable liquid. When shipped by rail, water, or highway, it must be packaged in authorized containers, and shippers must comply with all DOT regulations regarding loading, handling, and labelling.

Before any connection or contact is made between the tank truck and the unloading line or other unloading equipment, the tank truck should be electrically grounded. *Caution: All containers filled from the truck should be bonded (electrically connected) and grounded to the truck before filling operations are started.*

Air pressure should never be used for unloading tank trucks of methanol. Nitrogen pressure can be used as long as the methanol tank is a pressure vessel. Because the bulk storage of methanol in above- and below-ground tanks requires consideration of such factors as size of vents, diking, and separation distances, which in turn depend on other variables such as nature of the tank contents, tank-wall thickness, or protection, it is recommended that tank storage requirements be determined through consultation with qualified fire-protection engineers. (For guidance, refer to National Fire Protection Association pamphlet NFPA 30 or Factory Mutual Handbook of Industrial Loss Prevention.) Figure 16 shows an example of underground methanol storage.

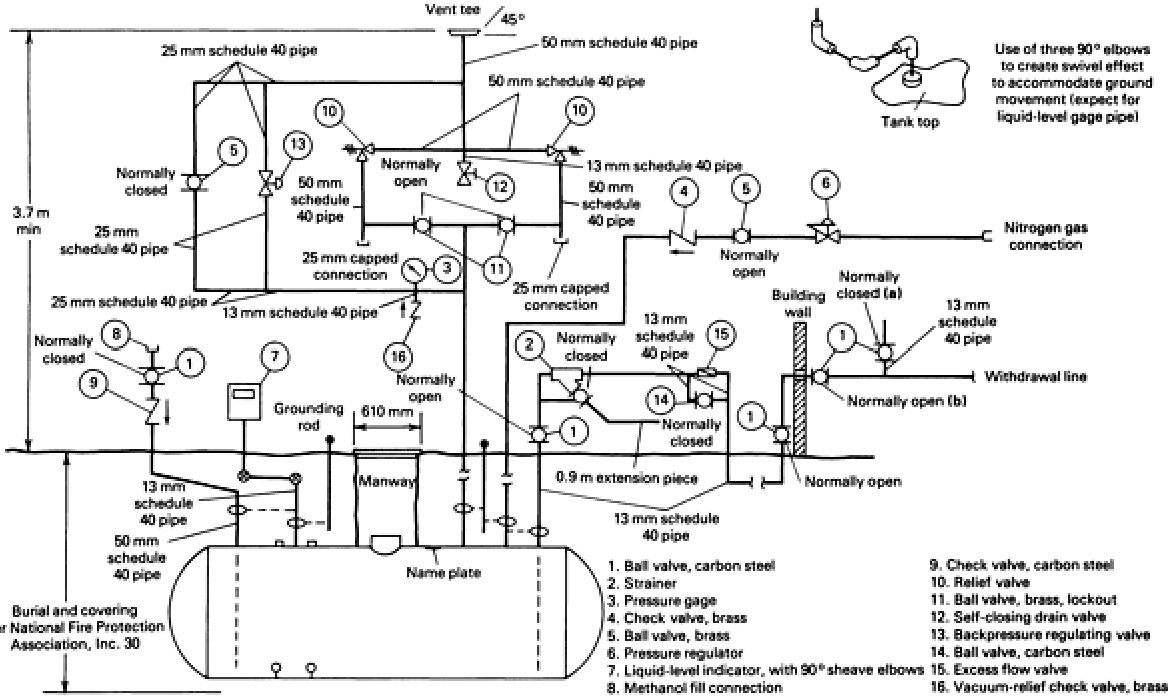

Fig. 16 Flow diagram of typical underground methanol storage. (a) Vapor bleed valve to be located at the high point of the houseline piping. (b) This valve can be eliminated if methanol piping between tank withdrawal connection and inlet to building is less than 6 m (20 ft) long.

Blending Equipment. Blending and flow-control systems for commercial nitrogen-based atmospheres are designed to be consistent with NFPA guidelines for generated atmospheres as well as with Factory Mutual guidelines. However, because gaseous components of the commercial nitrogen atmosphere system are independent with regard to storage, pressure, and flow rate, certain differences exist compared with atmosphere generator operation. The blending system ensures safe operation in both normal and emergency situations compatible with furnace design and processing conditions. Figure 17 illustrates generalized blending equipment schematics for two types of commercial nitrogen-based atmospheres. These schematics are consistent with the storage supply illustrations for protective and carbon-controlled atmosphere systems shown in Fig. 14.

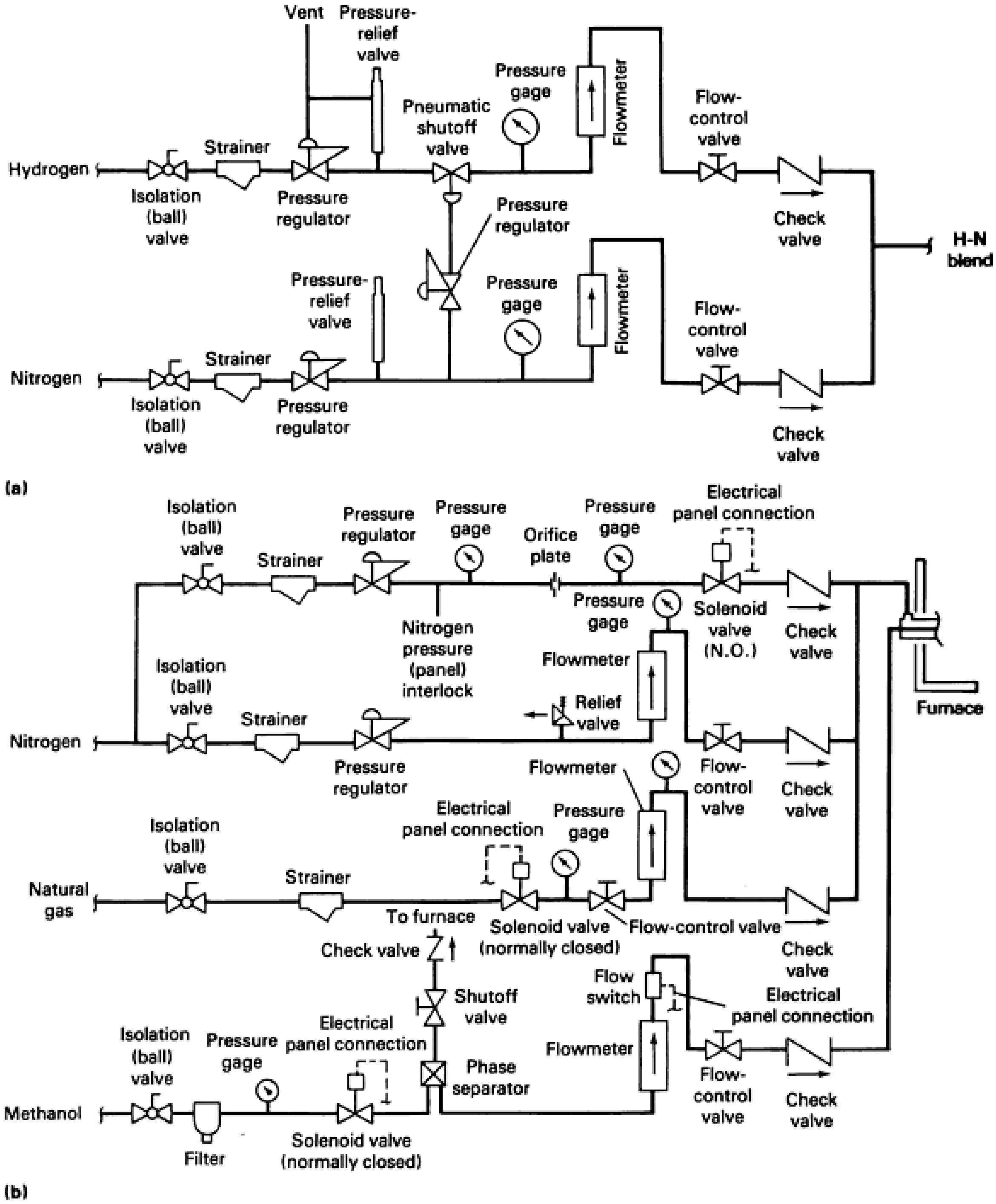

Fig. 17 Flow diagrams of commercial nitrogen-based atmosphere-blending equipment. (a) Two-component blend system. (b) Three-component blend system

In most applications, nitrogen is the predominant component, comprising 50 to 100% of the atmosphere. The enriching gas is typically hydrogen, but it may also be methane, propane, or liquid methanol. Figure 17 shows a two-component blend system. Each leg consists of a pressure regulator, relief valve, pressure gage, flowmeter, control valve, and check valve. Nitrogen pressure is used to open a normally closed pneumatic valve on the hydrogen leg. It is, therefore, not possible for the combustible gas to flow into the furnace until the nitrogen is also available for flow. If nitrogen pressure is lost for any reason, flow of the combustible component will be interrupted automatically. An alternative method of interlocking combustibles to the nitrogen is through use of a nitrogen flow sensor. Typically this will be done by a flow switch or by a magnetic sensor on the nitrogen flowmeter. The hydrogen-shutoff solenoid also should be interlocked to

furnace temperature to prevent the flow of the combustible component into a furnace at less than 760 °C (1400 °F) to prevent the formation of an explosive mixture.

Figure 17(b) shows a nitrogen-methanol-methane blend panel typically used for carburizing applications. The design is more complex than the protective-atmosphere system because of the number of components and the more involved nature of the batch-carburizing process for which this methanol panel is designed.

Each leg typically consists of the same major components as the two-component system in Fig. 17(a): pressure regulator, relief valve, pressure gage, flowmeter, flowcontrol valve, and check valve. Because the combustible components are interlocked to nitrogen pressure, a loss of nitrogen pressure will shut off the methanol and methane. The combustibles are also interlocked to furnace temperature and to the electrical power supply to the furnace and panel. A drop in furnace temperature below 760 °C (1400 °F) or a loss of electric power will shut off the combustibles.

This panel typically includes a separate nitrogen-purge system that is preset with a pressure regulator orifice plate flow control. In the event of low furnace temperature or electric power loss, an alarm sounds, the nitrogen purge commences, and flow of combustibles is shut off. The nitrogen purge is also interlocked to the inner furnace doors through a microswitch circuit so that charging or quenching a load will initiate the high-flow purge. In this mode, the purge will last from 5 to 60 min.

Commercial Nitrogen-Based Atmosphere Applications. Tables 8, 9, and 10 compare commercial nitrogen-based atmospheres with comparable generated atmospheres used in relevant heat-treating processes. Shown are the generated atmospheres typically in use and the nitrogen-based alternative. Protective atmosphere applications in Table 8 indicate the potential of commercial nitrogen-based atmospheres as alternatives to exothermic, endothermic, and dissociated ammonia atmospheres in a broad range of annealing operations. The nitrogen-based alternatives illustrated are pure nitrogen, nitrogen-hydrogen, nitrogen-methanol, and nitrogen-hydrocarbon.

Table 8 Compositions of protective generated atmosphere and commercial nitrogen-based atmosphere systems

Application	Input atmosphere	Furnace atmosphere analysis, %					
		N_2	H_2	CO	CH_4	Trace impurities	
						H_2O	CO_2
Carbon steel sheet, tube, wire	Exothermic-purified	80	12	8	. . .	0.01	0.5
	N_2-5% H_2	95	5	. . .	. . .	0.001	. . .
Carbon steel rod	Exothermic-purified	100	. . .	. . .	. . .	0.01	0.5
	Exothermic-endothermic blend	75	15	8	2	0.01	0.5
	N_2-1% C_3H_8	97	1	1	1	0.001	0.01
	N_2-5% H_2-3% CH_4	90	7	2	1	0.001	0.01
	N_2-3% CH_3OH	91	6	3	. . .	0.001	0.01

Copper wire, rod	Exothermic-lean	86	. . .	. . .	. . .	3	11
	N_2-1% H_2	99	1	. . .	. . .	0.001	. . .
Aluminum sheet	Exothermic-lean	86	. . .	. . .	. . .	3	11
	N_2	100	. . .	. . .	. . .	0.001	
Stainless steel sheet, wire	Dissociated ammonia	25	75	. . .	. . .	0.001	. . .
	H_2	. . .	100	. . .	. . .	0.0005	. . .
	N_2-40% H_2	60	40	. . .	. . .	0.0005	. . .
Stainless steel tube	Dissociated ammonia	25	75	. . .	. . .	0.001	. . .
	H_2	. . .	100	. . .	. . .	0.0005	. . .
	N_2-25% H_2	75	25	. . .	. . .	0.005	. . .
Malleable iron anneal	Exothermic-purified	98	. . .	2	. . .	0.01	0.5
	N_2-1% C_3H_8	97	1	1	1	0.001	0.2
Nickel-iron laminations	Dissociated ammonia	25	75	. . .	. . .	0.001	. . .
	N_2-15% H_2	85	15	. . .	. . .	0.001	. . .

Table 9 Compositions of reactive atmospheres for brazing and sintering applications

Application	**Input atmosphere**	**Furnace atmosphere analysis, %**					
		N_2	**H_2**	**CO**	**CH_4**	**Trace impurities**	
						H_2O	**CO_2**
Copper braze carbon steel	Exothermic-rich	70	14	11	1	0.05	4
	Endothermic	40	39	19	2	0.05	0.1
	N_2-5% H_2	95	5	. . .	. . .	0.001	. . .

	N_2-3% CH_3OH	91	6	3	. . .	0.001	0.01
Silver braze stainless steel	Dissociated ammonia	25	75	. . .	. . .	0.001	. . .
	N_2-25% H_2	75	25	. . .	. . .	0.001	. . .
Metallize ceramics	Dissociated ammonia + H_2O	25	75	. . .	. . .	3	. . .
	N_2-10% H_2-2% H_2O	90	10	. . .	. . .	2	. . .
Glass-to-metal seal	Exothermic	75	9	7	. . .	3	6
	N_2-10% H_2-2% H_2O	88	10	. . .	. . .	2	. . .
Carbon steel sintering (6.4 to 6.8 g/cm^3, or 0.23 to 25 lb/in.^{3} density, <0.4% C)	Endothermic	40	39	19	2	0.05	0.1
	N_2-5% H_2	95	5	. . .	. . .	0.001	. . .
	Endothermic	40	39	19	2	0.05	0.2
Carbon steel sintering (6.8 to 7.2 g/cm^3, or 0.25 to 0.26 lb/in.^{3} density, >0.4% C)	N_2-endothermic	87	8	4	1	0.01	0.05
	N_2-8% CH_3OH	76	16	7	1	0.005	0.05
	N_2-8% H_2-2% CH_4	90	8	1	1	0.005	0.01
Brass, bronze sintering	Dissociated ammonia	25	75	. . .	. . .	0.001	. . .
	Endothermic	40	39	19	2	0.05	0.3
	N_2-10% H_2	90	10	. . .	. . .	0.001	. . .
Stainless steel sintering	Dissociated ammonia	25	75	. . .	. . .	0.001	. . .
	H_2	. . .	100	. . .	. . .	0.001	. . .
Tungsten carbide							
Sintering and brazing	Dissociated ammonia	25	75	. . .	. . .	0.001	. . .

Sintering	H_2	. . .	100	. . .	. . .	0.001	. . .
Presintering	N_2-20% H_2	80	20	. . .	. . .	0.001	. . .
Nickel sintering	Dissociated ammonia	25	75	. . .	. . .	0.001	. . .
	N_2-10% H_2	90	10	. . .	. . .	0.001	. . .

Table 10 Compositions of carbon-controlled atmospheres for selected applications

Application	Input atmosphere	Furnace atmosphere analysis, %					
		N_2	H_2	CO	CH_4	Trace impurities	
						H_2O	CO_2
Neutral harden	Endothermic + CH_4	39	40	19	2	0.05	0.1
	N_2-2% CH_4, or 1% C_3H_8	97	1	1	1	0.001	0.01
	N_2-5% CH_3OH-1% CH_4	84	10	5	1	0.005	0.01
Carburize	Endothermic + CH_4	37	40	18	5	0.05	0.1
	N_2-20% CH_3OH + CH_4	37	40	18	5	0.05	0.1
	N_2-17% CH_4-4% CO_2	70	16	7	7	0.005	0.05
	N_2-20% CH_4-5% H_2O	55	28	10	7	0.01	0.05
Carbonitride	Endothermic + CH_4 + NH_3	36	40	18	5	0.05	0.1
	N_2-20% CH_3OH + CH_4 + NH_3	36	40	18	5	0.05	0.1
	N_2-17% CH_4-4% CO_2 + NH_3	68	18	7	7	0.005	0.05
	N_2-20% CH_4-5% H_2O + NH_3	53	30	10	7	0.01	0.05
Lamination decarburize	Exothermic + H_2O	75	9	7	. . .	3	6
	N_2-10% H_2-4% H_2O	83	10	1	. . .	3	3

	N_2-5% CH_3OH-4% H_2O	79	10	2	. . .	3	6

In most instances, the nitrogen atmosphere has a lower level of combustible components, carbon monoxide and hydrogen. The nitrogen atmosphere also will normally contain lower trace impurities, carbon dioxide and water vapor. In some applications, more than one system is applicable, depending on the furnace design and the grade of material processed.

Reactive atmospheres are required for such heat-treating applications as brazing and powder-metal sintering. The atmosphere reacts with the metal surface to remove all metal oxides. In brazing, a chemically clean metal surface is required to ensure proper filler-metal flow and diffusion of the filler metal into the base metal. In powder-metal sintering, reduction of powder surface oxides is necessary to promote diffusion and thus to obtain effective bonding within the powder compact. The reactive nature of these atmospheres also applies to carbon transfer. In brazing, residual carbonaceous lubricants on the materials and organics in the brazing paste must be removed by the atmosphere for proper flow of filler metal. In carbon steel powder-metal sintering, lubricants must be removed in one section of the furnace and carbon made available to the steel in another section to achieve proper part chemistry. Table 9 summarizes the compositions of reactive atmosphere alternatives, both with respect to major constituents and to trace impurities.

Carbon-controlled atmospheres transfer carbon from the atmosphere to the surface of the metal part ($\overline{C}$) through controlled gas-metal reactions. The two most common reactions are:

$$2CO \text{ € } \overline{C} + CO_2 \quad \textbf{(Eq 38)}$$

$$CO + H_2 \text{ € } \overline{C} + H_2O \quad \textbf{(Eq 39)}$$

Because carbon transfer is required of many of these applications, it is common to find higher concentrations of carbon monoxide and hydrogen in these atmospheres than in the protective and reactive atmospheres. The compositions of typical carbon-controlled atmosphere systems are provided in Table 10.

Carbon-controlled atmosphere systems are used in surface carburizing steel parts, in neutral hardening, and in decarburize annealing of steel motor laminations. The essential requirement of all applications using these atmospheres is control. In neutral hardening, the atmosphere carbon potential must match the surface carbon of the steel to prevent decarburization or carburization. The surface carburization of steel parts requires not only the desired carbon potential in the atmosphere, but also the correct carbon availability to provide the proper case depth. Decarburization of motor and transformer laminations requires controlled carbon removal from the steel without unwanted oxidation of the steel surface. The systems presently employed in these applications are exothermic- and endothermic-generated atmospheres, and nitrogen-hydrocarbon and nitrogen-methanol blended atmosphere systems.

Dissociated Ammonia-Based Atmospheres

Dissociated ammonia (class 601) is a medium-cost prepared furnace atmosphere providing a dry, carbon-free source of reducing gas. Typical composition is 75% hydrogen, 25% nitrogen, less than 300 ppm residual ammonia, and less than -50 °C (-60 °F) dew point.

Principal uses of dissociated-ammonia furnace atmosphere include bright copper and silver brazing; bright heat treating of selected nickel alloys, copper alloys, and carbon steels; bright annealing of electrical components; and as a carrier mixed gas for certain nitriding processes, including the Floe system of nitriding, which is a method of controlling white layer formation.

The high hydrogen content affords a strong deoxidizing potential, which is an advantage in removing surface oxides or preventing oxide formation during high-temperature heat treatment. Care should be exercised, however, in selecting heat-processing applications that might result in unwanted hydrogen embrittlement or surface-nitriding reactions.

Other less general uses involve dissociated ammonia fully or partially burned with air in a slightly modified exothermic-gas generator. These secondary atmospheres fall into two general classifications: lean combusted ammonia (class 621), which is considered inert and nonflammable with from 0.25 to 1.0% hydrogen and the remainder nitrogen, and rich combusted ammonia (class 622), which is a moderately reducing atmosphere usually containing from 5 to 20% hydrogen

and the balance nitrogen. A very high moisture content is present following combustion and primary cooling. It is often necessary to further dehydrate these gases with additional equipment in the form of refrigerant and desiccant dryers. These treated gases provide very high-quality atmospheres of low-to-moderate reducing ability. Practical uses, however, are restricted because the process requires consumption of relatively costly anhydrous ammonia as the primary feedstock and because added investment is required in addition to operating costs of exothermic generators and dryers.

Required Equipment. Dissociated ammonia ($N_2 + 3H_2$) is produced from commercially supplied anhydrous ammonia (NH_3) with an ammonia dissociator. This equipment raises the temperature of ammonia vapor in a catalyst-filled retort to approximately 900 to 980 °C (1650 to 1800 °F). The gas is then cooled for metering and transport as a prepared atmosphere. At these reaction temperatures in the presence of catalyst, ammonia vapor dissociates into separate constituents of hydrogen and nitrogen. The simplified reaction is:

$$2NH_3 + \text{heat} \rightarrow N_2 + 3H_2 \qquad \textbf{(Eq 40)}$$

where two volumes of ammonia vapor yield four volumes of dissociated ammonia.

The basic ammonia dissociator (Fig. 18) consists of either an electrically heated or gas-fired chamber containing one or more catalyst-filled alloy retorts, followed by a water-cooled indirect heat exchanger. Operation is simple and continuous, incorporating a product gas flowmeter with either manual or automatic process flow control, and suitable automatic heating-chamber temperature controls. Safety devices include items such as pressure switches, temperature-monitoring instruments, and pressure-relief valves. Periodic checks of operation consist of observing pressures, temperature, and flow rate, and occasional analysis of product gas for unreacted ammonia content.

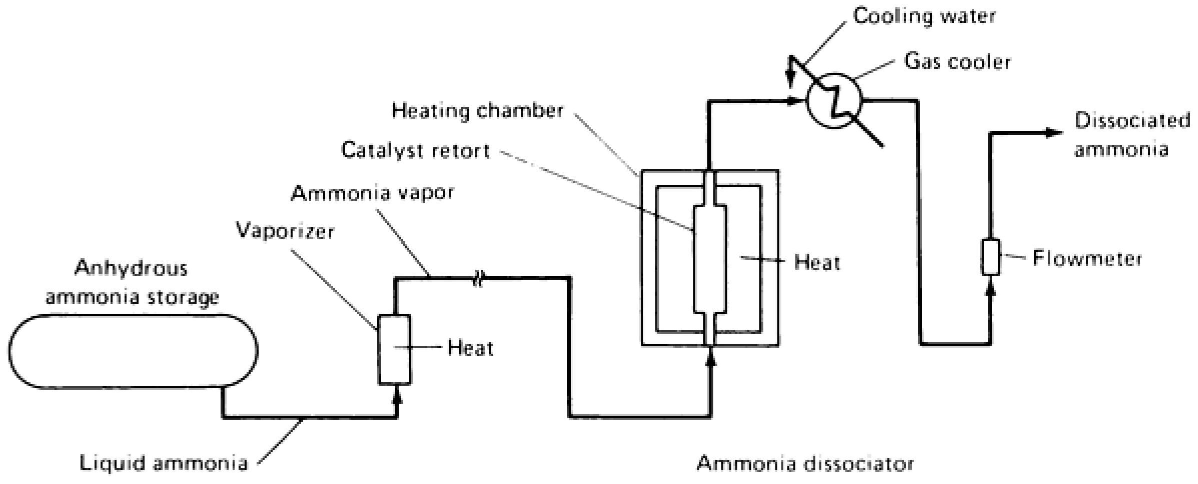

Fig. 18 Simplified process schematic of ammonia dissociator system

Liquid anhydrous ammonia as a feedstock material is obtained by commercial delivery in pressurized cylinders, by pressurized tank truck, or by rail tank car. The ammonia is transferred to a stationary on-site bulk storage vessel. Because liquid ammonia is supplied at high pressure, only pressure and flow regulation are required for conveyance to points of use.

To ensure suitable and efficient dissociator operation, liquid ammonia should first be converted to vapor, usually with a tankmounted vaporizer. This is a chamber using an immersion-type electric heater or steam coil. Some smaller dissociators may have a self-contained vaporizer using residual process heat, thus permitting operation directly from cylinder supplies.

Operating Economics. Typical operating consumptions to produce 28 m^3 (1000 ft^3) of dissociated ammonia are:

Consumption	Value
Anhydrous ammonia, kg (lb)	10 (22.0)
Dissociator electric energy, MJ (kW · h)	75 (21)
Vaporizer electric energy, MJ (kW · h)	14 (3.9)
Cooling water, L (gal)	284 (75)

To obtain the highest-quality furnace atmosphere and to minimize possible dissociator maintenance, an oil-free metallurgical grade of ensured dry anhydrous ammonia should be used.

Safety Precautions. *Caution: Ammonia vapor and dissociated ammonia are flammable when mixed in certain proportions of air.* They should be treated with any combustible gas relative to handling or to its use as a furnace atmosphere. Ammonia vapor also is extremely corrosive to certain materials such as copper and copper-bearing alloys. Care should be taken in the selection of piping materials and other devices in contact to prevent corrosion failure and resultant leaks. *Caution: Additionally, because ammonia is stored at high pressure and has a high rate of expansion, stored cylinders should not be exposed to temperatures exceeding 50 °C (120 °F), otherwise dangerously excessive pressures will result.* Ammonia piping above 25 mm (1 in.) diam should have welded steel joints with adequate pressure rating, and extra-heavy (schedule 80) steel pipe should be used.

Ammonia may also cause certain physiological effects in air concentrations over 100 ppm, resulting in eye and respiratory irritation (see Table 11). It is extremely pungent, however, and the strong odor will generally give adequate warning of any leak.

Table 11 Physiological effects of contamination of air by ammonia in various concentrations

Ammonia concentration in air, ppm	Physiological effect
53	Smallest concentration at which odor can be detected
100	Maximum concentration allowable for prolonged exposure
300-500	Maximum concentration allowable for short exposure ($\frac{1}{2}$-1 h)
408	Least amount causing immediate irritation to the throat
698	Least amount causing immediate irritation to the eye
1720	Least amount causing coughing

2500-4500	Dangerous for short exposure ($\frac{1}{2}$ h)
5000-10,000	Rapidly fatal for short exposure

Caution: Dissociated ammonia with its high percentage of hydrogen makes it necessary to establish furnace operating practices appropriate for hydrogen atmospheres, and these should be carefully observed. Particularly important are safety procedures associated with nitrogen purging to prevent air infiltration. Adequate internal furnace circulation should be used to avoid entrapment of the low-density gas in upper portions of furnace chambers. Most ammonia dissociators are monitored with safety devices, which should be periodically tested to ensure fail-safe operation.

Hydrogen Atmospheres

Commercially available hydrogen is 98 to 99.9% pure. All cylinder hydrogen contains traces of water vapor and oxygen. Methane, nitrogen, carbon monoxide, and carbon dioxide may be present as impurities in very small amounts, depending on the method of manufacture. Hydrogen is produced commercially by a variety of methods, including the electrolysis of water, the catalytic conversion of hydrocarbons, the decomposition of ammonia, and the water-gas reaction. It is also obtained as a by-product in the electrolytic manufacture of sodium hydroxide and the catalytic cracking of petroleum oils.

Hydrogen is a powerful deoxidizer, and its deoxidizing potential is limited by moisture content only. Its thermal conductivity is approximately seven times that of air. Its principal disadvantage is that it is readily absorbed by most common metals, either by occlusion or by chemical combination, at elevated temperature. Absorption of hydrogen can result in serious embrittlement, especially in high-carbon steels. It may also reduce oxide inclusions in steel to form water, thus building sufficient pressure at elevated temperature to cause intergranular fracture of the steel. Dry hydrogen will decarburize high-carbon steels at elevated temperature by reacting with carbon to form methane.

Impurities. The hydrogen best suited for metallurgical purposes is made by the electrolysis of distilled water. In most heat-treating procedures requiring hydrogen, water vapor and oxygen are objectionable, and the hydrogen must be purified before it can be used. Oxygen is removed by a room-temperature catalytic process that combines the oxygen with hydrogen to form water vapor. Essentially all water vapor is then removed by means of activated-alumina dryers, yielding a gas with a dew point of -50 °C (-60 °F). See Fig. 19 for a curve relating dew point and moisture content.

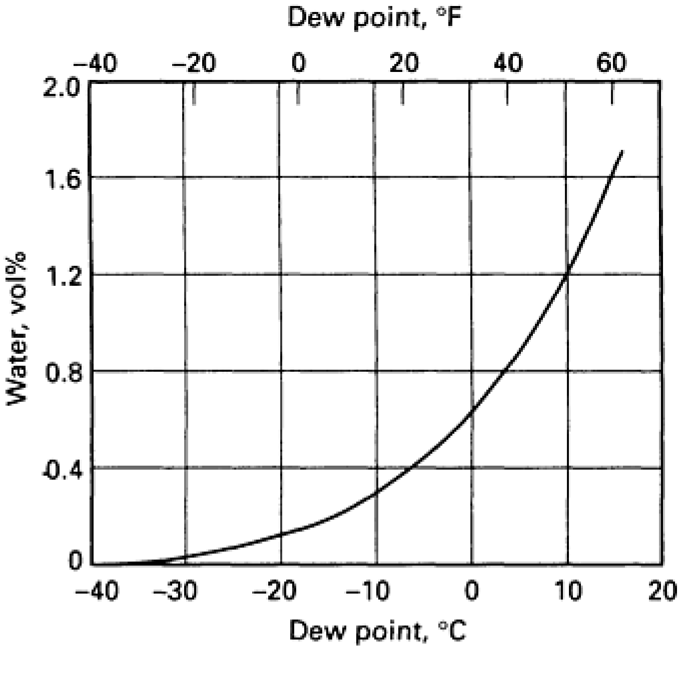

Fig. 19 Relationship between dew point and moisture content of gases

Applications. Dry hydrogen is used in the annealing of stainless and low-carbon steels, electrical steels, and several nonferrous metals. It is used also in the sintering of refractory materials such as tungsten carbide and tantalum carbide, in the nickel brazing of stainless steel and heat-resisting alloys, and in copper brazing, direct reduction of metal ores, annealing of metal powders, and the sintering of P/M compacts. Data relating to metal-oxide equilibriums in hydrogen atmospheres are given in Fig. 20.

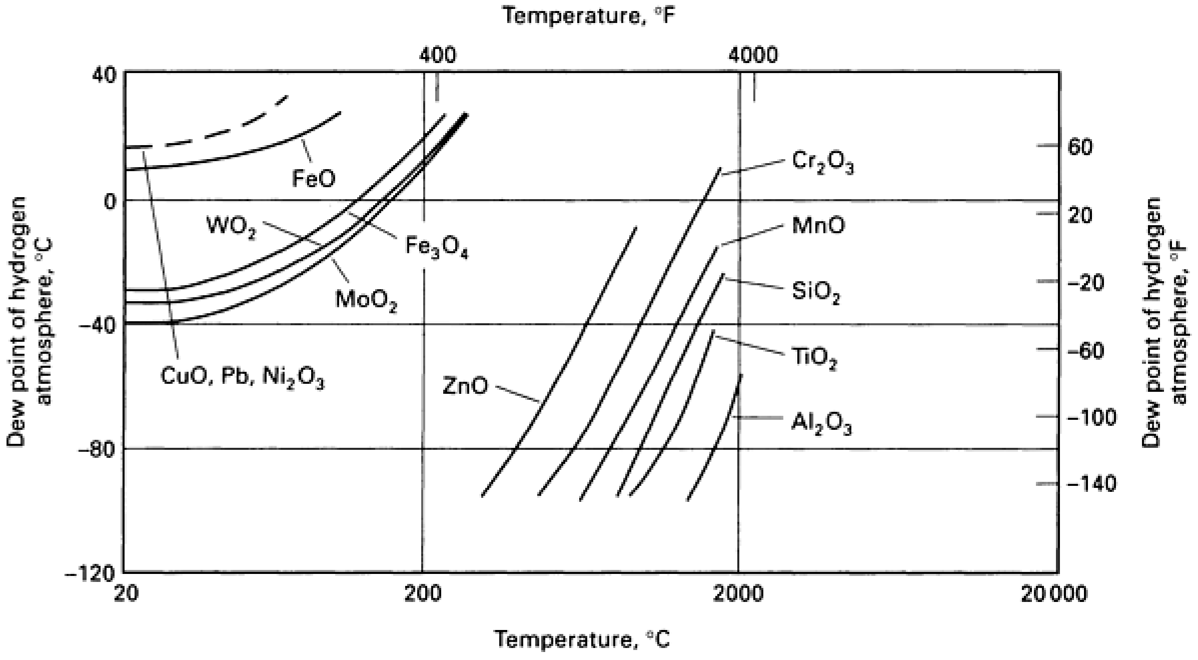

Fig. 20 Metal-metal oxide equilibriums in hydrogen atmospheres

Example 1: Sintering of Stainless Steel P/M Parts in Hydrogen.

Stainless steel powder parts are sintered in a dry (-40 °C, or -40 °F dew point) hydrogen atmosphere at 1275 °C (2325 °F), following preheating in dissociated ammonia at 425 °C (800 °F). Electric furnaces are used for both preheating and sintering. Details of the equipment used are given in Table 12.

Table 12 Equipment requirements for sintering stainless steel powder metallurgy parts in hydrogen

Production requirements	
Load weight, kg (lb)	9 (20)
Heating cycle, min	40
Output per hour, kg (lb)	14 (30)
Equipment requirements	

Burnoff furnace	Pusher, electrically heated; forced circulation
Size of hearth, mm (in.)	255 by 150 by 915 (10 by 6 by 36)
Length of cooling chamber, m (ft)	1.8 (6)
Power, hp (kW)	27 (20)
Operating temperature, °C (°F)	425 (800)
Atmosphere, m^3/h (ft^3/h)	Dissociated ammonia, 4.2 (150)
High-heat furnace	Open chamber, electrically heated; front push, rear pull
Size of hearth, mm (in.)	255 by 610 (10 by 24) (preheating) 255 by 915 mm (10 by 36 in.) (high heating)
Length of cooling chamber, mm (ft)	2.4 (8)
Power, hp (kW)	47 (35)
Operating temperature, °C (°F)	1275 (2325)
Atmosphere, m^3/h (ft^3/h), °C (°F)	Dry hydrogen, 9.9 (350); dew point, -40 (-40)

Supply. Hydrogen is usually obtained in cylinders. Small quantities are supplied at a pressure of 14 MPa (2 ksi) in steel cylinders that contain 5.5 m^3 (193 ft^3) of hydrogen measured at standard conditions of 20 °C (68 °F) and atmospheric pressure. Larger quantities can be supplied in banks of about 12 interconnected cylinders that are mounted on portable dollies and contain a total of about 90 m^3 (3200 ft^3) of gas. For even larger requirements, trailers are used, containing a total of 810 m^3 (28,600 ft^3) of hydrogen at 17 MPa (2.5 ksi); the capacity of a railroad tank car is 5665 m^3 (200,000 ft^3).

In-Plant Generators. Large amounts of hydrogen are supplied by generators that decompose ammonia or partially burn hydrocarbon fuels. Purification is accomplished by adsorption of unwanted gases or by diffusion of raw hydrogen through molecular filters that are capable of producing a gas of 99.5% purity.

Safety. *Caution: The explosive range of hydrogen in air is so great that it should be considered explosive in all ranges.* Whenever hydrogen is used in a furnace, an adequate supply of inert gas for purging should be readily available, either from storage or from a generator. Nitrogen and products of combustion are commonly used for purging.

Steam Atmospheres

Steam may be used as an atmosphere for scale-free tempering and stress relieving of ferrous metals in the temperature range of 345 to 650 °C (650 to 1200 °F). The steam causes a thin, hard, and tenacious blue-black oxide to form on the metal surface. This oxide film, which is about 0.00127 to 0.008 mm (0.00005 to 0.0003 in.) thick, improves certain properties of various metal parts.

Effects of Steam Treating. The service life of cutting edges of high-speed steel tools such as drills, reamers, taps, and milling cutters is increased from 50 to 100% when the tools are steam treated after being tempered and finish ground. During machining operations, the oxide film prevents metal chips from welding to the tool and retains cutting oil to reduce heat of friction.

Steam treating decreases the porosity of sintered iron compacts and provides increased compressive strength and resistance to wear and corrosion. Steam penetrates the pores of compacts and forms the oxide internally as well as on the surface. The oxide seals the pores and partially fills the voids, thus increasing compressive strength. The hardness of the film, in addition to its ability to hold oil, increases wear resistance. The density of the film, coupled with its ability to retain oil, increases corrosion resistance.

Cast iron and steel parts steam treated at 345 °C (650 °F) or higher have increased resistance to wear and corrosion. Steam-treated cast iron valve bodies also have less porosity.

Processing Considerations. Before parts are processed in steam atmospheres, their surfaces must be clean and oxide-free, to permit the formation of a unique coating. To prevent condensation and rusting, steam should not be admitted until workpiece surfaces are above 100 °C (212 °F). Air must be purged from the furnace before the temperature exceeds 425 °C (800 °F), to prevent the formation of a brown coating instead of the desired blue-black coating.

Charcoal-Based Atmospheres

Charcoal-based atmosphere generators (AGA classes 402 to 421), which are on the way to becoming obsolete, are now used mainly by small-scale manufacturing plants that desire a generator of low initial cost for intermittent operation. The principal uses of charcoal-based atmospheres at present are for the manufacture of malleable iron castings and for providing atmosphere in small toolroom heat-treating furnaces.

Composition and characteristics of a class 402 charcoal-based atmosphere are given in Table 3. These gases are produced by passing air through a bed of hot charcoal. The air is supplied by a blower and measured by a flowmeter. Incoming air burns with the charcoal at the bottom of the combustion chamber to form a mixture of nitrogen, carbon dioxide, and water vapor. This reaction heats the charcoal in the upper portion of the combustion chamber to incandescence. The incandescent charcoal converts carbon dioxide to carbon monoxide and water vapor to hydrogen. These hot, dry gases pass around the charcoal storage hopper, heating the charcoal and driving off the moisture and volatile matter through a burnoff can at the top of the hopper. The hot, dry atmosphere is taken off at the side of the generator and passed through a filter to remove fly ash.

Charcoal-based atmosphere is produced by the reaction:

$$2C + O_2 + 3.8N_2 \rightarrow 2CO + 3.8N_2 \qquad \textbf{(Eq 41)}$$

Theoretically, this reaction would produce 34% CO and 66% N_2. Actually, however, the following mixture is normally obtained because of moisture and volatiles in the charcoal and the less-than-100% efficiency in converting all of the carbon dioxide:

Atmosphere constituents	**Concentration, %**
CO_2	1.0-2.0
CO	30.0-32.0

H_2	1.5-7.0
CH_4	0.0-0.5
N_2	bal

Although the generator may operate at as low as 50% of rated capacity, lower percentages of carbon dioxide and water vapor are attained at the rated output because of the hotter charcoal bed. The type of charcoal used also influences hydrogen and water-vapor content of the atmosphere.

Normally, the atmosphere is neutral to higher-carbon steels, but the carbon potential may be increased by additions of about 0.5% of natural gas in the furnace, causing further breakdown of carbon dioxide and water vapor in the atmosphere. Channeling of gases through the incandescent charcoal bed or excessive moisture content of the charcoal can cause high carbon dioxide and water-vapor contents that will decarburize high-carbon steels.

Charcoal-based atmospheres may be used for hardening, annealing, and normalizing high-carbon steels without scale formation or decarburization. A gray-green oxide forms on steels containing appreciable amounts of chromium. At high temperatures, the great affinity of chromium for oxygen causes a breakdown of carbon monoxide. The relatively low hydrogen content of these atmospheres makes them particularly suitable for making malleable iron castings.

The principal disadvantages of charcoal-based atmospheres are the high operating cost, the absence of suitable means for automatic control, the intermittence of operation imposed by the need to recharge charcoal and remove ashes, and the corrosion of alloy furnace parts in the area of high-temperature combustion.

Exothermic-Endothermic-Based Atmospheres

These atmospheres (classes 501 and 502), the compositions and characteristics of which are previously described in the section "Classification of Prepared Atmospheres" of this article, are re-formed exothermic-based atmospheres that are less reducing than conventional endothermic-based furnace atmospheres.

Applications

Potentially, exothermic-endothermic-based atmospheres could be substituted for exothermic, endothermic, and nitrogen-based atmospheres in virtually every application for which any one of these three atmospheres is recommended. They may also be used as a carrier gas in carburizing and carbonitriding. In practice, however, it is not practical to mix exothermic-endothermic atmospheres in existing headers with straight endothermic atmospheres because of the differences in specific gravity and chemistry. This limitation may not apply to the use of the combination exothermic-endothermic type of generator, provided one generator for one furnace can be economically employed to produce both exothermic and endothermic atmospheres for use at the same time.

Generation

Generation of exothermic-endothermic atmospheres begins with the combustion of a mixture of air and fuel gas in a refractory-lined combustion chamber. This reaction supplies the external heating required to maintain a satisfactory temperature in a secondary, or endothermic-stage, reaction. Products of combustion from the first stage are dehydrated, and a predetermined quantity of a hydrocarbon fuel is added to them. This mixture is then reacted in contact with a catalyst contained in an externally heated alloy tube.

The primary air-fuel mixture yields very close to perfect combustion. For normal operations, 0.5% CO or O_2 in the generated gas is satisfactory. This reaction, using natural gas as the fuel, yields 11 volumes of combustion products. Removal of the water formed in the reaction reduces the total to 9.225 volumes. In the secondary reaction, 7.3 volumes of combustion products and 1 volume of natural gas react to produce 10.5 volumes of atmosphere of the following nominal composition:

Composition	Concentration, %
CO_2	0-0.2
CO	17
H_2	20
N_2	bal

Equipment. Figure 21 is a flow diagram of a typical exothermic-endothermic generator. In operation, the flow rates of air and gas are regulated by fixed and variable orifices and balanced pressure ratio regulators to maintain the mixture at a predetermined ratio. A gas pump introduces the mixture into a refractory-lined combustion chamber (exothermic unit A in Fig. 21). The products of combustion then pass through a water spray cooler (atmosphere cooler B). After the combustion products have cooled, a measured volume of a hydrocarbon fuel is blended with them. The ratio of the products to the hydrocarbon fuel is controlled by fixed and variable orifices and balanced pressure-ratio regulators, and the mixture is introduced under pressure by a gas pump into a catalyst-filled U-shaped alloy retort (endothermic unit C in Fig. 21), which is contained in the refractory-lined combustion chamber and is heated by the primary-stage combustion. From the retort, the gas mixture passes into atmosphere cooler D. From here, it is piped through an atmosphere outlet and into the furnace.

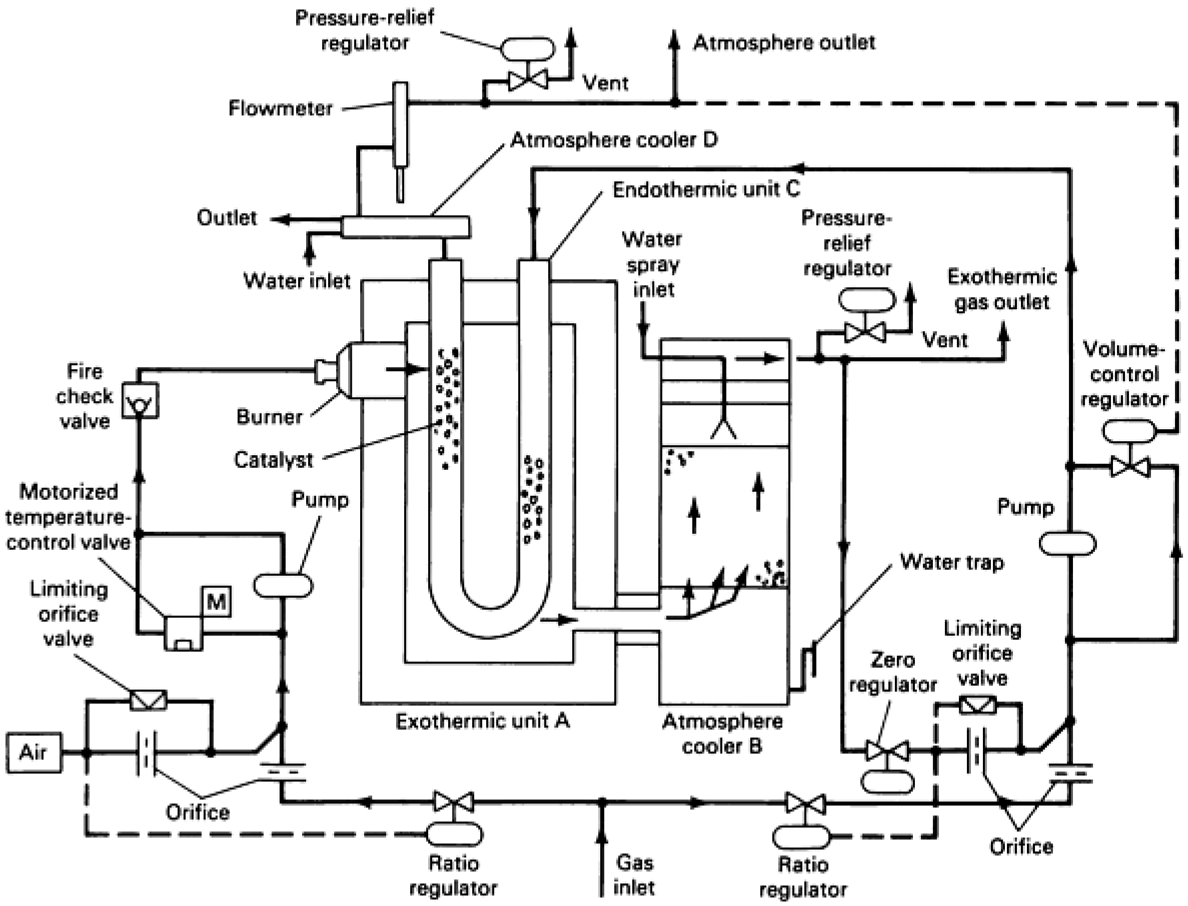

Fig. 21 Flow diagram of an exothermic-endothermic gas generator

The volume of atmosphere needed for a given work load is influenced by the size of workpieces comprising the total work load and the type of furnace used for heating. See Table 13 for production and equipment requirements for hardening small parts made of 1070 steel in an exothermic-endothermic-based atmosphere.

Table 13 Equipment requirements for hardening small parts made of 1070 steel in an exothermic-endothermic atmosphere

Production requirements	
Number of parts per load	2625
Weight of each part, kg (lb)	0.0069 (0.015)
Maximum net weight of load, kg (lb)	18 (40)
Production rate, kg (lb)	7.5 loads (135, or 300) per h
Equipment requirements	
Hardening furnace	Gas-fired radiant-tube single-row pusher type with automatic quench
Size of hearth, m (ft)	0.9 (3) wide by 2.9 ($9\frac{1}{2}$) long
Heat input, W/h (Btu/h)	2.2×10^5 Watts (7.5×10^5)
Operating temperature, °C (°F)	900 (1650)
Capacity of generator, m^3/h (ft^3/h)	68 (2400)
Type of atmosphere	Class 502
Capacity of oil-quench tank, L (gal)	1250 (330)
Type of oil, °C (°F)	Fast, 180 (360) flash point
Temperature of oil, °C (°F)	70 (160) (controlled)
Oil agitation	Medium

Operation of Generator. When the generator is used for the manufacture of endothermic-based gas, it should be operated at approximately 1010 °C (1850 °F). If the temperature is too low, reaction will be incomplete; if the temperature is too high, life of the retort will be greatly shortened. All of the previously described precautions to be observed when operating an endothermic generator should be adhered to when endothermic-based atmosphere is being produced.

When the same generator is used for producing an exothermic-based gas, there is no need to change the operating conditions. Therefore, by closing the gas valve in the secondary stage, the unit purges itself of endothermic gas by producing exothermic gas. When used as an exothermic generator, with about 90% perfect combustion, it will produce a gas having the following approximate composition:

Composition	Concentration, %
CO_2	10.0-11.0
O_2	0-1.0
CO	0-2.0
H_2	0-2.0
N_2	86.0-89.0

When the generator is producing endothermic gas, it can, at the same time, supply an exothermic-gas volume of approximately 25% of its rated endothermic capacity.

When changing over from production of exothermic to endothermic gas, it is recommended that a period of about $\frac{1}{2}$ h be allowed to establish equilibrium in the generator. Gas-analysis equipment, either manual or automatic (as described in the section "Analyzing Atmosphere Requirements" of this article), should be employed to determine when equilibrium conditions for the desired atmosphere have been established.

Generator Maintenance. A typical maintenance schedule for exothermic-endothermic atmosphere generators includes:

Daily

- Check flow of cooling water
- Check dew point and secondary gas analysis, and make adjustments as necessary
- Check instruments

Weekly

- Check primary gas analysis and make adjustments as necessary
- Check operation and linkage of temperature-control valve
- Lubricate as required

- Check drive belts

Monthly

- Check for leaks
- Check operation of combustion and fuel safeguard equipment, such as manual reset shutoff valves, pressure switches, and firecheck
- Check and clean air filter as required
- Check cooling distribution on atmosphere cooler B (Fig. 21)
- Check atmosphere cooler D (Fig. 21) for water leaks by dew point before and after, and excessive soot deposits in the aftercooler by taking readings of pressure of atmosphere before and after it passes through the cooler

Atmospheres for Backfilling and Quenching in Vacuum

Backfilling a vacuum furnace with a cooling gas is performed to induce a more rapid cooling rate. Backfilling also is used to suppress vaporization of oil in integrated oil-quenching vacuum furnaces and to provide an atmosphere for carburizing and nitriding.

Quenching. Inert gases, nitrogen, and, in rare circumstances, hydrogen, are used for cooling. If surface integrity of workpieces is to be maintained and damage to furnace parts avoided, contaminants in the cooling gas must be kept at a low level. Commercial gases are readily available with contaminant level below 0.01%.

Backfilling and forced circulation accomplishes a more rapid cooling rate, facilitates hardening, and, in some requirements, produces annealing of metal alloys. It also enhances efficient use of the equipment. Cooling gas is usually introduced into the vacuum chamber at the end of the high-temperature soaking period. When internal pressure reaches some predetermined level, either slightly negative or positive relative to atmospheric pressure, the gas is circulated through the load and then through appropriate heat exchangers located outside the heating zone. Design of the furnace and its structural strength dictate the maximum pressure level.

Figure 22 shows the effect of gas selection. Because cooling rates were established with identical loads and equipment, differences are attributed to differences in heat conductivity, heat capacity, viscosity, and density of the gases tested.

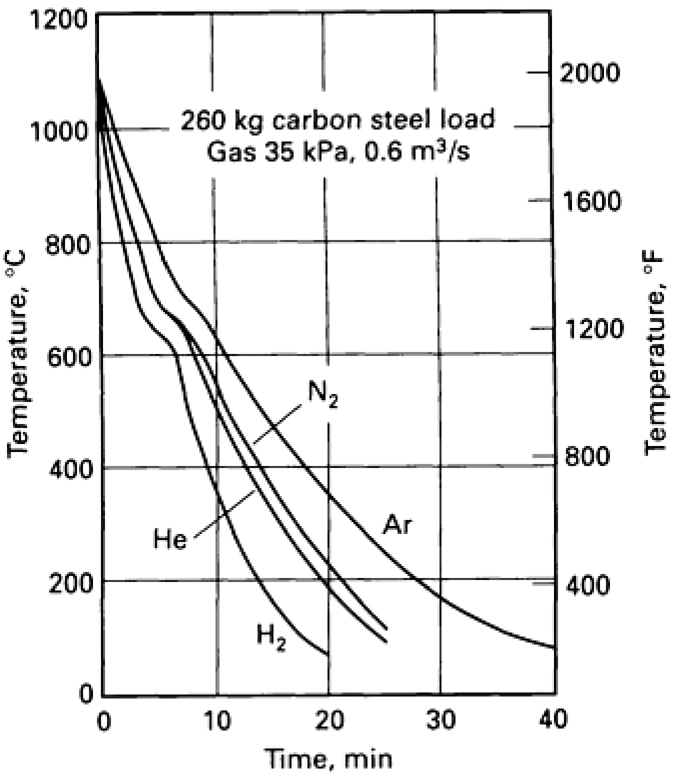

Fig. 22 Effect of four gases on cooling rate

Figure 23 illustrates the effect of pressure when the same cooling gas, load, and equipment are used. Slightly negative pressure provides sufficient cooling to harden air-hardening materials such as air-hardening stainless steels and tool steels. Positive pressure provides a sufficient cooling rate to harden materials such as M2 tool steels. The mass of the load and part cross-section dimensions also govern the cooling rate and must be recognized as cooling-rate factors.

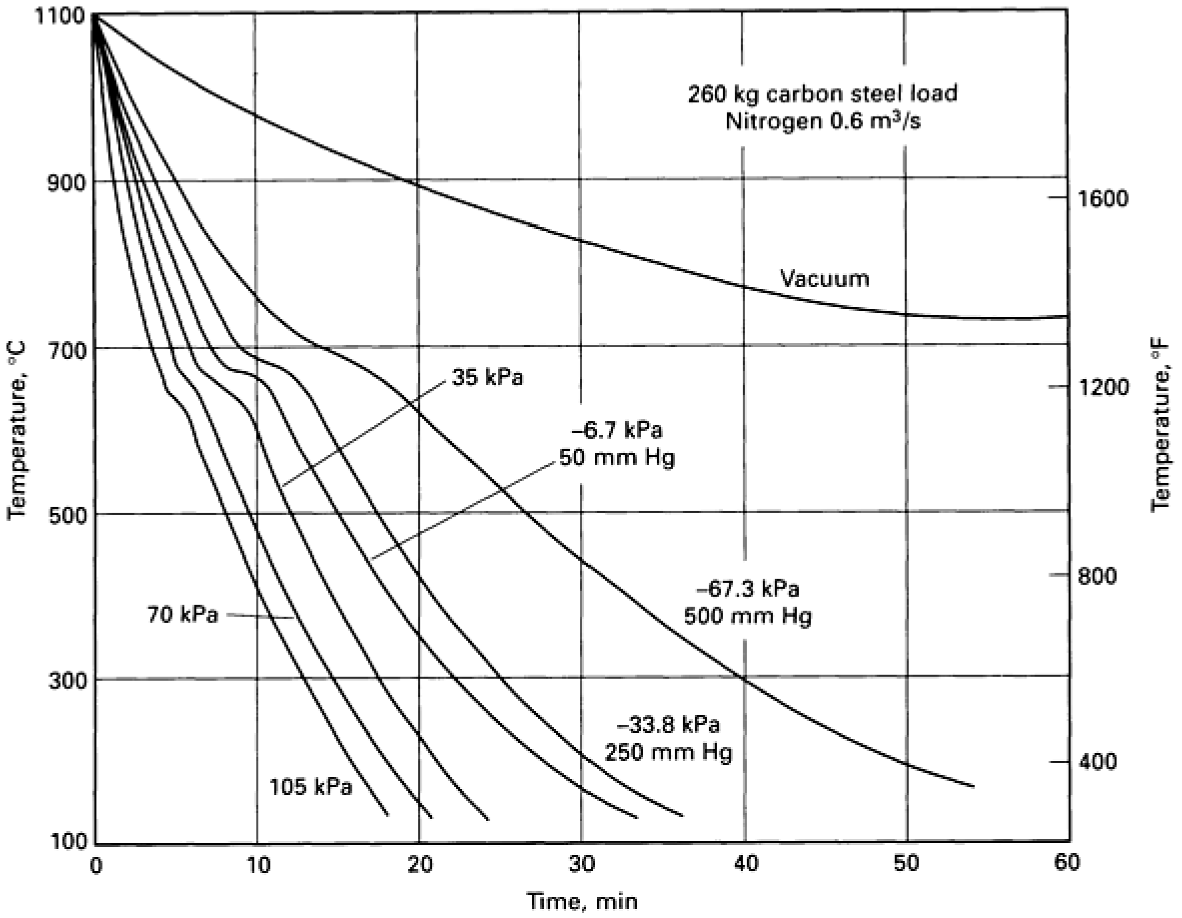

Fig. 23 Effect of circulating gas pressure on cooling rate

Vacuum Furnace Gas-Carburizing Atmospheres. Vacuum furnaces may be used for carburizing by the injection of any one of several atmospheres that will induce carburizing at appropriate temperatures. Nitrogen enriched with a hydrocarbon gas is most frequently employed.

Vacuum furnace carburizing is normally carried out in the temperature range of 870 to 980 °C (1600 to 1800 °F). In the carburizing and diffusion process, surface-carbon contents of 1% or more are formed initially. The high-carbon case is then diffused in vacuum until the surface-carbon content and case depth are acceptable.

The diffusion process may be carried out in a series of interrupted periods during the carburizing cycle or at the end of the carburizing portion of the cycle. An interrupted carburizing cycle produces a less severe drop in carbon content and a higher hardness relative to case depth. Surface-carbon content and surface hardness remain comparable in both diffusion processes.

Vacuum carburizing entails some problems with sooting and distribution of the carburizing atmosphere. Soot monitoring with subsequent enrichment control can minimize the soot problem, and forced circulation of the carburizing atmosphere assists in minimizing the distribution problem. Additional information is available in the article "Vacuum Carburizing" in this Volume.

Ion-Carburizing Atmospheres. A hydrocarbon gas that is ionized by a high-voltage system in a vacuum is a suitable atmosphere for ion carburizing. Methane is a good source of carbon and is frequently employed. With a voltage differential between an anode, which may be chamber walls, and the work load serving at the cathode, a plasma will be generated at a critical vacuum pressure (Fig. 24). Migration and impingement of the resulting ions on the surface of the load produce the carburizing potential. Ion carburizing is much more rapid than conventional atmosphere carburizing, and the surface-carbon content approaches saturation. Other diluting gases are added for carbon control.

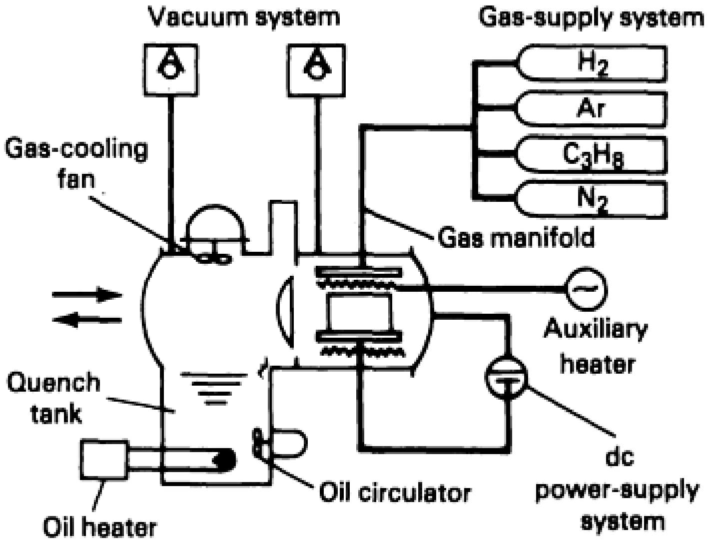

Fig. 24 A two-chamber plasma-carburizing furnace that consists of a plasma-carburizing chamber and an oil-quenching chamber

An AISI 1018 steel can be ion carburized to a depth of 1.0 mm (0.040 in.) with a 10-min cycle in an atmosphere of methane at 1.3 to 2.7 kPa (10 to 20 torr) and a temperature of 1050 °C (1925 °F). Carburizing is followed by a 30-min diffusion cycle in vacuum at the same temperature. Approximately 400 V is required to produce the plasma.

Additional information is available in the article "Plasma (Ion) Carburizing" in this Volume.

Ion-Nitriding Atmospheres. Ion nitriding is similar to ion carburizing, with the exception that the atmosphere gas generates nitrogen ions, and the process is carried out at lower temperatures (Fig. 25). Ammonia or mixtures of hydrogen and nitrogen are suitable sources for the nitrogen ions.

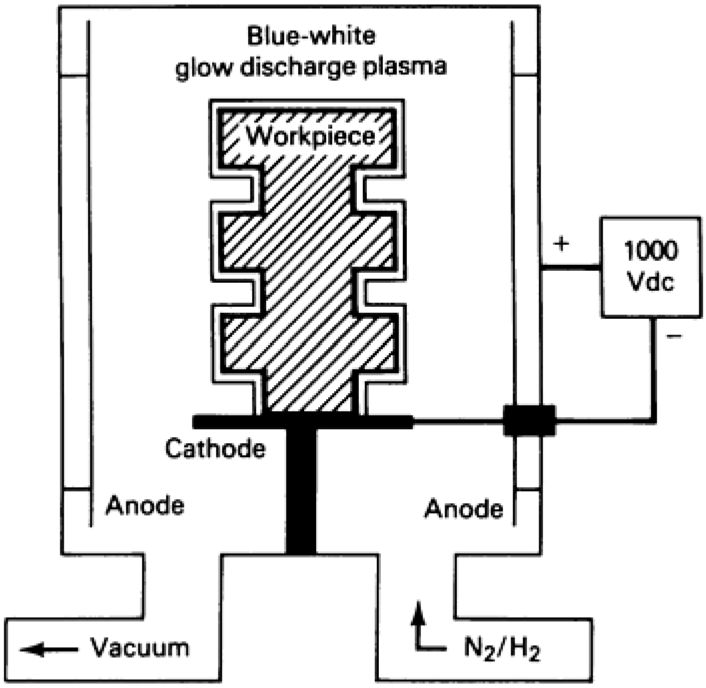

Fig. 25 Schematic showing basic elements of an ion-nitriding system. High-kinetic-energy nitrogen-ion

bombardment on workpiece surface is indicated by blue-white glow discharge around the components.

A typical cycle of 8 h at 510 °C (950 °F) with a mixture of 75% hydrogen and 25% nitrogen at a pressure of 0.9 kPa (7 torr) and a current density of 0.8 mA/cm^2 will produce a nitrided case of 0.30 mm (0.012 in.) in AISI 4140 steel. Approximately 400 V is required to generate the plasma. Other alloys, such as 300 series stainless steels, M2 tool steels, and nitralloy, respond to the ion-nitriding process.

Additional information is available in the article "Plasma (Ion) Nitriding" in this Volume.

Partial Pressure. Nitrogen and inert gases are used in vacuum furnaces at partial-pressure vacuum levels to suppress vaporization of a constituent in the composition of the load. A gas is injected in small quantities by a needle valve. The deliberately leaked gas raises the pressure to some stable level between the ultimate vacuum of the pumping system and atmospheric pressure. For example, the vaporization of copper during the brazing of heat exchangers is suppressed by the leaking of nitrogen into the furnace and maintaining a level of 0.27 kPa (2.0 torr). For more information, see articles "Plasma (Ion) Nitriding" and "Plasma (Ion) Carburizing" in this Volume.

Analyzing Atmosphere Requirements

Analysis of the atmosphere requirements of heat-treating furnaces is influenced by several factors. Cost of operation is always one of the main considerations in selecting an atmosphere system. Another prime factor is the capital investment required to purchase the hardware, make the installation, and satisfy the associated safety requirements. Certain circumstances dictate that all cost considerations be subordinated to achieve high levels of heat-treating accuracy to satisfy stringent metallurgical specifications.

The degree of validity of any analysis is determined by the thoroughness of investigation and the definitive parameters placed on the project.

Influence of Required Processes. Many installations are built in which multiple processes are anticipated. In such instances, the atmosphere system must be capable of a reasonable response time. For example, a batch furnace may be used for carburizing in one cycle, followed by clean hardening of medium-carbon steel in the next, without a long delay between heats. This processing schedule means the carbon potential will vary from 0.9 to 0.3% C. With an endothermic-based atmosphere, this variance means a dew point change from -12 to 18 °C (10 to 64 °F). With a nitrogen-based atmosphere, the carburizing cycle can be completed with additions of carbon-bearing material and an oxidant, and the hardening cycle can be accomplished by eliminating the additives.

In some installations, the volume of atmosphere is based on the process requirements rather than on the amounts of atmosphere required to overcome air infiltration to the furnace chamber. This volume basis is used when the atmosphere provides an element in carburizing parts with large surface areas; for example, in sintering, the amount of hydrogen required becomes a function of the amount of oxide or sulfur to be reduced.

Thus, distinctions need to be made between the need of an atmosphere to exclude unwanted air and the requirement that it enter into a precise chemical reaction. As the process specifications become more exacting, the need for precision of the chemical reaction increases and the need for reliable atmosphere control becomes more urgent.

Influence of Furnace Design. Furnace design and the selection of atmospheres are interdependent. In any atmosphere furnace the degree of tightness is a critical factor, and among the various types of atmosphere furnaces--pusher tray, batch tray, cast link belt, roller hearth, mesh belt, rotary retort, bell, gantry, and others--the furnace designer basically has only three ways to load and four ways to unload the work.

Slot-Opening Loading. The first way of loading and unloading an atmosphere furnace is through a slot. Sufficient atmosphere must be provided to prevent air from entering through the slot, and the amount can be significantly reduced by the use of curtains or flame screens, and by elevating the working hearth above the slot opening when possible.

Vestibule or Cold Chamber Loading. The second way of loading and unloading is through a cold chamber vestibule linked with the furnace. The most common use of a vestibule is with a pusher tray or batch tray furnace. A loaded tray is placed in the vestibule and the outer vestibule door is closed. The vestibule remains closed until sufficient time has elapsed to purge the vestibule of air. This purging occurs either by atmosphere leakage from the furnace around the inner

furnace door or by admission of atmosphere gas through a direct line that is opened for a predetermined time. Sufficient atmosphere for approximately five volume changes must pass through the vestibule to be ensured that contamination will be minimized when the inner furnace door is opened to admit the work tray. Any mechanism that operates through the vestibule wall must be equipped with packing glands, and these must be maintained. The atmosphere in the vestibule also undergoes a temperature change when the inner door is raised and lowered, subjecting the vestibule gases to rapid volume increases followed by decreases. The furnace door closing must not be so rapid as to cause a contraction of the gases in the vestibule greater than the flow of gas to the vestibule for normal purging.

Stationary- or Movable-Base Loading. The third way of loading and unloading is to place the work on a stationary or movable base and to raise the work into the furnace or place the furnace over the base. The furnace chamber over the work is purged with atmosphere, and the furnace is taken through a time-temperature cycle. When that cycle is completed, the work is uncovered and removed.

Quench Tank Unloading. The fourth way of unloading a furnace is to have the work fall directly into a quench tank at the discharge end (see Fig. 24). To protect the atmosphere, an eductor must be installed to draw atmosphere from the quench chute just above the fluid line. If the quenching medium has a water base, the eductor will prevent water vapor from contaminating the atmosphere. If the quenchant is oil, the eductor will prevent oil splash and fumes from unbalancing the atmosphere. One mechanism that has been successfully used in direct-quenching applications is a laminar-flow quench-fluid spray between the quench-tank eductor and the liquid quenchant in the quench chute.

Fans to Increase Atmosphere Uniformity. An additional furnace design consideration having a direct influence on the atmosphere is the use of fans. By increasing the flow of atmosphere gas across the faces of the work being processed, fans increase the effective concentration of the gases and accelerate chemical reactions in applications where the atmosphere is the source of a desired chemical ingredient. This is particularly significant in case hardening. A properly designed fan thoroughly mixes the atmosphere as the various chemical reactions take place, and improves temperature uniformity in dense loads. The result is more uniform part-to-part response to a process within a load.

Influence of the Availability and Dependability of Utilities. The availability and dependability of utilities influence the location of industrial plants. In heat-treating operations, large amounts of energy are consumed. As the cost of energy increases, energy cost and availability receive more management attention and planning, particularly in heat-treating operations that have had their energy supplies curtailed.

In the past, heat-treating operations required a supply of natural gas, which was inexpensive; electricity, which was readily available; and water, which was needed for cooling purposes. These utilities not only were required for the furnaces, but also were the required ingredients for the generation of heat-treating atmospheres. In many instances, natural gas was the preferred form of energy. It was used not only as fuel for furnaces but also as an acceptable feedstock for the atmosphere generators.

As energy supplies have become more expensive and less available, it has been relatively simple to go to alternate or dual fuels to heat furnaces. Finding substitute atmosphere feedstocks has been somewhat more complicated, but solutions are available. Commercial nitrogen produced by air-reduction plants provides an alternative in two forms. For large volumes, the air-reduction plant can be located at or near the using site, or nitrogen from a central air-reduction plant can be transported and stored as a liquid, at the using site. With the developing technology of utilizing methanol with nitrogen, it is now possible to establish a heat-treating operation requiring carburizing atmospheres without dependence on natural supplies.

Influence of Estimating Atmosphere Quantities. As energy costs increase, the customary practice of employing an atmosphere generator of greater capacity than required adversely affects operating costs. This is especially true of endothermic atmosphere generation. The atmosphere feedstock is passed through a catalyst-filled heated reaction tube, which requires considerable energy to reach gas-cracking temperature. Little energy is required to maintain the reaction tube temperature over the range of minimum flow to maximum flow of reactive gases through the tube. For instance, a 68 m^3/h (2400 ft^3/h) endothermic generator at full flow will require a little over 1 m^3/h (36 ft^3/h) of natural gas per 3 m^3/h (100 ft^3/h) of produced gas. The same generator operating at one-third capacity or 23 m^3/h (800 ft^3/h) output will require a little over 1.3 m^3/h (47 ft^3/h) of natural gas per 3 m^3/h (100 ft^3/h) of produced gas. The differences on a 102 m^3/h (3600 ft^3/h) generator were even more pronounced. At 102 m^3/h (3600 ft^3/h) output, the required natural gas is 0.8 m^3/h (28.7 ft^3/h). At 68 m^3/h (2400 ft^3/h) output, the required natural gas is 0.937 m^3/h (33.1 ft^3/h), and at 34 m^3/h (1200 ft^3/h) output, the required natural gas is 1.2 m^3/h (40.9 ft^3/h). Because natural gas is the major cost factor in producing endothermic atmosphere, a 30% variation in operating cost is significant.

Furnace Atmosphere Control in Heat Treating

Revised by John G. Rowe, Union Carbide Industrial Gases Inc., Linde Division

Introduction

THE PURPOSE of atmosphere control is to maintain consistent levels of the various constituents that make up the atmosphere and to determine if changes in those levels are required in order to produce a desired result under a given set of conditions. Controls are required for various heat-treating operations that use a variety of different atmospheres. All methods of atmosphere control can effectively be divided into two groups: those involving control of the atmosphere once it is inside the furnace and those involving control of the atmosphere supply before it is introduced into the furnace. Such control is achieved through the use of atmosphere control devices.

Atmosphere Control Devices

The control devices available for the wide variety of furnace atmospheres used can be categorized into three major types: oxygen probe, infrared, and dew point. Direct oxygen or dew point monitoring devices are also often used for applications such as bell furnace annealing. The oxygen probe is an *in situ* type device; that is, it directly samples the atmosphere to be measured. The electrical signal generated by an oxygen probe is directly proportional to the carbon potential of the atmosphere. Infrared control measures a sample drawn from the furnace. Infrared control is usually used to measure carbon monoxide and/or carbon dioxide levels. Dew point control also analyzes a drawn sample external to the furnace.

These control devices can effectively control endothermic, exothermic, nitrogen-methanol, nitrogen-hydrocarbon, and nitrogen-hydrogen-type atmospheres. Infrared control is most often utilized for endothermic and exothermic generator operation and, in some cases, for exothermic furnace atmospheres as well. Nitrogen-hydrogen atmospheres are typically controlled by dew point.

It is good practice to regularly compare the carbon potential determined through an analyzer to the actual carbon potential of the atmosphere as determined through shim analysis. A shim is a thin low-carbon metal sample that, when placed in the furnace, will quickly carburize to a level equal to the furnace carbon potential. Adjusting the control system to match the carbon potential indicated by a shim test will improve the accuracy of the entire system.

The above-mentioned control devices can be modified and incorporated together to form an automatic control system for any given set of conditions, utilizing normal instrumentation and final control devices. The system is ultimately a product of the needs of the user and justifiable economics. As metallurgical reproducibility of any given process becomes more important, the need for atmosphere control to produce chemical stability becomes a necessity. A second imperative not to be overlooked in the application of atmosphere-control devices is the safety aspects of operating atmosphere supply systems and industrial furnaces.

Oxygen probes have been extensively used for control of carburizing furnaces. Accuracy of carbon-potential control through use of oxygen probes is estimated to be approximately ±0.05% carbon in actual practice because of the limitations of temperature control and temperature variations in typical heat-treating furnaces. Because of the fast response rate, on/off control systems utilizing solenoid valves for regulating propane, natural gas, or liquid enrichment are adequate for batch furnaces. *In situ* probes or probes exposed directly to the furnace atmosphere control carbon potential by adjusting the set point on the control instrument to the carbon level desired in the furnace. The oxygen probe supplies to the control station an electrical signal related to the carbon potential. High-and low-deviation contacts are adjusted throughout the control instrument and either contact is made by the electrical signal from the probe. The low-deviation contact controls the solenoid valve that supplies enriching gas or liquid to the furnace. The high-deviation contact can be made to control the solenoid valve to add air or an oxidizer to the furnace. Carbon-concentration reproducibility of ±0.02% is frequently achieved using systems of this type, provided that the cycle, temperature, and furnace conditions remain constant.

The oxygen probe is based in theory on a hot ceramic electrochemical cell. The probe will respond to oxygen, hydrogen, carbon monoxide, water, and carbon dioxide and thus can determine the oxidization potential of a gas. The output of the oxygen probe is a direct measurement of the oxidation potential of the atmosphere at the process temperature of the furnace. Therefore, when the probe temperature is close to the furnace temperature, the response of the probe is a direct indication of whether the atmosphere will oxidize or reduce steel, provided that the composition of the atmosphere with

regard to the proportions of carbon gases and hydrogen is known. Under such conditions, the probe will give a reliable indication of the oxidation/reduction situation for all furnace temperatures.

The oxygen probe is a closed-end tube usually constructed of lime-stabilized zirconia or yttria-stabilized material for temperatures up to 1600 °C (2900 °F). When such a probe is subjected to elevated temperatures, the nonporous sheath material acts as a solid electrolyte that permits the passage of oxygen ions when the inner and outer surfaces are subjected to atmospheres of different oxygen partial pressures--for example, a reference gas such as air, because its O_2 content is constant at 20.9% by volume at sea level, and the process furnace atmosphere, respectively. The electromotive force (emf) thus generated, and measured via the electrodes attached to the sheath, is related directly to, and provides an accurate quantification of, atmosphere characteristics in terms of its oxidizing/reducing, or, in some endothermic-atmosphere applications, carburizing/decarburizing tendencies at a known temperature (Ref 1). The electrodes mentioned above are in physical contact with the zirconia on both the inside and outside of the tube and usually are constructed of platinum because of its high chemical resistance at elevated temperatures. When the probe is subjected to elevated temperatures, there is a difference between the oxygen partial pressures on the two sides of the probe, and electricity will flow through a circuit connecting the two sides. This flow of electricity is from the higher pressure to the lower. If the oxygen pressure on one side is known, the oxygen pressure on the other side can be determined:

$$E = K\ x\ t \log \left\{ \frac{[O_2]_{known}}{[O_2]_{unknown}} \right\}$$

where T is absolute temperature, $[O_2]$ is oxygen partial pressure, K is a constant, and E is the electromotive force generated. This measurement can be made using a simple panel meter without electronics (Ref 2).

Continuous carburizing furnaces and straight hardening furnaces usually use proportional control in conjunction with the oxygen-probe control. Experience in control of continuous furnaces has shown that proportional control is normally required in order to cope with on-going disturbances involving movement of work, opening of doors, and the like. Compensation for these disturbances is rapid because of the rapid response rate of the oxygen probe. In the proportional-control system, the output voltage is supplied to a two-mode controller, and the controller positions a motorized or pneumatic control valve that regulates the flow of enriching gas to the furnace. Such carbon control is advantageous when short treatment cycles of 20 min or less are used, because compensations of 2 to 3 min or less are required for disturbances in such applications.

Oxygen probes often are used to monitor a furnace atmosphere while control is accomplished manually by adjusting flowmeters on enriching lines to the furnace. This is often used when the cost of control systems cannot be justified. The cost of replacing the consumable probe and the cost of simple on/off control systems must be weighed against human error, process accuracy, and reproducibility.

Endothermic generators also can be controlled by use of the oxygen probe. In this case, because of the difficulty of placing an *in situ* probe in the retort of the generator, the probe is used to sample atmosphere from the output line of the generator. The electrical signal from the probe is then wired to the control instrument that activates the solenoid valve located on the air-bypass line to the mixer. Thus, the air/gas ratio is automatically adjusted to give the desired properties of the endothermic gas.

Infrared Analyzer. An infrared-type analyzer can be utilized for specific analysis of simple or complex mixtures of vapors and liquids and can be used to detect any components that absorb infrared energy. Carbon monoxide and carbon dioxide are the most common gases measured by infrared control. An infrared-type analyzing system could be of a design utilizing two separate or twin infrared radiation cells. One is referred to as a reference source and gives a known signal in response to the reference gas. The other cell is used as a sample cell and would vary from the known reference cell depending upon the elements in the gas contained inside that cell. When the gases in both cells are the same, they are in balance.

If the gas-absorbing infrared radiation in the sample cell is increased, more infrared radiation is absorbed, and consequently the beams become unequal. Movement of a membrane within the detector varies the electrical capacity of the condenser, resulting in an electrical signal proportional to the difference between the two beams. This signal is amplified and fed into an indicating meter.

These same principles are utilized for both furnace control and atmosphere-generator control. Infrared analyzers may be used to control systems other than carbon monoxide and carbon dioxide in furnace applications. However, because many heat-treating systems are based on carbon dioxide analysis, infrared carbon dioxide control is very common. Carbon dioxide control and/or dew point control can be used for determining carbon potential in carburizing atmospheres. Infrared analyzers can also be used to monitor ammonia in nitriding atmospheres and carbon monoxide in other applications.

Dew Point Instrument. Use of a dew point measuring device is another method of controlling the carbon potential of a furnace atmosphere. It can also be used to determine the moisture content of any given atmosphere.

One type of dew point instrument utilizes an aluminum oxide sensor to generate an electrical signal that is proportional to the moisture content of the sample stream. The sensor consists of an aluminum base material with an aluminum oxide etched on its surface. The oxide is then covered with a thin permeable metal layer (see Fig. 1). The inner aluminum base and the outer metal layer form two electrodes in what is basically a capacitor. Moisture passes through the outer metal layer and is absorbed on the oxide. This changes the capacitance of the entire assembly proportionally to the moisture content in the atmosphere (Ref 3 and 4).

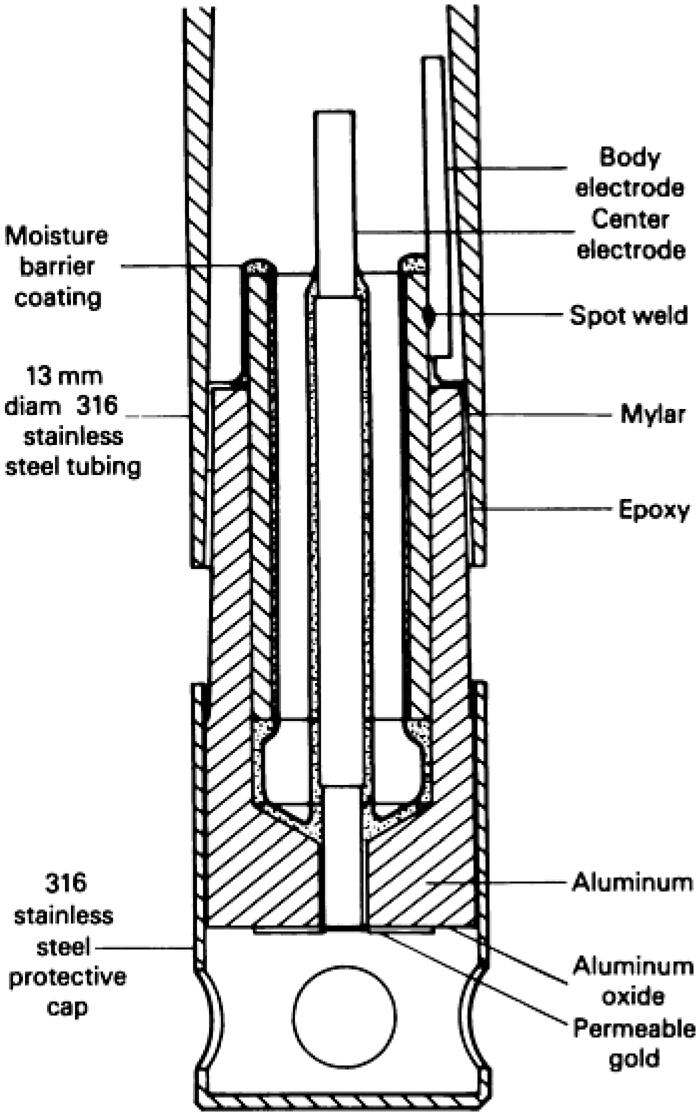

Fig. 1 The aluminum oxide sensor, a type of dew point instrument, measures water content of an atmosphere by change in capacitance between two electrodes. Source: Ondyne Inc.

Oxygen Analysis. Some applications involving heat processes require the use of analyzers to determine the oxygen content of a given processed gas. The most common practice for oxygen analysis in heat-treating furnaces is to determine the lack of oxygen. Depending on the level of oxygen desired or permitted in the process gas, specific ranges of concentration may have to be determined.

The magnetic oxygen analyzer is a common analyzing system used with heat-treating systems. Oxygen has an affinity for magnetic fields; most other gases do not. By adding a sample gas to a magnetic field and a detector, the change in resistance can be measured in a cell. The output from this cell is fed to a meter or a recorder and quite often is used as a permissive circuit in an atmosphere-control system.

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Atmosphere Control

For success in metallurgical atmosphere control, gas analysis instrumentation must be applied at the furnace and at the gas generator. This is true for endothermic as well as exothermic atmosphere applications. Analyzers and associated control systems applied to a furnace should never be expected to correct deficiencies in the basic atmosphere produced by the gas generator. Instrumentation dedicated to the furnace is designed to provide information and control relative to operation of the furnace and to the product being processed. Likewise, instrumentation dedicated to the generator is designed to provide information and control relative to operation of the generator and to the atmosphere produced by it.

Furnace Atmosphere

When controlling furnace atmospheres, it is important to control atmosphere composition, that is, the percentages of individual gases such as carbon monoxide, hydrogen, and so on. It is also frequently important to control atmosphere stability, the tendency of the atmosphere to move within, and out of the furnace.

Composition. The complexity of the furnace atmosphere control system is directly related to the degree of control required. For less critical applications, no active control system may be needed. Atmosphere supply adjustments can be made through occasional analysis of the atmosphere with portable instrumentation. With carburizing and hardening applications, a carbon probe and control systems are common. When greater precision is required, an infrared carbon monoxide instrument is added.

Stability. For atmosphere control of continuous (belt, roller hearth, and so forth) furnaces, atmosphere stability is an important factor. Room winds and drafts, caused by open doors in the plant for example, can cause the atmosphere inside the furnace to shift. In most cases, door curtains are sufficient to contain the atmosphere within the furnace. However, there are circumstances where curtains are ineffective, especially when large parts are frequently entering and leaving the furnace. In this case, blanketing the furnace doors with an inert gas flow can reduce or eliminate air entering the furnace. In some cases, a system capable of reacting to atmosphere changes may be needed.

Supply Atmosphere

Because the heat-treated product is treated in the furnace, there is a tendency to emphasize furnace atmosphere control and to overlook the generator. In many cases, automatic atmosphere control of the gas generator will resolve heat-treating atmosphere problems, simplify control of the furnace atmosphere, and in some cases reduce furnace monitoring to occasional spot checks.

There are two basic types of atmospheric supply systems: generated atmospheres (both endothermic and exothermic) and nitrogen-based atmospheres. The primary difference between generated and nitrogen-based atmospheres is the method of producing the final atmosphere composition. Generated atmospheres are produced by reacting natural gas, usually, and air inside a retort with a catalyst. The final product can be modified by downstream filtration. Nitrogen-based atmospheres, on the other hand, are produced by mixing one or more gases or liquids in the desired ratio. With nitrogen-methanol atmospheres, the alcohol dissociates inside the furnace to produce an atmosphere similar to endothermic.

Nitrogen-Based Atmospheres. Nitrogen-based atmosphere supply systems consist of a fluid supply source, normally a tank for each fluid component, and a flow control panel. The tank or tanks are located outside the plant, and the panel is normally situated inside the plant at the furnace. Figure 2 shows a typical supply arrangement. The flow control panel usually includes pressure regulation and flow control devices to ensure consistent supply. The atmosphere composition required in the furnace is mixed at the panel. Atmospheres similar to endothermic, exothermic, and dissociated ammonia are easily produced.

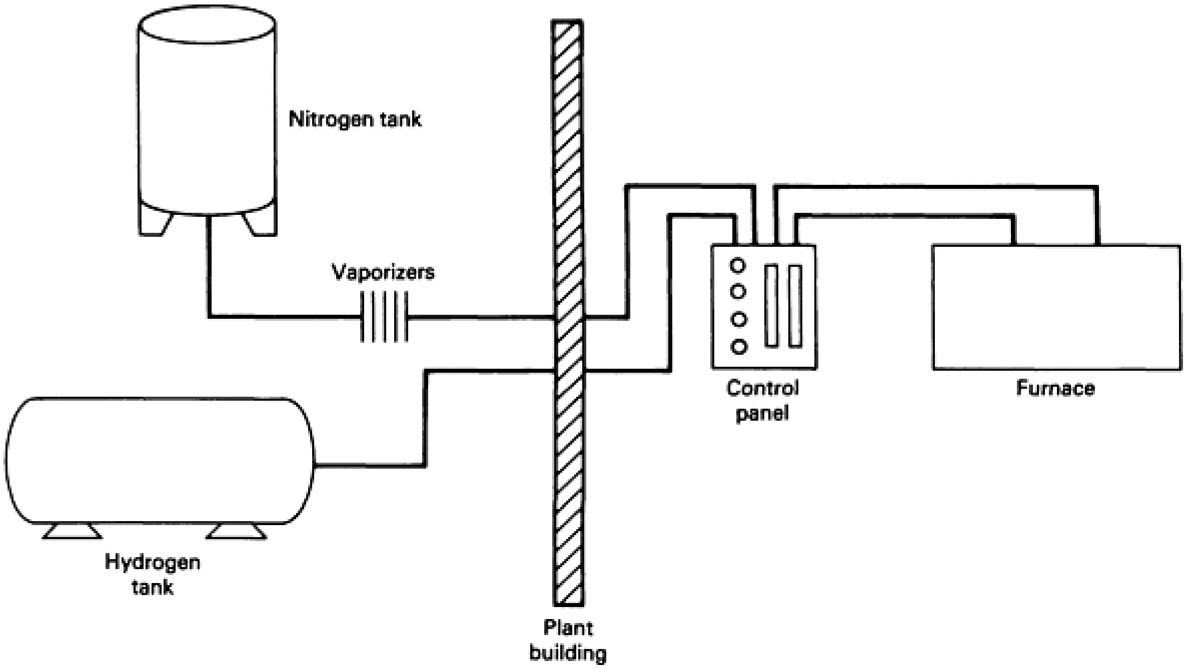


Fig. 2 Typical nitrogen-based supply system

No reaction or combustion takes place outside the furnace with a nitrogen-based system. This fact, along with the consistent, very high purity of the supply fluids, eliminates the need for supply analytical instrumentation.

Nitrogen-methanol atmospheres are used for carburizing and hardening applications as well as for some annealing and brazing operations. Nitrogen-propylene and nitrogen-hydrogen atmospheres are commonly used in annealing, brazing, and sintering. Pure hydrogen atmospheres are increasingly used in bell annealing furnaces.

Generated Atmospheres. Generated endothermic atmosphere is used in heat-treating furnaces for hardening, stress relieving, carbon restoration, and carburizing. The most recognized guides to endothermic generator operation are CO_2 and dew point. Any deviation from the relationship between the two indicates a generator problem, such as a leak or a carbon-coated catalyst. Figure 3 shows a proper carbon dioxide/dew point relationship.

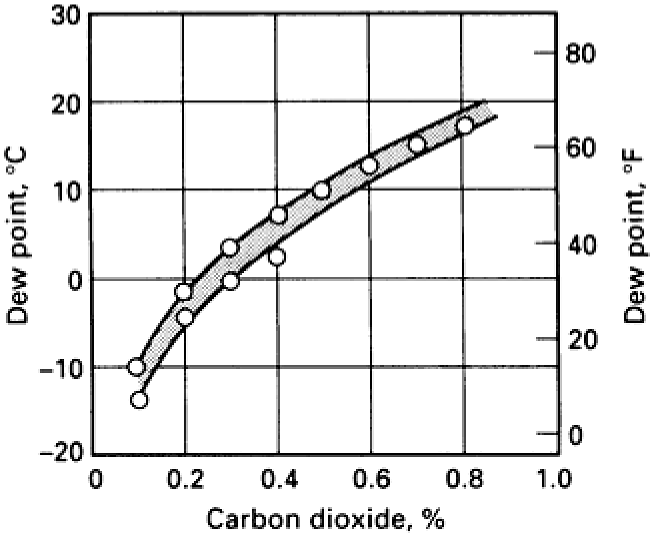


Fig. 3 Variation in the relation between dew point and carbon dioxide in the generation of an endothermic atmosphere, as obtained from four plants. The generator in each plant was operated at a different temperature, in the range of 1005 to 1095 °C (1840 to 2000 °F).

The nominal operating ranges for endothermic-atmosphere generators are -7 to 16 °C (20 to 60 °F) dew point and 0.2 to 0.7% CO_2. Generally, maintenance of an endothermic generator can be reduced by operating the generator near the lower end of the CO_2 range or near the higher end of the dew point range within the limits required by the furnace process. As a rule of thumb, the dew point will rise approximately 6 °C (10 °F) between a sample taken at the generator and a sample taken at the furnace before enriching gases are admitted to produce the desired carbon potential within the furnace chamber.

The following list describes typical endothermic generator problems that can be identified, corrected, or avoided through application of proper analysis and control:

- Carbon on catalyst
- Worn or clogged carburetor or mixer
- Poor temperature control
- Combustion products leaking into retort
- Barometric pressure change
- Humidity change
- Hydrocarbons from quench oil or engine exhaust drawn into generator with air
- Change in natural gas composition
- Sticking regulators
- Dirty flowscope orifices

When it is determined that carbon is present on the catalyst, a "burnout" procedure is followed to restore catalyst activity. Burnout is accomplished by turning off the natural gas and allowing air to pass through the catalyst. Oxygen combines with the excess carbon to form CO_2. Using the CO_2 analyzer to track the CO_2 buildup and decay, the entire burnout procedure can be monitored to completion efficiently. Operators often allow burnout to continue for excessive periods of time. By following the CO_2 readings on the analyzer, burnout usually can be completed in less than one hour. The necessity for burning out a generator is greatly reduced when the generator is controlled by CO_2 or dew point analysis, because large upsets commonly induced by manual adjustments are eliminated. In some cases, endothermic generators have been controlled at 0.20% CO_2 (dew point of -4 °C, or 25 °F) for one year without requiring burnout; this is exceptional and largely contingent on generator design, controls used, and manufacturing cycles in operation.

Generated exothermic-type atmospheres are used where inert atmospheres are required. Applications are common in the metal-treating industry for bright annealing of copper, decarburization annealing of motor laminations, processing of aluminum, and ferrous and nonferrous annealing of coils, wire, and strip. Exothermic atmospheres are also used as an inert blanket in production of glass, in food processing, and in rubber curing. Various chemical processes and storage facilities employ inert atmospheres produced by exothermic-gas generators.

Analyzer Recommendations

Typical analyses of various exothermic atmospheres are listed below, along with recommended analyzers. Total combustibles analyzers are applied most frequently to monitor and/or control exothermic atmospheres. Very rich (20% or higher total combustibles) and very lean (less than 1% total combustibles) exothermic atmospheres are most accurately monitored and/or controlled by an infrared analyzer sensitized to an appropriate range of carbon monoxide.

Rich exothermic atmospheres typically consist of 10 to 25% combustibles (approximately equal parts CO and H_2), 5% CO_2, 3% H_2O, with the remainder N_2. Recommended analyzers to control and/or monitor rich exothermic atmospheres are:

- Infrared analyzer calibrated for 0 to 10 or 20% carbon monoxide
- Total combustibles analyzer (catalytic type) calibrated for 0 to 15%, 20 or 25% combustibles

Lean exothermic atmospheres consist of 1 to 10% combustibles (approximately equal parts CO and H_2), 12% CO_2, 3% H_2O, with the remainder N_2. Recommended analyzers to control and/or monitor lean exothermic atmospheres are:

- Total combustibles analyzer (catalytic type) calibrated for 0 to 1, 2, 5 or 10% combustibles
- Infrared analyzer calibrated for 1, 2, 5, or 10% carbon monoxide
- Oxygen analyzer for 0 to 1.0% or 2% oxygen to monitor lean atmospheres to ensure minimum oxygen

Nitrogen (lean exothermic) atmospheres typically consist of 0.2% combustibles, 0.1% oxygen, 12% CO_2, 3% H_2O, with the remainder N_2. Recommended analyzers to control and/or monitor nitrogen atmospheres are similar to lean exothermic analyzers but with lower ranges specified for greater accuracy; infrared analyzers calibrated for 0 to 0.1% or 0 to 0.5% carbon monoxide are generally preferred over total combustibles analyzers when best accuracy is required.

Exothermic atmospheres with CO_2 and H_2O removed may be produced by passing exothermic atmospheres through a MEA (monoethanolamine) or a molecular sieve scrubber to remove CO_2 (<1000 ppm) and H_2O). The atmosphere can be a N_2 or a N_2 + combustibles atmosphere. In addition to applying the above analyzers, an infrared analyzer calibrated for 0 to 0.1% carbon dioxide provides an excellent means of monitoring CO_2 scrubber efficiency as well as prompt indication of carbon dioxide buildup or variation.

Control Valve and Motor Adjustment Procedure

Figures 4 and 5 summarize application of analyzers to exothermic- and endothermic-gas generators, indicate analyzer sample take-off locations, and show proper locations for installation of control valves for automatic atmosphere control. The effectiveness of an automatic atmosphere analysis control system is directly related to the proper setup of the control valve and motor. Proper control valve port size and driven-motor speed are important to system success. In both Fig. 4 and 5, the control valve should drive open when analysis point is below set point. If set point is moved below analysis point, valve should drive closed.

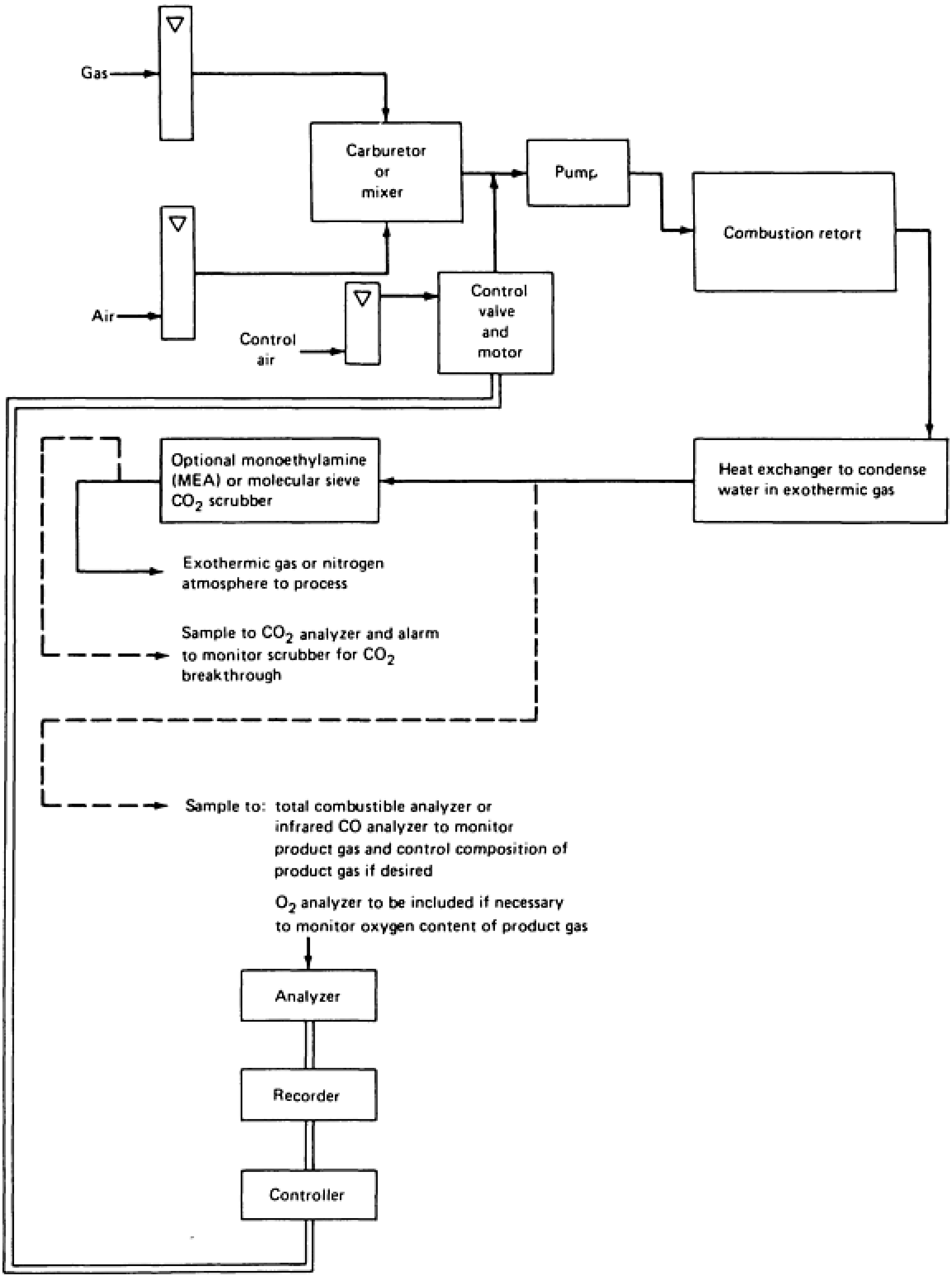


Fig. 4 Typical analyzer and controller applied to exothermic-gas or nitrogen generator

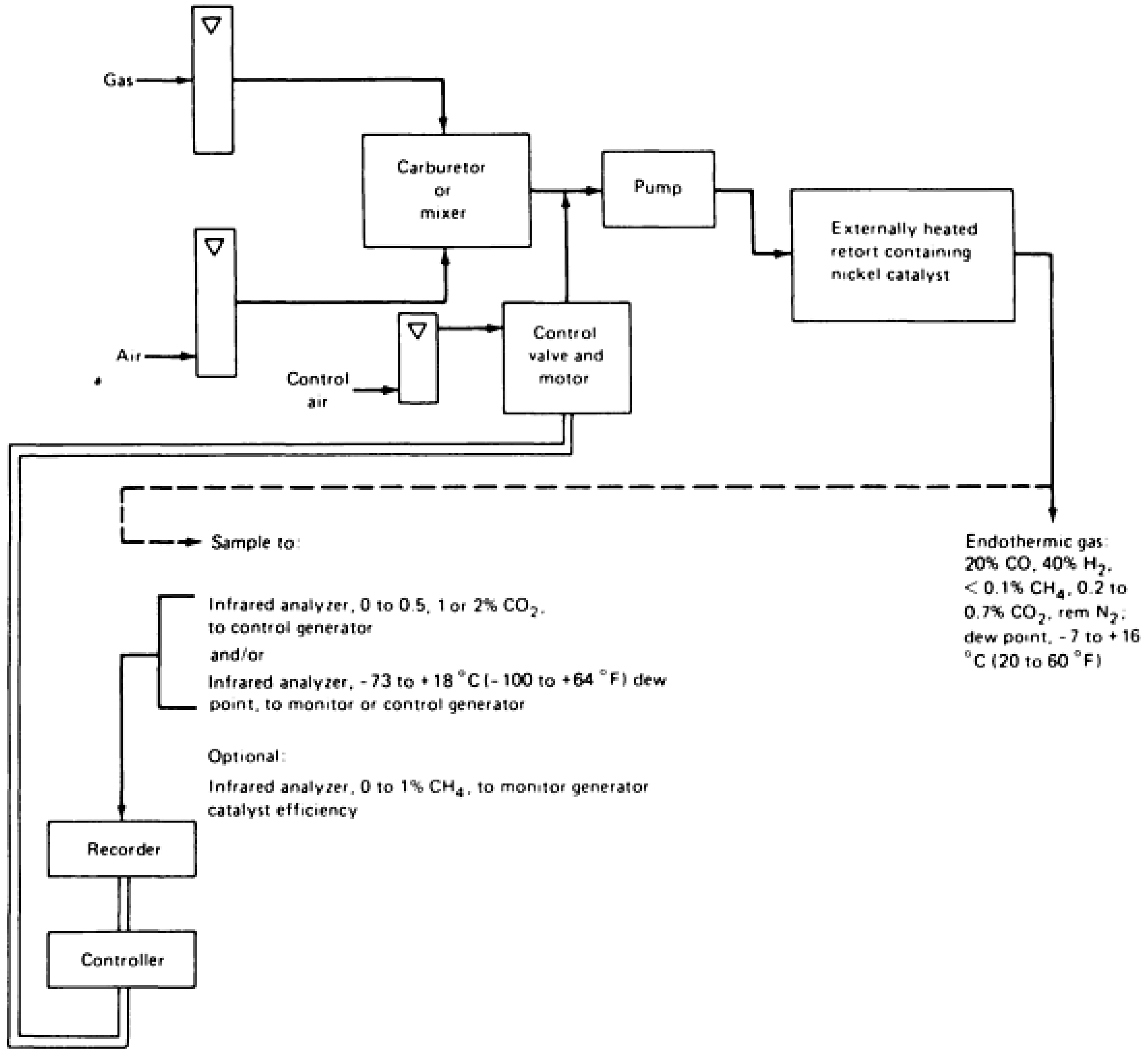


Fig. 5 Typical analyzer and controller applied to endothermic-gas generator

Increasing air to the endothermic generator (Fig. 5) increases CO_2 and dew point. Increasing air to the exothermic generator (Fig. 4) decreases CO or total combustibles. During the first week or two of operation, the control valve on the endothermic generator may keep seeking a position at full motor travel, and it will be necessary for the operator to manually reset to midposition, adjust carburetor or mixer to obtain desired set point, and switch back to automatic. This is a normal sequence caused by gradual cleaning and conditioning of catalyst in the endothermic generator.

Control of Surface Carbon Content in Heat Treating of Steel

Revised by the ASM Committee on Control of Surface Carbon Content*

Introduction

MOST HEAT-TREATING ATMOSPHERES are gaseous mixtures containing carbon monoxide, carbon dioxide, methane, nitrogen, hydrogen, and water vapor. The relative amounts of these gases depend on the type of generator gas used, the processing temperature, and the amount of gas added during processing. For example, endothermic generator gas produced by catalytic reaction of natural gas with air results in the following composition (approximate percentages by volume): 20 CO, 40 H_2, 40 N_2, 0.1 to 0.5 CO_2, 0.2 to 1.2 H_2O, and 0.2 to 0.8 CH_4. A synthetic endothermic atmosphere may be obtained by injecting 40% N_2 with 60% CH_3OH into the furnace at the heat-treating temperature. In

gas carburizing, a common commercial practice is to use an endothermic gas as a carrier and to enrich it with natural or propane gas additions.

Note

* * M. Stefan Stanescu, *Chairman*, Airco Industrial Gases; Raymond L. Davies II, Carbon Control Instruments; Neil Cornellssen, Siemens Energy and Automation, Inc.; S. Allan Stephens, Stephens Analytical Equipment Inc.; Dennis M. Hablewitz, Barber-Colman Company; Tim Kenney, Panametrics

Gas Reactions

There are several possible gas reactions that can occur in a heat-treating atmosphere because of the presence of many gas species. The most important reactions are described briefly:

$$H_2 + CO_2 \;\text{€}\; H_2O + CO \qquad \textbf{(Eq 1)}$$

$$H_2 + \frac{1}{2}O_2 \;\text{€}\; H_2O \qquad \textbf{(Eq 2)}$$

$$CO + \frac{1}{2}O_2 \;\text{€}\; CO_2 \qquad \textbf{(Eq 3)}$$

Equations 1, 2, and 3 are homogeneous gas reactions that are generally assumed to be in equilibrium in furnace atmospheres above 790 °C (1450 °F).

Equations 4, 5, and 6 are gas-solid reactions, where *C* represents carbon in solution in the steel:

$$2CO \;\text{€}\; C + CO_2 \qquad \textbf{(Eq 4)}$$

$$CO + H_2 \;\text{€}\; C + H_2O \qquad \textbf{(Eq 5)}$$

$$CH_4 \;\text{€}\; C + 2H_2 \qquad \textbf{(Eq 6)}$$

The carbon potential in the gas phase determines the carbon concentration at the surface of the steel parts being processed. Equations 4 and 5 are much faster reactions than Eq 6, as discussed in the section off kinetics. Thus, to maintain a given carbon potential in the gas atmosphere, the following reactions are important for replenishing CO and H_2 and for maintaining the appropriate low concentration levels of CO_2 and H_2O because they introduce methane (enriching gas) into the furnace:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \textbf{(Eq 7)}$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \textbf{(Eq 8)}$$

Equations 7 and 8 are usually considered to be nonequilibrium reactions.

Control of Carbon Potential

Traditionally, control of carbon potential has been achieved, in principle, by controlling either water vapor concentration (dew point), carbon dioxide concentration, or oxygen partial pressure. It is accomplished by the addition of methane or air to the furnace atmosphere.

The principle of carbon-potential control can be shown by the following equilibrium reaction:

$$2CO = C + CO_2 \quad \textbf{(Eq 9)}$$

The equilibrium constant for Eq 9 (K_1) is given by the relationship:

$$K_1 = \frac{a_c P_{CO_2}}{P_{CO}^2} \quad \textbf{(Eq 10)}$$

where a_c is the activity of carbon, and PCO_2 and P_{CO} are the partial pressures of CO_2 and CO, respectively. The expression:

$$a_c = \frac{K_1 P_{CO}^2}{P_{CO_2}} \quad \textbf{(Eq 11)}$$

can be derived from Eq 10. The quantity a_c is related to the carbon potential by the equilibrium relationship shown in Fig. 1, where a_c is plotted against weight percentage of carbon in austenite for various isotherms between 815 and 1040 °C (1500 and 1900 °F). Because K_1 is temperature dependent only and P_{CO} in the carrier gas remains essentially constant (20 kPa, or 0.20 atm is typical), the carbon potential may be controlled by varying PCO_2. The calculated isothermal equilibrium relationship between percentage of CO_2 and weight percentage of carbon in an endothermic-based-atmosphere containing 20% CO is shown in Fig. 2. The experimentally determined relationship between percentage of CO_2 and weight percentage of carbon has been obtained by several investigators. Although the experimental values determined by different investigators are not in exact agreement with one another or with calculated values, they generally are in close enough agreement so that control of percentage CO_2 can be used as a reliable means for controlling carbon potential.

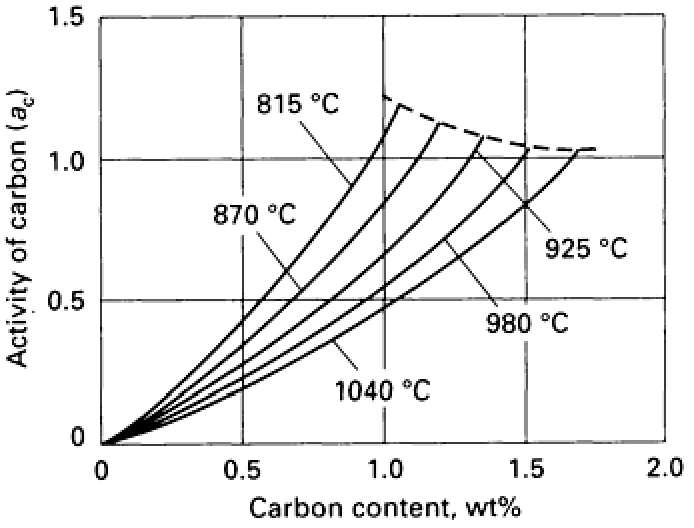


Fig. 1 Isothermal equilibrium relationship between activity of carbon and carbon concentration in austenite for various temperatures

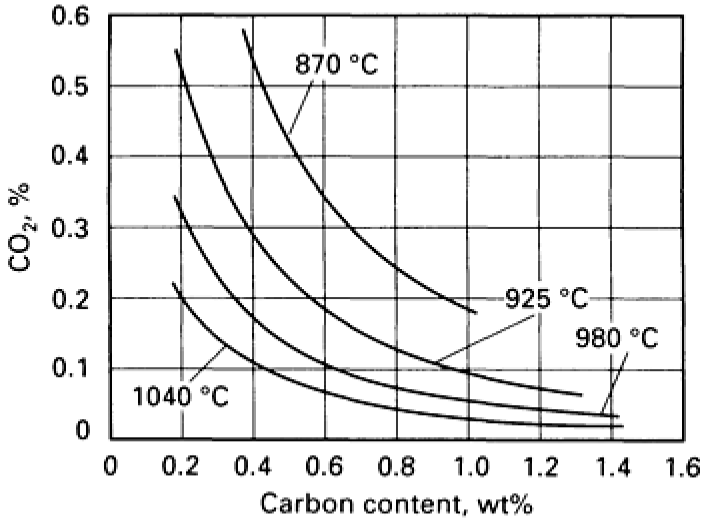


Fig. 2 Calculated equilibrium relationship between carbon dioxide concentration and carbon content in an endothermic-based atmosphere. Carbon monoxide content is assumed to be 20%.

The principle of control of carbon potential by control of H_2O vapor pressure (dew point) may be demonstrated easily by the following equations. Under equilibrium conditions, the partial pressure of H_2O is related to the partial pressure of CO_2. The following well-known water-gas reaction can be used to show this relationship:

$$H_2 + CO_2 \rightleftarrows H_2O + CO \qquad \textbf{(Eq 12)}$$

The equilibrium constant for Eq 12 (K_2) is given by:

$$K_2 = \frac{P_{H_2O} P_{CO}}{P_{H_2} P_{CO_2}} \qquad \textbf{(Eq 13)}$$

and the following expression for P_{CO_2} may be derived from Eq 13:

$$P_{CO_2} = \frac{P_{H_2O}}{K_2 P_{H_2}} P_{CO} \qquad \textbf{(Eq 14)}$$

Substitution of the right side of Eq 14 for P_{CO_2} in Eq 11 gives:

$$a_c = K_1 K_2 \frac{P_{CO}}{P_{H_2O}} P_{H_2} \qquad \textbf{(Eq 15)}$$

Because K_1 and K_2 are temperature dependent only and P_{CO} and PH_2 remain essentially constant in the carburizing atmosphere, the carbon potential can be controlled in principle by controlling the vapor pressure of H_2O (dew point). The calculated equilibrium relationship between dew point and weight percentage of carbon for an endothermic-based atmosphere containing 20% CO and 40% H_2 is shown in Fig. 3. Although the experimental values determined by different investigators are not in exact agreement with one another or with calculated values, they generally are in close enough agreement so that control of dew point can be used as a means of controlling carbon potential.

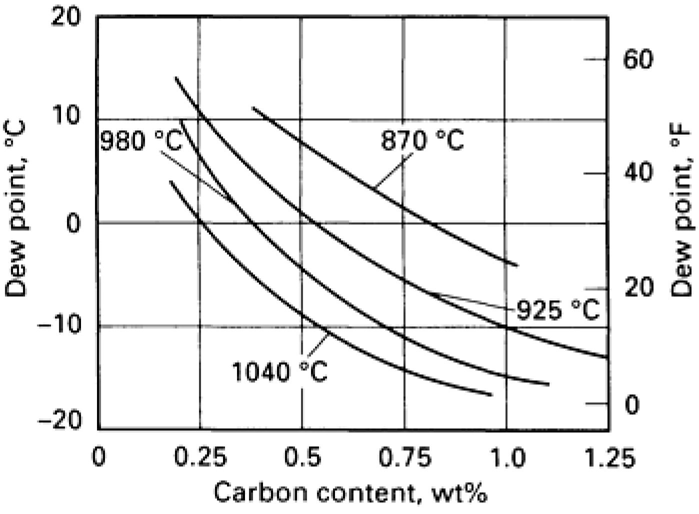


Fig. 3 Calculated equilibrium relationship between dewpoint and carbon content in an endothermic-based atmosphere. Carbon monoxide and hydrogen contents are assumed to be 20% and 40%, respectively.

Based on simple thermodynamic considerations, control of oxygen partial pressure (PO_2) can in principle be used to control carbon potential. Under equilibrium conditions, PO_2 is related to the partial pressure of P CO_2. The following well-known expression can be used to show this principle:

$$\mathrm{CO} + \frac{1}{2}\mathrm{O_2} \text{ € } \mathrm{CO_2} \qquad \textbf{(Eq 16)}$$

The equilibrium constant for Eq 16 (K_3) is given by:

$$K_3 = \frac{P_{CO_2}}{P_{CO}P_{O_2}^{1/2}} \qquad \textbf{(Eq 17)}$$

and the following expression for P CO_2 may be derived from Eq 17:

$$P\ \mathrm{CO_2} = K_3\ P_{O_2}^{1/2} P_{\mathrm{CO}} \qquad \textbf{(Eq 18)}$$

Substitution of the right side of Eq 18 for P CO_2 in Eq 11 gives:

$$a_c = \frac{K_1 P_{CO}}{K_3 P_{O_2}^{1/2}} \qquad \textbf{(Eq 19)}$$

Because K_1 and K_3 are temperature dependent only and P_{CO} remains essentially constant in the carburizing atmosphere, the carbon potential can be controlled by monitoring the partial pressure of oxygen.

Kinetics

As stated, the concept of equilibrium conditions presupposes that an infinite length of time for reaction, necessary to ensure true equilibrium, is available. In actual heat treatment of steel, however, reaction times are important factors. Some reactions are fast and take control of the heat-treating process; these are the reactions of chief concern. Intergas reactions determine the atmosphere composition and the carbon potential it will exhibit. Gas-solid reactions are responsible for the actual carbon transfer and so determine the rate of case formation.

Homogeneous Gas-with-Gas Reactions. Some gas-with-gas reactions, such as those given in Eq 12, 2, and 16, are fast. In a well-mixed atmosphere of uniform composition, fast reactions reach equilibrium and characterize, to a large extent, the gas and its carbon potential.

Other reactions, such as those given in Eq 7 and 8, are comparatively slow. These are endothermic reactions that require considerable energy absorption but that are important as replenishment reactions. They are, however, less important in characterizing the gas, especially in terms of effective carbon potential.

Hetergeneous gas-with-solid reactions, such as those defined by Eq 4, 5, and 6, are relatively slow. These are the reactions by which carbon is transferred to steel surfaces, and carbon potential is displayed and made effective. The reaction in Eq 6 is particularly slow, and this reflects the fact that CH_4 is a relatively stable molecule and does not dissociate readily. The reaction given in Eq 5 is said by some investigators to be the fastest of all carburizing reactions and the most influential in determining the rate of case formation.

Carburization of a surface involves three factors not present in gas-with-gas reactions, and one of these factors becomes rate controlling.

Movement of Molecules to the Metal Surface. Reaction in contact with the metal surface is usually required. Usually reactions occurring away from the metal surface result simply in soot deposition, which hinders carburization. Turbulent mechanical circulation of the gases over the metal surfaces keeps the gases well mixed and uniform in composition, and maintains flow of the supply gases to the main stream of reacting gases. The amount of energy and time required for mixing can be significant, especially where workloads are densely packed in the baskets and gases do not have uniform access to all parts of the load.

Reactions between Gases and Metal Surfaces. Carburization occurs when the proper gas molecules interact with a metal surface and transfer carbon to that surface. As the carbon is released by the gases, it is incorporated (dissolved) into the surface layer of the metal. These reactions are rate controlling with respect to the overall process, especially in the early hours of the process. The concentration of the active species affects the rate at which the proper molecules contact the metal surface and consequently affects the rate at which the gas mixture gives up carbon to the surface. Conversely, the concentration of decarburizing H_2O and CO_2 molecules (relative to equilibrium concentrations) determine whether some of the carbon transferred will be reincorporated promptly into a gas molecule. Such considerations determine whether, at a given temperature, a given gas mixture will carburize steel at the maximum rate or at a considerably lower rate. Consequently, increasing methane concentrations well above equilibrium values (that is, without corresponding decreases in CO_2 and H_2O) will not necessarily result in the expected increase in carburizing rates.

Dilution of the carburizing gas mixture with an inert gas such as nitrogen will slow carburization by reducing the rate at which carbon-donating molecules contact the metal surface. To this reduction is added the effect of the inert diluent on carbon potential. Generally, that effect is a drop in carbon potential. However, in the endothermic-gas technique, concentrations of inert diluent up to at least 40% do not seriously impair the carburizing power or the carburizing rate of a well-prepared gas mixture. Despite these known factors, the mechanisms of reactions between gases and metal surfaces are too complex and conditions at the work surfaces too difficult to evaluate, for accurate mathematical prediction of reaction rates for a given gas composition in a production carburizing furnace.

Diffusion of Dissolved Carbon from the Metal Surface. When carbon has become part of the metal surface, it usually represents an increase in carbon concentration over that of the core, except where the surface has been previously decarburized. With this increased carbon concentration, the carbon begins to diffuse toward the leaner core at a rate that is a function of this concentration gradient, of case depth, and of temperature. Initially, this diffusion rate is high; carbon diffuses inwardly at a rapid rate, and surface concentration increases slowly. As the surface carbon activity approaches equilibrium with the gas carbon activity after about 2 h at 925 °C (1700 °F), the rate of inward transfer diminishes until it becomes rate controlling. Beyond that point, acceleration of carburization requires that either the carbon potential or the carburizing temperature be raised.

Kinetics in Practice. Recognizing that transfer of carbon from the gas to the steel surfaces can be rate controlling for the first several hours of a carburizing cycle, it is advisable to:

- Employ high-power circulating fans in the furnace to move the atmosphere rapidly and to keep it thoroughly mixed
- Direct the movement of gases as much as possible to maximize circulation through the work load and to

minimize short circuiting in the region of the fan

- Allow sufficient space for movement of gas between and around workpieces
- Use atmosphere compositions that initially will provide a carbon potential well above the concentration desired in the work surface. This will facilitate carbon transfer at a maximum rate while the case is shallow and carbon demand is high
- Reduce carbon potential during processing in time to establish carbon concentration in the surface at the desired set point before processing is complete
- Anticipate the total carburizing time required for a given case by referring to published data or by means of calculations based on Fick's law of diffusion. Use this as a guide in evaluating the rates of case formation obtained

Process Control in Gas Carburizing

Control of a gas-carburizing process involves accurate measurement and adjustment of temperature, time, flow of carrier gas or atmosphere, and flow of enriching gas. Initial set points for these parameters are established from equilibrium data or from experience. Set points may be changed as necessary to maintain required properties of the workpieces. In some installations, certain parameters such as temperature and carrier-gas, or base atmosphere, flow are fixed, and the time of exposure and the flow of enriching gas are varied to achieve differences in case depth and surface carbon content.

Control-System Features. Regardless of the variable being controlled or the instrumentation being used, a major feature of every control system should be a set of signal devices that warns operating personnel of major malfunctions. For instance, a power failure normally renders the atmosphere control system inoperative. It also shuts down the furnace heating system. If the furnace temperature drops below 760 °C (1400 °F), there is an increased danger of an explosion. A temperature-activated, battery-powered audible or visible alarm warns of a decrease in temperature in time to allow the furnace doors to be opened and the combustible mixture to be burned out or purged with an inert gas before the temperature drops below the danger point.

If the furnace pressure drops below a predetermined minimum because of loss in atmosphere flow supply, there is again a danger of explosion due to air infiltration. Such a condition should activate an alarm system that triggers a purge system.

The reserve supply of inert gas should be monitored and an alarm system installed that will signal a drop in the gas supply to a predetermined dangerous level. There should always be enough inert gas in reserve to purge the combustibles out of all connected furnaces.

In general, the control system should comply with National Fire Protection Association (NFPA) 86C recommendations.

Under normal operating conditions, control is maintained by periodic checking of the control parameters against set points or specified values, followed by adjustment of heat input, enriching-gas flow, or other process variables as necessary. Case depth often is specified as effective case depth (to 0.40% C, or to 50 HRC), which indicates the hardened case depth. The effective case depth is influenced by steel composition and by process variables: temperature, time at temperature, carbon potential of the atmosphere, and efficiency of the quench.

Accuracy. For a constant atmosphere composition, especially where there is no change in carbon dioxide content, a change in temperature of about 10 °C (18 °F) can produce a change of as much as 0.1% in carbon potential. Therefore, accurate control of carbon potential is achieved only when there is accurate control of temperature.

Normally, an atmosphere-control system must respond to variations of 0.01 to 0.02% in carbon dioxide content; however, this degree of control is not sufficient in high-temperature carburizing, where the set point may be below 0.1% carbon dioxide. Then, reproducibility of ±0.005% or better is usually recommended.

Inherently, carburization is a slow, forgiving process; a part is usually at elevated temperature for several hours. Therefore, periodic fluctuations in temperature or in carbon potential are usually of little consequence. As long as average conditions are maintained, without large or prolonged excursions from set-point conditions, it is unlikely that parts will be adversely affected. Likewise, a few minutes' difference from programmed time in the furnace usually will be of little consequence.

Only carburizing and diffusion times, not total furnace time, should be counted toward the time required to develop a given depth of case. Preheating time is disregarded because little carburizing takes place in this part of the cycle. Any equalizing time following diffusion also may be disregarded; during cooling from the diffusion temperature to the quenching temperature, any diffusion that occurs will not substantially increase case depth.

Controlling the Process. For control of carburization, there is no substitute for alert, vigilant, well-trained operators. There are many ways a carburizing furnace and its controls can malfunction. For instance, failure of a thermocouple or plugging of the atmosphere-sampling tube can cause the process to go out of control. Any soot buildup on the parts will stop continuous carburizing reactions. These and many other relatively common occurrences can be detected by operators, and corrective action can be taken before there is an adverse effect on parts in the furnace.

Moreover, considerable thought and preparation should go into the initial preproduction planning for carburizing a new part or for putting new or renovated equipment into operation. The following is a checklist of items to be considered in setting up for production:

- *Temperature distribution:* Uniformity of temperature throughout the heated zones of the furnace and correct location of thermocouples should be ensured
- *Effects of loading:* Full trayloads of parts may have to be checked and subjected to complete metallurgical examination to determine distribution of case depth, hardness, and other properties in parts throughout the load. Light loading is inefficient in terms of energy usage, but heavy loading can cause nonuniform atmosphere flow through the work. Bulk loading of parts randomly heaped in baskets is likely to cause unacceptable case depth and hardness variability
- *Variations in carbon concentration:* Test bars for carbon determination should be placed in different furnace loads and at varying locations on trays. Results of tests should be analyzed statistically to ascertain the process capability of the furnace
- *Variations in properties:* Effects of the positions of parts in the load on asquenched or quenched and tempered properties should be analyzed statistically
- *Atmosphere introduction:* In continuous furnaces for shallow cases and with fast pushing cycles, most of the enriching gas is piped into the furnace close to the discharge end and possibly flowed countercurrent to the work. For slow cycles and deep cases, the main flow of enriching gas into the furnace should be nearer to the charging end. In either instance, most of the enriching gas should enter at the point where the work load has reached the carburizing temperature
- *Dew-point characteristics:* In continuous furnaces, it should be ascertained whether the last furnace zone (diffusion zone) can develop the required dew point, with some latitude for adjustment. A small measured quantity of air may be introduced to increase the dew point and lower the carbon potential. Some operators prefer to inject exothermic gas instead of air at the discharge end
- *Hardenability of the steel:* Wherever possible, properties of the parts should be determined for heats of steel at both the top and bottom limits of the hardenability band
- *Dimensional variations:* Parts requiring close tolerances should be measured before and after hardening to evaluate dimensional changes

When a furnace is first put into operation, when it has been overhauled or relined with new firebrick, or after a long furnace shutdown, it is usually necessary to dry out and condition the furnace before it is used for carburizing production parts. Conditioning consists of bringing the empty furnace to the operating temperature and then admitting a carburizing atmosphere and allowing the atmosphere to react with the internal components of the furnace for at least several hours to as long as several days. Conditioning ensures that the internal components of the furnace will be essentially at equilibrium with the carburizing atmosphere, so that chemical reactions between the atmosphere and the workpieces will not be slowed because of reactions between the atmosphere and the furnace lining.

Set points for control of the carburizing atmosphere are usually estimated by referring initially to a plot of carbon potential versus dew point (see Fig. 4), or of carbon potential versus carbon dioxide concentration (see Fig. 5). After control has been established and the furnace is conditioned, it may become necessary to adjust set points to ensure that the desired surface carbon content is obtained consistently and reliably. Charts such as Fig. 4 and 5 also may be used to estimate the effect of a given change in set point.

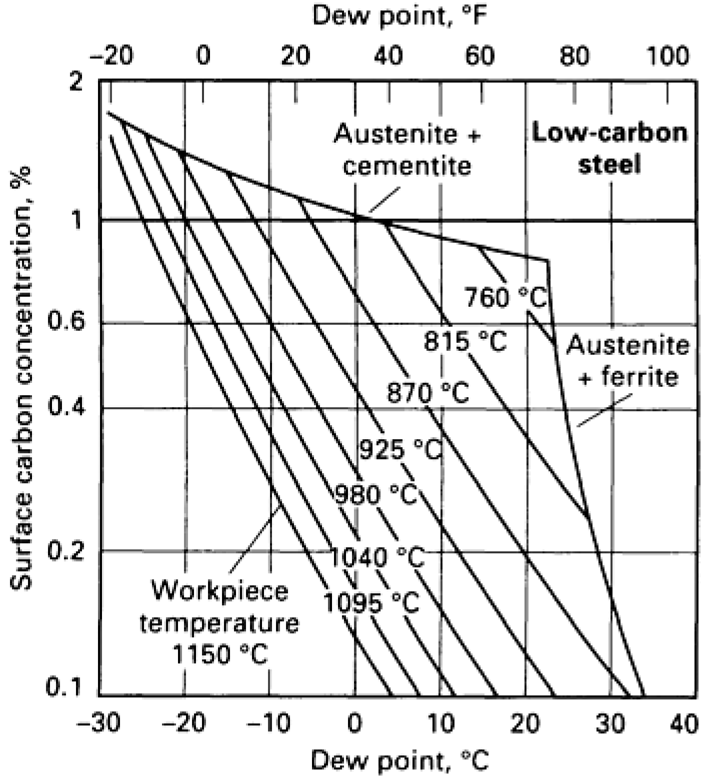


Fig. 4 Variation of carbon potential with dew point for an endothermic-based atmosphere containing 20% CO and 40% H_2 in contact with plain carbon steel at various workpiece temperatures

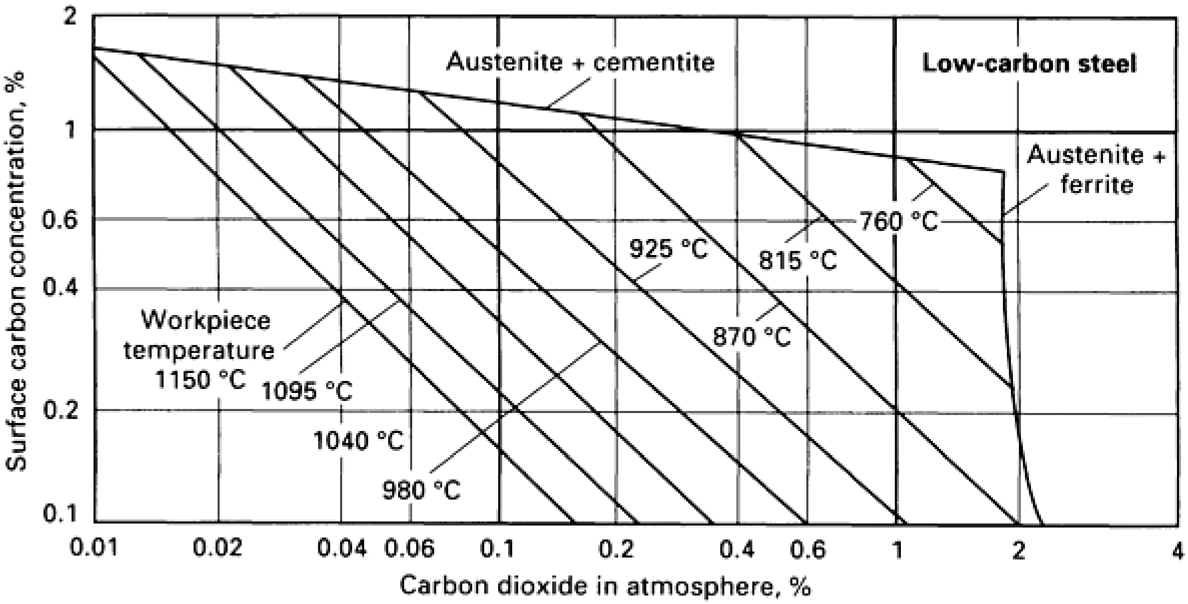


Fig. 5 Variation of carbon potential with carbon dioxide concentration for an endothermic-based atmosphere containing 20% CO and 40% H_2 in contact with plain carbon steel at various workpiece temperatures

Temperature control should be maintained with an average deviation from the control set point of no more than ±3 °C (±5 °F) for good control of results. However, a control cycle of ±6 °C (±10 °F) is usually acceptable. In a continuous four-zone carburizing furnace, thermocouples should be placed near the end of the first (preheat) zone because workpieces should be at carburizing temperature when they enter the second (carburizing) zone. Thermocouples should be placed in the centers of the second zone and the third (diffusion) zone. In the fourth (equalizing) zone, thermocouples

should be close to the discharge end; this will ensure that the workpieces have reached the required temperature for subsequent quenching, which is usually about 815 °C (1500 °F).

There should be provision for two thermocouples in each furnace zone. They should be as close as possible to the workpieces. One thermocouple is for the temperature recorder/controller, and the second is for an overheat potentiometer set at the overtemperature of that zone. If a hole or crack develops in a thermocouple-protection tube, the thermocouple will come in contact with the reducing furnace atmosphere and will malfunction. When this happens, the protection tube and thermocouple must be replaced.

Circulation of the atmosphere influences temperature uniformity throughout the furnace. Without good circulation, there is no effective temperature control, and wide differences in temperature can exist between the outer and inner sections of the work basket. This is true for both continuous and batch furnaces.

Atmosphere Control. Generator gas that contains 0.1 to 0.3% CO_2 and that has a dew point of about -10 to 5 °C (15 to 40 °F) is ideal for use in a carburizing atmosphere. Reactions in the gas generator are controlled by regulation of the gas-to-air ratio in the mixing valve before the hydrocarbon gas is cracked in the retort tubes of the generator. Increasing the air flow increases the dew point, and increasing the natural gas flow decreases the dew point. It is usually preferable to generate a carrier gas with a composition favorable to trouble-free generator operation. Production of carrier gas with a carbon dioxide content of less than 0.1% may cause excessive sooting in the generator, requiring frequent burnouts.

An oxygen probe or infrared control system may be used to automatically control the generated endothermic atmosphere so that it maintains a constant composition.

The atmosphere formed by incomplete combustion of natural gas, propane, or other hydrocarbon is assigned a predetermined set point. When the generated atmosphere is not on the set point, a signal is sent to a motorized valve that either increases or decreases the flow rate of hydrocarbons for a given constant rate. Control could be implemented with either hydrocarbon or an air trim system. The amount of trim should be ±15% of the total flow.

An oxygen probe could be installed using two distinct setups.

In Situ Method. The probe is inserted through the top of the cooling chamber to a point 25 to 50 mm (1 to 2 in.) above the catalyst. At this point, the temperature should be at least 900 °C (1650 °F), although the preferred temperature range is 925 to 980 °C (1700 to 1795 °F). The head of the probe and the lead wire must be cooled with forced air.

Sample-Reheat Method. The probe is inserted into a sample port on the atmosphere exhaust line. This method may require maintenance to remove the deposition of soot from the sample line.

Automatic control of the generated atmosphere, which would maintain a constant composition, could contribute to a more effective process. However, automatic control of the generated atmosphere is not as accurate as an automatic carbon-potential control that monitors the atmosphere of a heat-treating furnace.

At no time should the carburizing atmosphere in the furnace be controlled by varying the dew point or carbon dioxide of the generator gas. If the furnace atmosphere is too rich, raising the generator-gas dew point to decrease the carbon potential will not work effectively. The reactions in the generator will not stay in equilibrium with this method of control.

The carbon potential of a carrier gas is neutral; the actual source of carbon is the enriching gas. Thus, the carbon potential of the furnace atmosphere can be controlled by varying the flow of the enriching gas. Altering the enriching gas will raise or lower the CO_2 or H_2O content, which, in turn, determines the carbon potential of the steel.

It should be noted that the reactions are not in equilibrium with latter stages of a carburizing batch. The enriching gas flow is initially found by experience and subsequently continuously monitored by automatic controls until the cycle is completed.

An oxygen probe or infrared control system may be used in controlling the carbon potential automatically in the batch furnace atmosphere or continuous furnace atmosphere zones. The atmosphere of each zone is assigned a predetermined set point. When the atmosphere is not on the set point, a signal is sent to a motorized valve, which either increases or decreases the flow of the enriching gas. A normally closed on-off solenoid valve may be used instead of a motorized

control valve. The equalizing zone generally is controlled by admission of a predetermined amount of air to keep the carbon potential at its intended value.

Sampling of Atmospheres for Analysis

In the carburizing of steel, three properties of the finished case are important:

- Surface concentration of carbon
- Case depth
- Carbon gradient

Case depth depends primarily on carburizing time and temperature; it often can be presumed to depend only on time because the temperature used in a given plant is often standardized. The other two case characteristics depend strongly on the carbon potential of the atmosphere and on accurate control of carbon potential. Carbon control is difficult unless the amounts of both carburizing and decarburizing constituents present in the atmosphere can be analyzed and controlled. The first requisite of analysis is that a representative sample of the furnace atmosphere be obtained.

The sample of gas should be taken from a point in the furnace chamber as close as possible to the work being treated. This will lessen the likelihood of obtaining a sample of stagnant gas, such as may be present near the furnace wall. The sampling point should also be as far as possible from the atmosphere inlet ports and from burner tubes. When the furnace has forced circulation through the work load, a sample taken from the atmosphere as it leaves the work will most nearly reflect its effective operating condition.

Velocity of Gas Flow. Empirical data indicate that when carbon dioxide or water vapor is to be measured, the velocity of gas flow through the sampling probe should be at least 1.2 m/s (240 ft/min). This velocity almost completely prevents reactions between constituents by reducing the time that the gas is in the intermediate temperature range, which exists mainly in the portion of the tube that passes through the furnace wall. With lower velocities, the water-gas reaction will take place at lower temperatures and thus raise the concentration of carbon dioxide and decrease the concentration of water vapor. If the carbon potential of the atmosphere is high, carbon monoxide will decompose into carbon dioxide and soot. This will further increase the concentration of carbon dioxide and also will affect the water-vapor content through the water-gas reaction.

When sooting occurs in the probe, the sample delivered to the analyzer has a higher carbon dioxide content than actually exists in the furnace. Based on analysis of the sample, the controller would increase the flow of enriching gas, which would put the furnace out of control and compound the sooting problem in the probe. This condition can be detected by observing the flow rate of enriching gas. If it is significantly higher than the normal value for the indicated carbon dioxide content it indicates out-of-control furnace atmosphere. Probe sooting also may be suspected if a manual check of dew point reveals an abnormally low water-vapor content for the indicated carbon dioxide content.

An alternative method of preventing a gas reaction during cooling is water cooling of the sample probe. The water cooling prevents water-gas reaction in the sample probe. This method should not be used with dew-point analyzers when the temperature of the cooling water is below the dew point of the atmosphere. Accurate measurement of dew point will not be obtained until the sampling line is dry. For other types of analyzers, a water trap is required in the sampling line to keep condensed water out of the analyzer. Even with a trap, however, it is good practice to keep the sampling line dry and to ensure that water does not enter the atmosphere analyzer.

Probe sooting also can be prevented by inserting a high-purity quartz liner into the probe to eliminate any catalytic effect of the probe material on chemical reactions within the probe.

If a flow rate below 1.2 m/s (240 ft/min) is used without a water-cooled sample probe, analysis will be sensitive to flow rate. Flow sensitivity can be checked by varying the flow rate from $\frac{1}{2}$ to $1\frac{1}{2}$ times the normal value and by noting any change in analysis that results.

Probe Materials and Design. The probe should be made of a heat-resisting alloy that does not react with the gas sample. Probes made of iron-chromium alloys are preferred to those made of high-nickel alloys because nickel catalyzes the breakdown of carbon monoxide into carbon dioxide and soot.

If the sample flow rate required by the analyzer is known, the internal diameter of the sampling probe that will provide the desired velocity can be calculated. Permanent probes smaller than 6.4 mm (in.) in diameter are not recommended because it is difficult to prevent them from becoming plugged with soot. To facilitate cleaning, a 25 mm (1 in.) diam pipe with tee and cap often is used as the outlet through the furnace wall. When the probe is mounted in a horizontal position, it must be made with heavy-wall tubing or must be placed inside a larger tube for increased mechanical strength.

One of the more effective methods of ensuring proper flow rate is to provide a separate sample pump for each furnace, furnace zone, or carrier-gas generator being controlled. The sample pump pushes the sample gas from the furnace or generator to the analyzing instrument. This minimizes sample contamination due to leaks in the sample line because there is always a positive pressure in the portion of the line downstream from the pump. If a sample pump fails, only one sampling point, not the entire controlled system of a multiple-point recorder-controller, is affected.

Another method for measuring the atmosphere composition of each furnace or each zone of a continuous furnace is shown in Fig. 6. This central sampling installation uses one pump for one sampling port and the analyzing instrument(s), and a second separate pump for all other sampling ports to keep them purging.

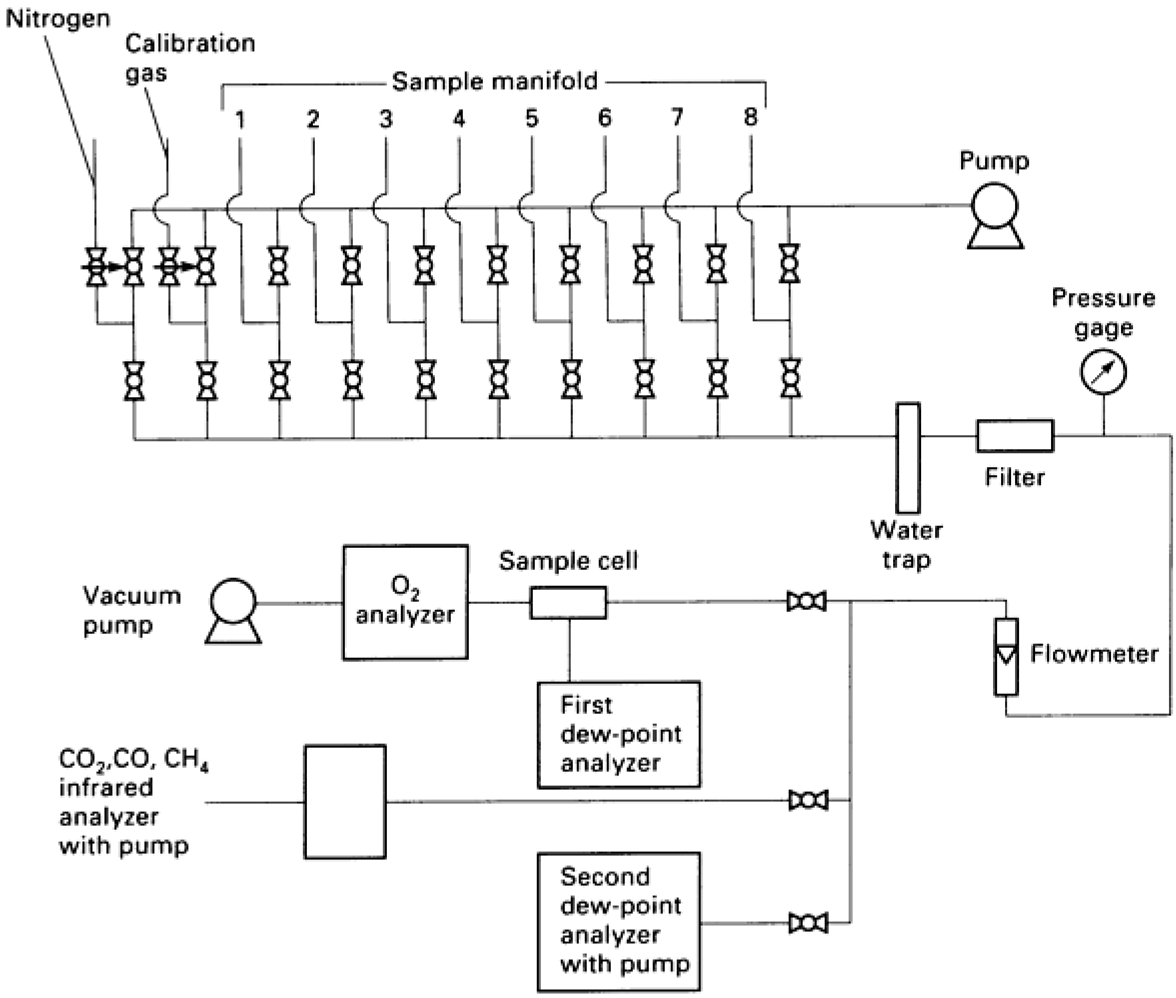


Fig. 6 Central atmosphere-sampling system that incorporates a sample manifold

The sample gases flow continuously through all sample lines. This reduces significantly the time required to purge the individual sample line selected for analysis and increases the accuracy of the entire analysis. Furthermore, the instruments can be purged with nitrogen and used to measure the sample gas when needed.

This central sampling system consists of a manifold with two shutoff valves for each sampling line (see Fig. 6). The two shutoff valves can be replaced with one three-way selection valve for each sampling line.

Permanent sampling probes should have a tee with a cleanout plug. Even though the instrument may have a filter of its own, it is wise to install a separate filter about 0.6 m (2 ft) from the gas-sampling tube in the furnace to collect any soot or dirt. An ideal filter for this purpose is the type used for compressed-air lines, which has a replaceable porous metal filter cartridge and a transparent plastic bowl. Another common type has a glass-wool filter cartridge. The filter cartridge can be inspected periodically and changed when dirty, and any condensate in the filter can be drained off by a petcock on the filter. If condensate is observed in the filter cartridge after draining, the cartridge should be replaced.

The sample line may be of copper, aluminum, or stainless steel tubing, although copper should not be used if ammonia is present in the atmosphere. A plastic tubing that will not absorb moisture also may be used if it is protected from heat. For installations in which the sample line must pass through areas where the ambient temperature sometimes falls below the dew point, steam tracing or electrical heating of the sample line is required.

Procedures and Precautions. Before a gas sample is taken from a batch-type furnace without a charging vestibule or from a continuous furnace from startup, enough time should be allowed for purging of the furnace chamber and porous refractories. Otherwise, high atmosphere dew points will occur at the beginning of a cycle and will cause condensation in the sample line. For batch-type furnaces, this delay can be accomplished automatically with an electrical limit switch operated when the furnace door or cover seal is broken and a time-delay relay set up for the proper purging time. In continuous furnaces, the sample pump should be turned off, or the sample line should be blocked with a manual valve.

In pusher-type continuous furnaces, the periodic opening of the furnace doors may cause large changes in atmosphere composition. When manual instruments are used, samples should be taken at the same time in each push cycle (preferably just before a push), in order to compare results. Use of an automatic analyzer that continuously monitors the atmosphere will permit observation of the effects of venting, resealing doors, and changing the purge flows to the vestibules. With this as a guide, the amount of variation in atmosphere composition can be reduced.

Relationship between Control Systems and Analysis. Usually, automatic equipment for controlling atmosphere-mixture ratios and carbon potential is more reliable than manual equipment, which varies in effectiveness with the skill of the operator. However, regardless of whether the process is controlled automatically, there is no substitute for alert, intelligent personnel on the operating floor. It should not be assumed that automatic process controls are the answer to control problems. Equipment malfunctions have often been noticed by operating personnel in time to switch over to manual control and avoid ruining the parts in the furnace.

Generator output and furnace-atmosphere composition are controlled by recording analyzers. These should have proportioning-type controls rather than on-off or two-position control because of the time lag in the sampling lines and the slow response of some analyzers. The preferred procedure for controlling carburizing atmospheres is to hold the flow of carrier gas constant and to vary the flow of the enriching gas. The normal procedure for generators is to set the carburetor (or mixer) to produce a rich fuel-air ratio and then to control the flow of air in a bypass line around the carburetor.

When the carbon potential of an atmosphere is to be controlled and one constituent of the atmosphere is to be measured, the set point must be determined on the basis of chemical analysis of the carbon content of either shim stock or turnings from test bars. Equilibrium data can be used to determine the approximate set point, but equilibrium conditions do not always exist in furnace atmospheres. By setting the limit on the furnace to obtain the final equilibrium condition required, the enriching gas flow is minimized. The controller will take over the monitoring of the furnace near the end of the cycle to deliver much lower flow rates.

Control of temperature is usually accomplished automatically, with a single-point or multiple-point recorder-controller regulating the heat input to the furnace. When several furnaces or several zones in a single furnace need to be controlled, it may be necessary to use a separate (dedicated) temperature controller for each furnace or each zone, particularly if different set points are used. Location of thermocouples that sense the control point is important, especially in continuous furnaces under zone control or in situations where furnace doors are opened frequently.

Simple elapsed-time controllers frequently are used to trigger successive events in the carburizing cycle, such as successive pushes in a pusher furnace or the end of carburizing and the beginning of diffusion in a batch furnace. In some types of continuous furnaces cycle time is regulated by the speed at which parts are moved through the furnace.

For batch furnaces with programmed temperatures, atmosphere set points also must be programmed. Shims removed at the end of each temperature period will serve as guides in determining correct set points.

When a furnace or generator is first placed under automatic control, it is considered good practice to monitor carbon dioxide content continuously and to correct any variations caused by equipment condition. The following list gives the interdependent variables that must be considered to establish and maintain automatic control of the carbon dioxide content in a carburizing atmosphere:

- Type of furnace
- Condition of equipment, including tightness and ability to maintain uniform temperature
- Size and type of typical work load
- Composition and uniformity of carrier gas
- Composition and uniformity of enriching gas
- Frequency of sampling and controlling
- Type of control: on-off or proportional
- Sensitivity of controller
- Width of proportional band on proportional controllers
- Normal and maximum response times of the motor-driven control valve
- Flow rate through fully open control valve
- Normal time for atmosphere to stabilize following a change in a controlled variable

Dual controls offer certain advantages for improving the stability and responsiveness of automatic control systems when the atmosphere gas is not of uniform composition, or when there are frequent large variations from normal operating conditions. Under these conditions, measurement of a single constituent of the furnace atmosphere will not necessarily lead to the desired level of process control. In these cases, control through analysis of only one atmosphere constituent results in a relatively large percentage of off-quality production. Simultaneous analysis and control of two atmosphere constituents is usually sufficient to overcome the more common problems.

Dual control is most often accomplished by either infrared ratio control of both carbon monoxide and carbon dioxide, or simultaneous independent analysis of carbon dioxide and dew point. In infrared ratio control, a two-column analyzer is used, with one column sensitized to carbon monoxide and the other to carbon dioxide. The output from the two columns is sent by means of a tapped slidewire to a third unit that actually controls the flow of enriching gas. The use of a tapped slidewire allows the output of the analyzers to be read as the ratio $(P_{CO})^2/(PCO_2)$, which is directly proportional to carburizing potential.

A system for simultaneous analysis of both carbon dioxide and dew point normally consists of two independent analyzers connected to a single sampling line. In the usual arrangement, the carbon dioxide analyzer establishes primary control, and the dew-point controller activates an alarm circuit whenever the water vapor content of the atmosphere deviates from prescribed limits.

Infrared Analyzers

Infrared analyzers are based on the principle that any compound present in the mixture will absorb infrared energy in proportion to its concentration in the mixture. The wavelengths absorbed are different for each compound. Elemental gases such as hydrogen and oxygen do not absorb infrared radiation and therefore cannot be analyzed by this method.

Infrared analyzers are normally used to measure carbon monoxide, carbon dioxide, and methane. For automatic control of carburizing processes where the carrier gas and enriching gas are reasonably uniform in composition, infrared analysis of carbon dioxide was considered the most accurate method and was the most widely used. The oxygen probe has recently gained acceptance. Infrared analyzers are normally connected to a recorder-controller or a scanner-programmer-printer of either the single-point or multiple-point type, which actually performs the control function.

In multiple-point control assemblies, a single analyzer is coupled to a system of gas-sample valves and control circuits, one set of sample valves and a control circuit for each point being analyzed and controlled. After each analysis is made and the resulting control signal is transmitted to the appropriate control valve, an automatic switching mechanism disconnects the sample valves and control circuit and energizes the set of sample valves and the control circuit for the next control point. A maximum of eight different furnaces, furnace zones, or carrier-gas generators is usually recommended for a single analyzer.

An infrared analyzer responds rapidly when the analysis function is triggered by the recorder-controller. Even so, time is required for transmittal of the control signal, and for flushing of the sample cell in the analyzer, so that the composition of a new sample will not be altered by remnants of the previous sample. Successive analyses can be made at intervals of about 1 min, allowing approximately 30 s for flushing and analysis and the remaining 30 s for controlling.

Positive-Filtering Analyzer. In this type of analyzer (shown in Fig. 7), an electrically heated helix of nickel-chromium alloy wire is the source of infrared radiation. Radiation from this source is split into two beams by mirrors. Both beams are simultaneously interrupted by a motor-driven chopper. The resulting pulses of radiation cause alternate heating and cooling of gas in the two sides of the detector. A condenser microphone consisting of a movable metal diaphragm and a fixed metal plate is mounted between the two sides of the detector. A measurement of differential pressure can thus be obtained.

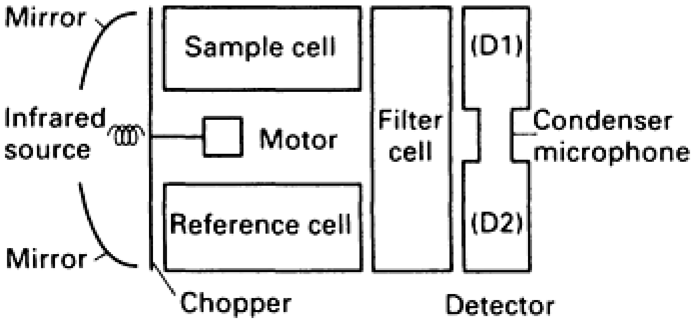


Fig. 7 Components of a positive-filtering infrared analyzer for measuring carbon monoxide, carbon dioxide, and methane contents of an atmosphere

The gas stream to be analyzed is continuously passed through the sample cell. The reference cell is filled with a gas that does not absorb infrared radiation, such as nitrogen or argon. A filter cell common to both beams is filled with a mixture of the background gases present in the sample-gas stream; the mixture should contain all constituent gases that absorb infrared radiation other than the specific gas being measured. The latest instruments on the market do not need to have the reference cell filled with a mixture of the background gases.

To sensitize the analyzer for measurement of carbon dioxide, both sides of the detector (D1 and D2) are filled with carbon dioxide. If the radiation in the two beams is identical, equal pulses of energy will strike both sides of the detector simultaneously, causing identical heating effects that will cancel each other and thereby produce no motion of the flexible membrane. If a gas containing some carbon dioxide is admitted to the sample cell, energy pulses reaching the D1 side of the detector (Fig. 7) will be reduced. The gas in D1 will be heated less than the gas in D2, and the pressure differential will cause a movement of the flexible membrane. The higher the concentration of carbon dioxide in the sample cell, the lower the energy level reaching D1, resulting in a higher signal output.

A positive-filtering infrared analyzer has good sensitivity and accuracy; the usual stated accuracy is 1% of full scale. Its direct-current output is 0 to 20 mA, 4 to 20 mA, or 0 to 100 mA. When a positive-filtering analyzer must be removed from service for repair, it can be returned to service without being conditioned prior to use.

Negative-Filtering Analyzer. In this type of analyzer (shown in Fig. 8), an electrically heated nickel-chromium alloy filament is the source of infrared radiation. Infrared energy passes through the sample cell and a filter cell and is separated into two beams by sensitizing cones. These two beams fall on detectors D1 and D2, which are thermopiles connected in series opposition to measure the difference in energy level of the two beams.

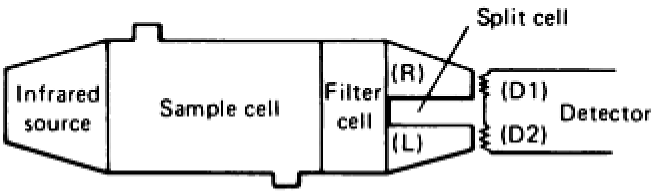


Fig. 8 Components of a negative-filtering infrared analyzer for measuring carbon monoxide, carbon dioxide, and methane contents of an atmosphere

Sensitization of the analyzer for measurement of carbon dioxide is accomplished by filling the right sensitizing cone (R in Fig. 8) with carbon dioxide, the left sensitizing cone (L) with a nonabsorbing gas such as nitrogen, and the filter cell with a mixture of interfering gases. Interfering gases are any gases present in the sample-gas stream that have any absorption lines that coincide with absorption lines for carbon dioxide. The newest such instruments on the market have deleted the filter cell as a component of the analyzer.

When no carbon dioxide is present in the sample flowing through the sample cell, radiation falling on detector D2 is undiminished, but radiation passing through the right sensitizing cone and falling on detector D1 is reduced to nil because of absorption by the pure carbon dioxide in the right cone. As a result, the two detectors produce a net signal that is proportional to the radiation unbalance.

If a gas sample containing some carbon dioxide is now passed through the sample cell, the radiation falling on detector D2 will be reduced by the energy absorbed in the sample cell. There will be no change on detector D1 because the pure carbon dioxide in the right sensitizing cone removes all radiation frequencies characteristic of carbon dioxide. The resulting change in net signal from both detectors is proportional to the concentration of carbon dioxide in the sample cell.

If a gas sample containing other gases that absorb infrared radiation is passed through the sample cell, an equal amount of radiation will be absorbed from the beams reaching both detectors, and the output of the analyzer will remain proportional to the amount of carbon dioxide present in the sample. If an interfering gas is present in the sample, the gas in the filter cell will ensure that its effect cannot be detected and that the output is still proportional to the carbon dioxide content.

A negative-filtering infrared analyzer has good sensitivity, good stability, and no moving parts. It has a nonlinear output so that the scale on the recorder is expanded at the low end of the scale (where most carburizing is controlled) and compressed at the high end. The stated accuracy at the low end of the scale is ±0.002% at a set point of 0.05% CO_2. When a negative-filtering analyzer is removed from service for repair, it must be conditioned for 24 h, after repairs have been made, before it can be put back into service.

Solid-State Detector Analyzer. This type of analyzer is similar in operation to the positive-filtering analyzer, except that the chopper is generally used to alternate the energy through the sample cell and the reference cell. The filter cell and condenser microphone detector are eliminated and replaced by a narrow band-pass interference filter placed on top of a solid-state detector, as shown in Fig. 9. The energy from the sample cell and reference cell is collected by end mirrors and directed to the filter/detector assembly. The band pass of the interference filter is set up in such a manner that the instrument becomes specific for either CO, CO_2, or methane. Because these detectors are very small, they can be stacked side by side, and multiple components can be analyzed in a single instrument. A solid-state detector infrared analyzer has good sensitivity and accuracy. The usual stated accuracy is 1% of full scale. Direct-current outputs are available as required, and repairs tend to be more routine than with either the positive-filtering analyzer or the negative-filtering analyzer.

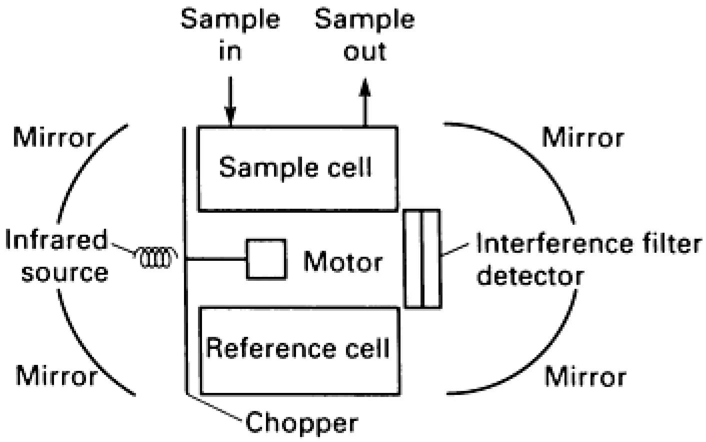


Fig. 9 Components of a solid-state detector infrared analyzer for measuring carbon monoxide, carbon dioxide, and methane contents of an atmosphere

Advantages of Infrared Analyzers. The use of an infrared analyzer-control system on endothermic generators and carburizing furnaces will result in narrower deviations in gas analyses. Such a system provides more uniformity of case depth and helps keep generators and furnaces free of soot.

Examination of the daily charge record of the analyzer will reveal changes in the condition of the atmosphere. For example, work on the natural gas pipelines in the field may cause a variation in the heat content of the natural gas. This will be indicated by the analyzer, and controls automatically restrict the effect of this change.

In one plant the chart revealed that rapid and severe increases in the carbon dioxide concentration and the dew point of the furnace atmosphere occurred with each opening of the discharge door of a continuous carburizing furnace. This problem was eliminated by improving the seal on the inner door and by adding a flame curtain to the outer door.

An infrared analyzer-control system will also compensate for the difference in the volume of natural gas required by a heavily loaded furnace on a short heating cycle and that required by a lightly loaded furnace on a long heating cycle. When a furnace or generator is being started, the system will provide a continuing check of atmosphere conditions so that equipment can be put into service as soon as proper operating levels are reached, without the necessity of frequent manual checking of dew point.

Limitations of Infrared Analyzers. An infrared analyzer is relatively expensive and complex, and its maintenance and repair require the skills of a trained electronics specialist. Malfunctions are not readily detectable; the unit may continue to operate despite failure of several components but will give erroneous readings. However, instruments that incorporate the most recent state-of-the-art technology include microprocessors having self-diagnostic features to announce and to identify analyzer malfunctions. Automatic control valves must be checked to ensure that they are operating properly and are not locked in the completely open or closed positions. The unit must be adjusted frequently to reflect changes in minor variables, such as a change in the energy content of the gas. Therefore, to ensure the accuracy of the system, trained personnel must daily recalibrate the unit against a gas of known composition.

Finally, when very high dew points are encountered, enough moisture may condense in the lines and be carried to the sample cell to damage the cell or render the system inoperative until the cell has been dismantled and cleaned. Damage caused by moisture may be prevented by installation of a moisture trap or an electrical warning system ahead of the sample cell.

Dew-Point Analyzers

Dew-point analyzers measure the partial pressure of water vapor in the furnace atmosphere. Dew point is defined as the exact temperature (at a given pressure) at which a mixture of gases will begin to precipitate its moisture content. When air and gas are mixed in consistent fixed proportions and the mixture is heated to allow chemical reactions to reach equilibrium, the dew point will reflect the chemical balance of the various components comprising the reacted products.

The use of dew point for controlling carbon potential is a fast, inexpensive, and relatively simple procedure. Control of endothermic-based atmospheres by the dew-point method is widely accepted in industry.

Manually operated instruments for measuring dew point are inexpensive, rugged, and simple, and serve satisfactorily under normal operating conditions. Automatic instruments are available also.

Dew-Cup Instrument. The simplest instrument for measurement of dew point is the dew cup, which appears in Fig. 10. The gas sample is drawn from the furnace or generator across the outside of a polished cup made of chromium-plated copper. The cup is enclosed in a glass container so that the moisture can be seen condensing on the cup surface when the dew point is reached. The cup surface is cooled progressively by dropping small pieces of dry ice in acetone (or methanol) inside the cup until the dew point is reached, as indicated by condensation on the cup surface at a temperature indicated by a thermometer in the acetone.

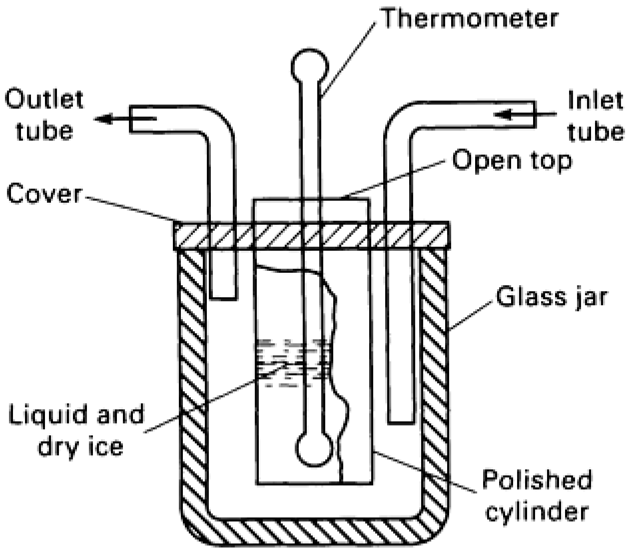


Fig. 10 Components of dew-cup apparatus for measuring dew point

The dew cup is most accurate for measurement of dew points above the freezing point of water. At dew points lower than 0 °C (32 °F), there is the possibility of supercooling, with an attendant low dew-point reading.

Use of the dew cup requires that the operator possess a considerable amount of skill and consistency. However, it is not recommended for close control. Incorrect dew-point readings may result if the atmosphere is sooty, if there are leaks in the dew cup or sampling lines, if the flow of atmosphere is too fast, if the temperature is lowered too quickly, or if the lighting conditions are poor in the area where the dew point is being observed.

Fog Chamber. The fog chamber, shown in Fig. 11, is another instrument for manually measuring dew point. It is used throughout industry because it is portable and gives consistent and accurate readings over an extremely wide range of dew points but requires no external cooling or mechanical refrigeration. The fog chamber operates on the principle that a rapidly expanding gas cooled adiabatically will produce a fog only when specific requirements of pressure drop, ambient temperature, and moisture content in the gas sample are satisfied.

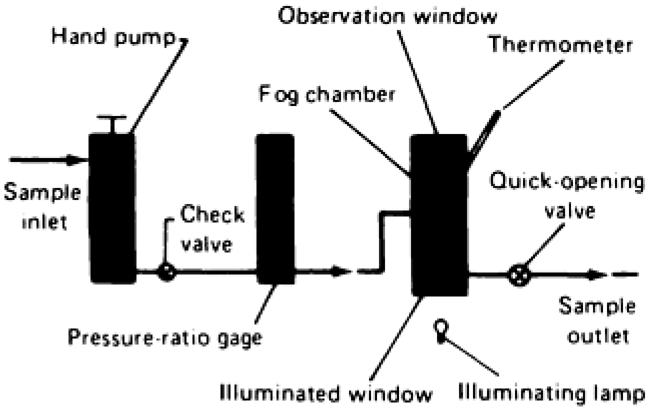


Fig. 11 Components of fog-chamber apparatus for measuring dew point

The atmosphere sample to be tested is drawn into the apparatus and held under pressure in an observation or fog chamber by a small hand pump. A pressure-ratio gage indicates the relationship between the pressure of the furnace atmosphere sample and the ambient atmospheric pressure. The temperature is indicated by a thermometer that extends into the observation chamber. The atmosphere sample is held in the observation chamber for several seconds to stabilize the temperature, after which the quick-opening valve is depressed, releasing the pressure and creating an adiabatic cooling. This may cause a visible condensation or fog to be suspended in the chamber. The fog is easily observed with a lens system that provides a beam of light in the fog chamber when the quick-operating valve is depressed. The procedure is repeated to find the end point, that at which the fog disappears. The dew point is then determined by referring to a chart that is based on the initial temperature reading of the thermometer and the pressure-ratio-gage reading at the point at which the fog disappeared.

Chilled Mirror. One of the first methods devised for automatic control of dew point involves the use of the chilled-mirror instrument, which is presented in Fig. 12. This method uses refrigeration and heating to condense and evaporate moisture from an illuminated mirror while the temperature of the mirror is being monitored. A photoelectric cell is used to detect the intensity of the light that the mirror reflects from the source of illumination. The intensity of this reflection depends on the amount of moisture present on the mirror. When the photoelectric cell registers a reflection that represents a deviation from a desired dew point, it generates an electric signal that in turn actuates appropriate auxiliary equipment at the furnace or atmosphere generator, which restores the dew point to the desired level.

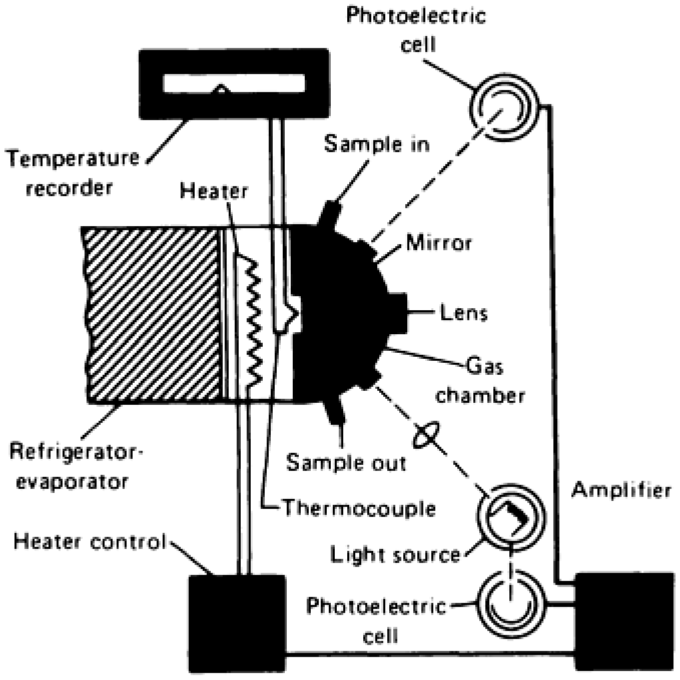


Fig. 12 Components of chilled-mirror apparatus for measuring dew point

This method is satisfactory for controlling relatively clean atmospheres, such as those consisting of mainly nitrogen or hydrogen, but it is not recommended for use with endothermic atmospheres unless maintenance problems created by dust and soot are solved. Chilled-mirror instruments are subject to errors when hydrocarbons or other vapors are present in the sample-gas stream.

Chilled-Metal Instrument. The chilled-metal method of determining dew point uses two refrigerated platinum electrodes that condense the moisture from a gas sample to complete an electrical circuit. The temperature of the electrodes is recorded as the circuit is completed, thus giving the dewpoint temperature. A heater is employed to evaporate the moisture from the sample chamber and electrodes, to prepare the instrument for another determination. Dirt and sooting present problems as with the chilled-mirror instrument. Figure 13 shows a chilled-metal instrument.

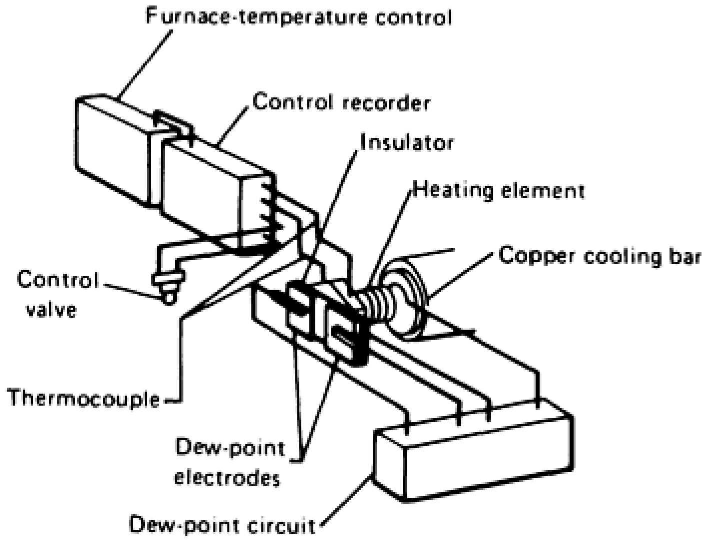
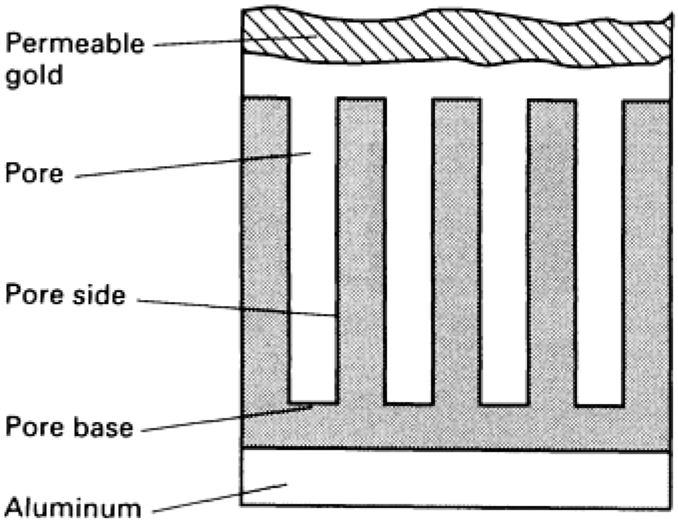


Fig. 13 Components of chilled-metal apparatus for measuring dew point

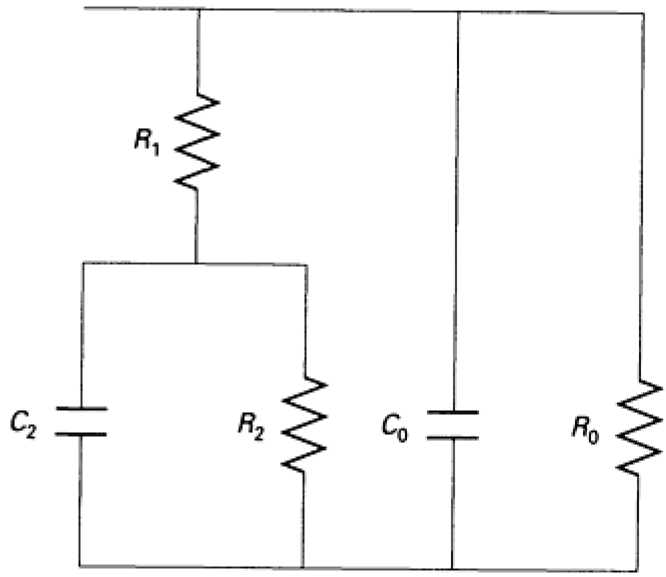
Lithium Chloride. Another type of dewpoint instrument that is widely employed for continuous automatic control uses as its basis for operation the behavior of a hygroscopic salt (lithium chloride) when in contact with water vapor. Dry lithium chloride will absorb water at room temperature and dissolve, forming a saturated solution. This solution may then be heated to the temperature at which the evaporation tendency of the moisture just matches the absorption tendency of the salt. This temperature is directly related to the dew-point temperature.

The instrument used consists of a thin metal tube wrapped with glass tape that is impregnated with dry lithium chloride. The tape is overwound with two silver wires and covered with a perforated metal guard. When the lithium chloride is exposed to moisture and becomes partly saturated, it becomes conductive, and a current is passed through the silver wire, driving off the moisture until equilibrium is achieved. The temperature is read from a sensor inside the metal tube. A limitation of this instrument is its susceptibility to contamination by raw ammonia, which makes it unacceptable for control of carbonitriding atmospheres.

Aluminum-Oxide Dew-Point Analyzer. The sensor in this analyzer consists of an aluminum substrate that is anodized to form a thin porous layer of aluminum oxide over which a very thin coating of gold has been deposited. The aluminum and gold form two electrodes of an aluminum-oxide capacitor (see Fig. 14). Water will diffuse through the gold layer and equilibrate on the pore walls. The number of water molecules absorbed on the oxide structure determines the conductivity of the pore walls. Each value of pore-wall resistance provides a value of electrical impedance that is related to the water vapor pressure, thus producing a dew-point reading.



(a)



(b)

Fig. 14 Aluminum-oxide dew-point sensor. (a) Layered construction. (b) Circuit equivalent. C_0, capacitance of aluminum-oxide layer; C_2, pore-base capacitance; R_0, resistance of aluminum oxide; R_1, pore-side resistance; and R_2, pore-base resistance

The aluminum-oxide dew-point analyzer is used for continuous automatic monitoring and control of heat-treating atmospheres. Because the maximum operating temperature of the aluminum-oxide sensor is 70 °C (160 °F), a sample gas stream must be taken from the furnace and cooled prior to taking the dew-point measurement. Current state-of-the-art liquid oil filters are the most efficient method of removing submicron solid metallic particles that may be deposited on the aluminum-oxide layer and are the source of inaccurate dew-point readings.

The standard furnace gas-sampling system used in an aluminum-oxide dew-point analyzer is shown in Fig. 15. The furnace atmosphere sample stream initially flows into the sample system via a stainless steel needle valve. The sample stream then passes through two filters: an oil filter containing polyethylene in liquid form to remove the solid particles, and a sintered stainless steel filter to entrap particles over 7 μm (280 μin.) in diameter. The sample stream then proceeds

to the sample cell, where the moisture-sensing probe is located, flows through a second needle valve, and finally exits the sample system via the vacuum pump.

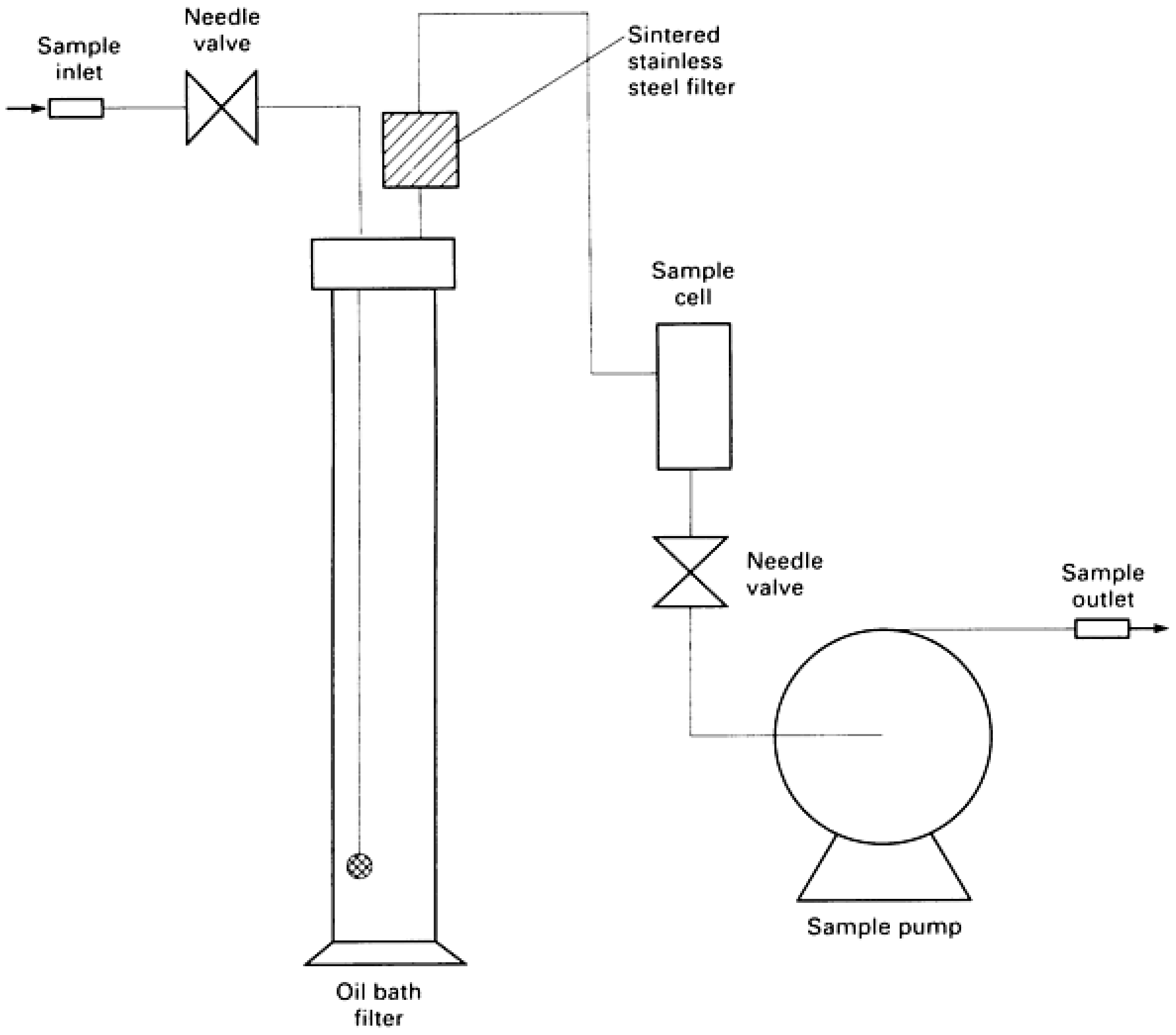


Fig. 15 Standard furnace gas-sample system incorporating an aluminum-oxide dew-point sensor in the sample cell

Limitations of Aluminum-Oxide Dew-Point Analyzer. This instrument cannot be relied upon to provide consistently accurate readings because it tends to drift with ambient and sample-gas temperatures. Furthermore, when exposed to the air or a wet gas atmosphere, it cannot be reused until the sensing probe has been either dried or recalibrated.

Silicon-Chip Dew-Point Analyzer. This instrument uses a capacitive-type sensor of silicon composition. An attached thermostatically controlled heating element maintains the temperature of the sensor in excess of the normal ambient or sample-gas temperatures. Because the sensor is calibrated at the elevated operating temperature of 45 °C (115 °F), the accuracy of the analyzer is unaffected by gas temperature variations below 45 °C (115 °F).

Instrument advantages include:

- Wide operating dew-point range: -80 to 80 °C (-110 to 175 °F)
- No temperature-induced error between -40 to 45 °C (-40 to 115 °F)
- Practically independent of flow rate
- High stability

- Rapid removal of moisture and hydrocarbon contaminants
- Extremely rapid response

Instrument limitations include:

- Does not tolerate gas samples containing oil, ammonia, or corrosive components
- Insufficient data to evaluate analyzer performance in hydrocarbon(s), carbon monoxide, and carbon dioxide atmospheres because instrument is a recent heat-treating innovation

Typical Limitations of Dew-Point Analyzers. Although dew-point analyzers can reflect changes in dew point with a fair degree of accuracy, these changes do not always correlate exactly with changes in carbon potential. An error of only a few degrees Celsius can represent an error of 0.1 to 0.2% C in evaluation of the carbon potential of a given atmosphere, which can be as much as a 25% deviation if the desired carbon content is near the eutectoid composition.

With respect to initial investment, automatic dew-point analyzers and controllers represent one of the lower-cost approaches to automatic control of carbon potential. However, the cost of maintenance of automatic dew-point equipment is a matter of some consequence. The equipment will tolerate virtually no dirt in the sampling system and consequently requires frequent cleaning and replacement. A refrigeration system is generally used to lower the gas temperature so that dew point can be measured, and problems may attend the operation of any refrigeration system.

In any dew-point-analysis system, condensed moisture in the sampling lines or filters will result in erroneous high readings that will continue until all moisture has been evaporated by purging the sampling lines and changing the filters. It is possible for condensate to form if the temperature within the sampling lines at any time falls below the dew point of the gas being analyzed. An efficient filtering system must be used with automatic equipment to keep contaminants out of the sampling system of the instrument.

In most automatic systems used for checking more than one unit, rather long purge times are required between dew-point readings if the dew points of the various units are not reasonably close together. For example, if the dew points in two furnaces differ by 20 °C (36 °F), long purge times between readings may be required for accurate results. In some automatic systems, it might be impossible to record successive dew points of -18 and 10 °C (0 and 50 °F) because formation of excessive moisture on the sensing head might render the system inoperative until the moisture can be purged from the system.

The silicon-chip dew-point analyzer (see the section "Aluminum-Oxide Dew-Point Analyzer" in this article) has a rapid response and removes excessive moisture very rapidly, but there is insufficient data to evaluate its performance in an atmosphere containing hydrocarbon(s), carbon monoxide, and carbon dioxide.

Other disadvantages of a dew-point system are the lack of a method of accurate calibration, such as is available with a system for controlling carbon dioxide, and the fact that calibration is required if the system is to reflect the hydrogen content of the atmosphere.

Oxygen Probes

In an endothermic-based or exothermic-based carburizing atmosphere, one of the reversible reactions, given as Eq 16, is:

$$CO + \frac{1}{2}O_2 \rightleftharpoons CO_2$$

The carbon potential of such an atmosphere is inversely related to the square root of the partial pressure of oxygen, as indicated in Eq 19. Therefore, by monitoring the concentration of oxygen, carbon potential can be defined without considering the concentrations of hydrogen, water vapor, or carbon dioxide. The only atmosphere constituent that directly influences the relationship is carbon monoxide. As long as the carbon monoxide content is reasonably constant, carbon activity can be controlled by controlling oxygen content. The advantage of this method of carbon-potential control is that it is less sensitive to changes in carbon monoxide and/or hydrogen content of the carburizing atmosphere. This can be

easily ascertained by comparing Eq 19, where it is observed that a_c is proportional to P_{CO}; with Eq 11 and 15, in which a_c is proportional to P^2CO and to the product $P_{CO}PH_2$, respectively.

An oxygen probe usually consists of two platinum electrodes separated by a solid electrolyte in the form of a gas-tight zirconia tube closed at one end (see Fig. 16). The probe, which is enclosed in a ceramic sheath or heat-resistant alloy, is inserted into the furnace. The furnace atmosphere enters the probe through a window in the sheath and contacts the outer electrode. The other electrode, inside the zirconia tube, is in contact with air, which serves as a reference gas of constant oxygen content. The difference between the partial pressure of oxygen in the furnace atmosphere and that in air induces an electromotive force (voltage), or emf, across the electrodes. The partial pressure of oxygen in the furnace atmosphere is determined by the voltage output (emf) of the sensor. Thus, carbon potential can be controlled by controlling the temperature in the furnace and the voltage output of the sensor because, as shown in Fig. 17, an isothermal relationship exists between carbon content (wt%) and the emf of the sensor. The voltage output of the sensor is fed directly into an electronic control circuit. The control circuit may be designed to operate in an on-off mode, a proportional mode, or a proportional-plus-reset mode, depending on the smoothness of response desired. The stated accuracy of most control systems based on the oxygen probe is ±0.05 wt% of carbon potential over the temperature range of the sensor.

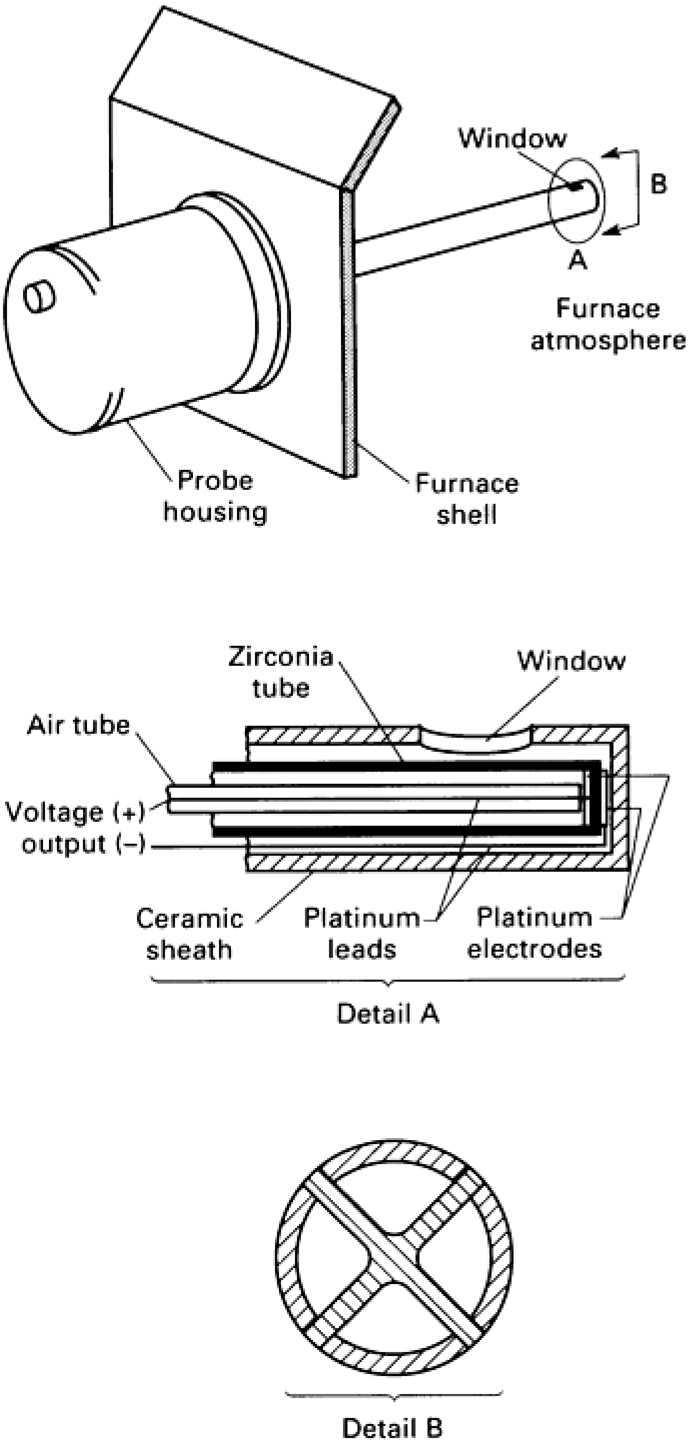


Fig. 16 Components of a typical oxygen probe for controlling carburizing atmospheres. Detail B shows construction of X-cap tip.

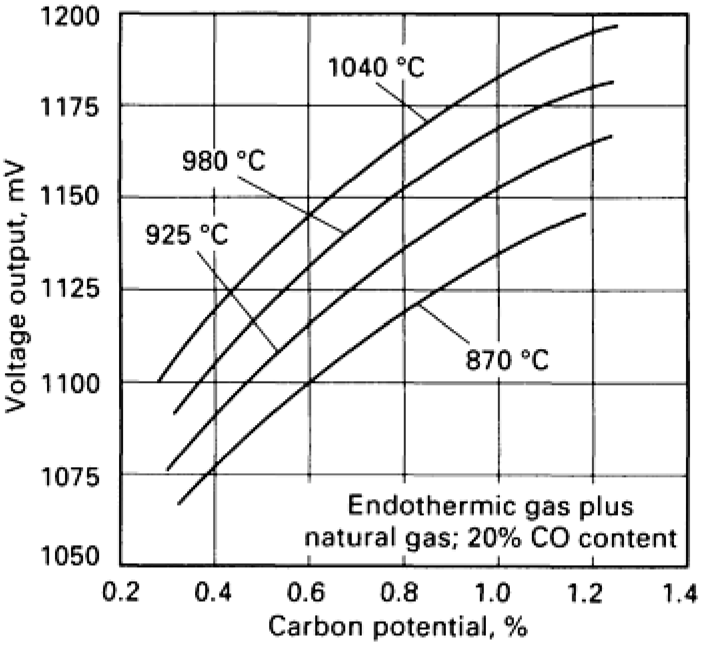


Fig. 17 Voltage across electrodes of a typical oxygen probe as a function of carbon potential at four temperatures, for endothermic gas enriched with natural gas and containing 20% CO

The correlation between the output of an oxygen probe and actual carbon potential has been confirmed experimentally, as shown in Fig. 17.

Advantages. The response of an oxygen probe is almost instantaneous and is directly related to changes in carbon potential. There is no loss in sensitivity at high temperatures, that is, 980 to 1040 °C (1800 to 1900 °F). Calibration, cleaning, and the maintenance associated with gas-sampling systems are not required; the probe is inserted directly into the atmosphere through a hole in the furnace wall. Sudden or substantial changes in the concentrations of carbon dioxide or water vapor do not cause pronounced control problems, as such changes do with infrared analyzers.

Disadvantages. The major disadvantage of oxygen probes is that the ceramic probe element must be replaced periodically, normally at intervals of one year or longer. Detachment of the outer electrode from the zirconia tube causes most probe failures requiring replacement. (The outer electrode is the one exposed to the furnace atmosphere.) Other causes of failure are mechanical and thermal shock, which crack the brittle ceramic components. In most instances, however, the increased reliability and decreased maintenance and supervision costs more than offset the expense of periodic replacement of the probe element.

The catalytic effect of the platinum outer electrode and the nickel alloy tube greatly reduces the accuracy of the probe. This catalytic effect can influence the hydrocarbon enrichment reactions represented by Eq 7 and 8, resulting in the atmosphere at the platinum electrode having a higher carbon potential than the atmosphere in the other portions of the furnace. This creates two problems:

- Because product formed has lower carbon content than expected, the magnitude of the error increases with the percentage of hydrocarbon enrichment
- Platinum electrode is plagued by increasing buildup of soot on its surface

To minimize the problems incurred by the catalytic effect described above, the following steps are recommended:

- Increase the furnace atmosphere flow at the sensing element
- Position the sensor near the circulation fan or in an area with a high furnace atmosphere flow. Note that furnaces lacking circulation fans are poor candidates for *in situ* oxygen probes

- Use an X-cap tip and open porting of the protection tube to maximize atmosphere flow (see Fig. 16)

Heavy sooting will impede atmosphere flow to the cell, thereby causing erroneous carbon-potential readings. Soot deposition usually occurs between the probe window and the furnace-shell portion of the insulating ceramic tube.

The installation of an air-purge system can eliminate the sooting problem. A low but controlled airflow rate of approximately 0.06 m^3/h (2 ft^3/h) can provide a gentle burnoff of the soot deposits without chilling the tube. The control must be set offline during the purge operation. Purge air must originate from a low-pressure source to prevent injection of a dangerously excessive volume of air into the probe. Oxygen probe manufacturers should be consulted for details.

Orsat Analyzer

The Orsat analyzer has long been the principal tool for analysis of furnace atmospheres. However, chromatographic and infrared analyzers have been gradually displacing it because of their greater speed and sensitivity. The Orsat analyzer has a comparatively low initial cost.

Operation of this equipment involves bubbling of a sample of an atmosphere through a series of solutions, each designed to absorb one of the gaseous constituents. Hydrogen, methane, ethane, and sometimes carbon monoxide are determined by controlled oxidation to water and carbon dioxide. The Orsat analyzer employs a fixed sequence of testing for the various constituents, and this sequence must always be followed.

Advantages. The Orsat analyzer has the advantage of low initial cost, simplicity of operation, portability, and ability to analyze accurately all constituents normally encountered in heat-treating atmospheres.

There are no complicated electrical circuits to maintain, and no standardization procedures are required. The operator must be certain only that solutions are reasonably fresh and that all connections are gastight. Although accuracy and reproducibility of results depend largely on the technique of the operator, satisfactory results can be obtained by nontechnical personnel after relatively short periods of training. Accuracy is actually dependent on the scale used. Higher concentrations are more accurate than lower concentrations. The ability to determine concentrations of all normal atmosphere constituents permits detection of air leaks, water leaks, or degeneration of the catalyst in the generator.

Disadvantages. The principal disadvantages of the Orsat analyzer are the long analysis time required compared to that required by the newer methods and the relatively large errors possible in determining the carbon dioxide contents of most furnace atmospheres. Automatic control of the furnace atmosphere is impractical.

Carbon dioxide and oxygen-content determinations can generally be made in about 5 min, whereas a full analysis requires 30 min or more. In contrast, a full analysis for all normal components of an atmosphere can be made in about 5 min with a gas chromatograph (see the subsequent section "Gas Chromatography") or in approximately 30 s using a set of infrared, oxygen, hydrogen, and dew-point analyzers.

To achieve high carbon potentials, carbon dioxide content must be maintained at low concentrations, generally from 0.1 to 0.5%. Hence, a small error in determination of carbon dioxide content will result in a relatively large inaccuracy in the ratio of carbon monoxide to carbon dioxide, which is used for determining carbon potential. Therefore, a method that provides more accurate analysis of carbon dioxide content is preferred whenever the heat-treating process employed requires close control of carbon potential.

Hot-Wire Analyzer

The hot-wire analyzer is based on the principle that carburization of steel (except high-alloy grades) is completely reversible. With the exception of nitrogen, poorly equilibrated atmospheres high in inert gases are a possible exception to this principle. The surfaces of thin and thick pieces of steel eventually come to essentially the same equilibrium with a gas of given composition and temperature. The electrical resistivity of steel is a linear function of carbon content over the range from 0.05% C to saturation. Therefore, a length of fine iron wire will exhibit a resistance proportional to its average carbon content, and at equilibrium, proportional also to the carbon potential of the surrounding gas. This is the potential that would be effective in carburizing loads of production parts.

Basic Design Configuration. The sensor of a hot-wire analyzer is a fine iron or iron-alloy wire, about 0.08 mm (0.003 in.) in diameter and about 32 mm ($1\frac{1}{4}$ in.) long that is shaped like a "U." This wire and its supporting structure are called the sensor tip and are mounted on a long holder that provides for room-temperature connections. The tip can be readily and economically replaced.

The sensor is housed in a protection tube that is a $\frac{3}{4}$ IPS pipe assembly, fitted for gas and electrical connections at the cold end and equipped with a small sampling hole at the hot end. This tube is inserted through the furnace wall or lid so that a sample of gas from the work load can be drawn over the sensor while the sensor is held substantially at work temperature.

The measuring circuit is a Wheatstone bridge equipped with compensators for furnace temperature and for calibration of the sensor. Suitable circuitry for driving an optional recorder is provided. Also included is circuitry for proportionally operating a control solenoid valve or a motorized proportional valve.

A pump and related flowmeters and valves are provided to ensure positive flow of sample gas over the sensor. This gear also provides protection of the sensor when the sample gas is not protective, including during standby periods.

The instrumentation is packaged in a 405 by 510 mm (16 by 20 in.) portable enclosure or in a 485 by 660 by 1650 mm (19 by 26 by 65 in.) free-standing panel. The latter package is also available with a small sensor-heating furnace, in which the sensor in its protection tube can be located and to which the sample gas from any remote point can be brought and then reheated to the preferred temperature before being passed over the sensor for measurement.

Advantages. The hot-wire analyzer can make an *in situ* measurement unaffected by sampling-system disturbances, and the measurement is of carbon potential rather than of gas composition. The readout is directly in terms of percent of carbon. Accuracy is normally ±0.05% C. The equipment is relatively simple and easy to maintain, and replacement components are readily available and inexpensive. The method is broadly applicable to any gas mixture exhibiting carbon potential, and measurements can be made either in the work furnace (*in situ*) or remotely in a small furnace that holds the sensor at constant temperature and reheats the sample gas before measurement.

Limitations of the hot-wire analyzer include:

- The hot-wire sensor cannot function in atmospheres so extensively rich that soot is deposited
- If the sensor is exposed to oxidizing gas above 425 °C (800 °F), it will be damaged (calibration shifted) or destroyed. Therefore, the sensor requires the protection of a good purge gas, such as nitrogen or endothermic generator gas
- If sulfur and some other contaminants are in the atmosphere, they can render the fine wire sluggish and insensitive
- In carbonitriding atmospheres, the sensor responds to nitrogen as well as to carbon, and therefore the readout consists of the sum of carbon and nitrogen
- A response speed below 815 °C (1500 °F) is too slow for automatic control of a short ($\frac{1}{2}$ h) cycle. However, speed of response is always faster than that of the work load; therefore, measurement is always feasible
- In high-nitrogen carburizing atmospheres ($\geq$70 vol% N_2) where equilibration is likely to be poor, the fine sensor wire can sometimes achieve higher carbon concentrations than the more massive workpieces; therefore, the readings might be too high

Economic Considerations. The hot-wire analyzer is among the least complicated single-point carbon-potential instruments and therefore is also one of the least expensive, considering original cost and upkeep. The most expensive component that needs occasional replacement is the alloy-protection tube.

The system requires attention from a trained operator and needs calibration two or three times a week.

Uses. The hot-wire method is useful for measurement and control of any atmosphere capable of transferring carbon to and from steel surfaces. The composition of the gas mixture need not fall into a conventional pattern, and the composition can be varied, such as when nitrogen additions are made or when peak shaving is practiced. The temperature range of application is 790 to 1040 °C (1450 to 1900 °F), and the carbon range is from 0.10% C to saturation.

Operation. The sensor is installed in its work furnace port under a flow of protective gas. Interlocks are usually arranged to activate furnace sampling and furnace control during the at-heat period. Low- and high-limit switches enable the sensor to bypass very lean or very rich sample gas without interruption of furnace control. When the protective purge gas is nitrogen, the sensor need not be withdrawn from its furnace port until it is to be replaced. The sensor is calibrated either by decarburizing it to its minimum reading or by carburizing it with a standard gas mixture. Under ideal conditions, average life of the sensor exceeds one month.

Hot-wire analyzers have been used to control endothermic-gas generators; batch carburizers; continuous carburizers, both pusher and belt; protected quench carburizers; bell carburizers; belt-hardening furnaces; rotary carburizers; and tool-hardening furnaces. They have been used with atmospheres made from drip feed of organic fluids, endothermic gas alone or enriched with natural gas or propane, appropriate combinations of a hydrocarbon fuel gas and an oxygen-supplying agent, and nitrogen modified for use in carburizing applications using suitable additives.

Gas Chromatography

Gas chromatography provides a relatively fast method for measuring the concentrations of practically all the gases present in an atmosphere. A small sample of the gas mixture is inserted into the analyzer, where a steady flow of a carrier gas such as helium carries it through the analyzer column. As the sample goes through the column, individual components are separated by adsorption or partitioning. Measurement of the thermal conductivity or ionization characteristics of the gas leaving the column provides a measure of the concentration of each constituent. Various types of analyzer columns are available by which almost any gas component can be analyzed. A chromatograph is shown in Fig. 18.

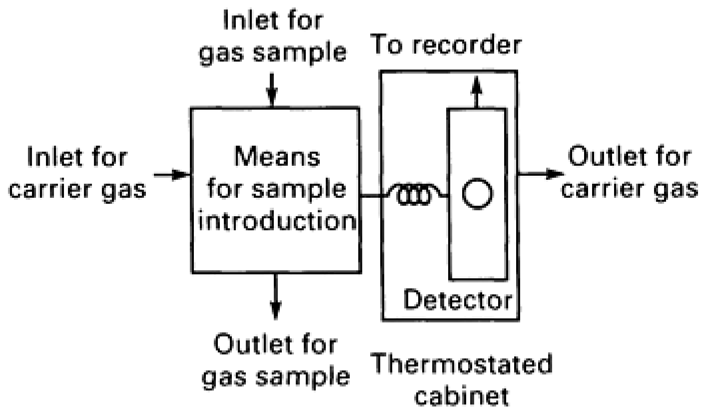


Fig. 18 Chromatograph for atmosphere analysis

Advantages. With present-day chromatographs, an analysis of each constituent, except water vapor, in an atmosphere containing carbon monoxide, carbon dioxide, methane, hydrogen, water vapor, and nitrogen can be made in approximately 5 min. If water vapor is analyzed, an additional 5 to 7 min are required.

The minimum full-scale ranges are 12% for hydrogen, 3% for water vapor, and 1% for each of the other gases listed. Reproducibility is ±1% of the full-scale reading, except for water vapor, for which it is ±2%. Laboratory analyzers are available with more sensitive detectors that can measure concentrations in parts per million. However, they do not have the stability that is needed in an automatic process-control device.

Although several constituents may be analyzed, automatic control usually is applied to only one. Because of the intermittent nature of the analysis, the input signal to the controller can be adjusted only once for each analysis cycle. The length of the cycle limits the analyzer to single-point control.

Limitations. Two limitations of gas chromatography are the fact that it provides only periodic, rather than continuous, analysis of the gas stream; and the difficulty of interpreting the chart record. With respect to the latter, the concentration of each constituent is recorded as a bar on the recorder chart, and each must first be identified from the recording sequence. Moreover, because the full-scale ranges differ for the various constituents, percentage of full scale must then be converted to percentage concentration.

Evaluation of Carbon Control in Processed Parts

Introduction

WHEN FABRICATED STEEL PARTS are heated in an atmosphere that will either carburize or decarburize the surfaces of the parts, an evaluation of the precise effect of the atmosphere on the parts is usually desirable. This is particularly important when the carbon content at the surface, and at significant depths below the surface, is to be controlled by adjusting the composition of the furnace atmosphere. Several methods of evaluating the carbon control of processed parts are considered in the following discussion.

In addition, methods for measuring the case depth produced by carburizing or carbonitriding are described in greater detail in the article "Methods of Measuring Case Depth," in this Volume.

Hardness Tests

Hardness tests for evaluating carbon control should be used with caution. The type of test selected should be one in which the depth of metal affected is properly related to the depth to which carbon control is desired. When hardness tests are used, one of three methods should be adopted only after all possible sources of error in the specific application have been thoroughly investigated:

- Surface hardness measurements taken under at least two conditions of loading (Rockwell C and superficial Rockwell 15N, for example)
- Superficial Rockwell 15N tests on steps ground below the surface to significant depths
- Microhardness measurements, either on steps or, preferably, on a cross section through the carbon control zone

Depth-of-penetration measurements such as those made in Rockwell tests generally do not measure hardness accurately at depths of less than 0.08 mm (0.003 in.) below the surface. Thus, if full hardness is required at the surface, as in wear applications, decarburization less than 0.08 mm (0.003 in.) deep may not be readily revealed by Rockwell testing at the surface. Such a condition would require microhardness testing or perhaps could be revealed by the proper use of a file. Conversely, the surface hardness test is not an accurate indication of carbon control if the carbon control is not effective to sufficient depth to support the penetrator during the hardness test. Lower or higher carbon content at a depth of 0.3 or 0.4 mm (0.010 or 0.015 in.) below the surface can also cause false readings.

Superficial Rockwell 15N testing on steps ground below the surface to significant depths gives a better indication of the depth to which carbon control is effective. For example, if a carbon restoration operation were being performed and the original decarburization were deeper than anticipated, the low carbon in the incompletely restored zone between the carbon-restored zone and the core could be detected by the step grind and hardness test method, whereas it might not affect a surface hardness reading.

Microhardness testing on a cross section through the carbon control zone is the most accurate of the hardness test methods for evaluating carbon control. With this method, each hardness impression is supported by metal of like composition. Variations in carbon content that affect hardness can be detected at any depth up to 0.06 mm (0.0025 in.). This method has the disadvantage of requiring a metallographically prepared cross section and special hardness-testing equipment that is usually available only in well-equipped laboratories.

When hardness testing is used to evaluate carbon control, it should be remembered that maximum quenched hardness is attained at about 0.80% C in plain carbon steels, and at lower carbon contents in alloy steels, depending on types and percentages of alloying elements present. If variations in carbon content above the level required to produce maximum

hardness are significant, hardness measurements are not capable of evaluating carbon control. Also, low hardness in quenched parts or test specimens can be caused by insufficient quenching or by excessive retained austenite, as well as by low carbon content. Therefore, evaluation on the basis of hardness measurements alone might lead to incorrect control measures. In instances where hardness measurements do not give adequate information, the techniques to be used are microscopic examination, analysis of consecutive cuts, analysis of shim stock, analysis of rolled wire, spectrographic analysis, and/or electromagnetic testing.

Microscopic Examination

Microscopic examination is the only method of determining surface carbon variations that shows the effects of such variations on microstructure. Because of this, it will indicate which corrective action must be taken to alter surface carbon concentration. Microscopic examination is also useful for determining whether an improper surface carbon content is detrimental to the part.

The effect of carbon content on microstructure varies from steel to steel. It also varies for a given steel, depending on whether the steel is annealed, unannealed, hardened, or tempered. The microscopic method is best used on steels with which experience has been gained in correlating results with those of other test methods of evaluating carbon control. Microscopic examination should be used to determine the microstructural constituents discussed below.

Ferrite. A layer of ferrite on the surface indicates total decarburization. There is usually partial decarburization below this layer.

Carbide (Cementite). An increase in the amount of carbide indicates carburization, and a decrease indicates decarburization. A fully annealed sample is almost always best for determining depth of carburization or decarburization by observing carbide variations. Size and frequency of carbide particles can be measured in order to estimate more accurately the percentage of carbide in the microstructure. Extreme carburization can result in massive amounts of carbides at the surface.

Pearlite. When the steel is annealed, pearlite indicates eutectoid carbon content. The ratios of pearlite to free ferrite and to proeutectoid carbide can be used to estimate how far and in which direction the structure deviates from that corresponding to the eutectoid composition.

Austenite. Carburization causes some steels to retain excessive amounts of austenite at the surface after heat treating. The proper etchant must be selected so that austenite is distinguished from ferrite and from massive carbide. Because both austenite and ferrite are soft, microscopic examination should be used to distinguish a sample with excessive retained austenite from one that has become decarburized.

Martensite. Variations in procedures used for etching martensitic structures (variations in metallographic preparation and in the etching reagents used) can indicate variations in carbon content. Familiarity with the microstructure of the steel is important for the correct interpretation of variations. Coarsening of martensite near the surface can indicate a variation in surface carbon.

As indicated, annealing of the sample is often desirable in order to obtain the best information; however, annealing must be carried out in the proper atmosphere, or severe errors may result from carburization or decarburization during the annealing cycle. The use of an inert atmosphere or a copper-plated sample is best. A neutral atmosphere tends to correct variations in surface carbon content, which makes it less desirable than an inert atmosphere.

The microscopic method is more sensitive than hardness testing, but it cannot detect very slight variations in carbon content and does not yield quantitative data suitable for plotting curves of atmosphere variables. Also, this type of evaluation is destructive, because cross sections must be cut perpendicular to the surface. When expensive parts are involved, appropriate testpieces should be processed along with the parts.

Analysis of Consecutive Cuts

The consecutive-cuts method of analysis can be used for the accurate evaluation of carbon control at any significant depth below the surfaces of parts. Because of the extremely accurate machining operations required to obtain reliable information, this type of evaluation is usually performed on cylindrical test bars treated with the work. After a test bar has

undergone the heat treatment to be evaluated, consecutive cuts of 0.03 to 0.3 mm (0.001 to 0.020 in.) or more are turned from the surface of the test bar, and the turnings from each cut are analyzed for carbon concentration.

The consecutive-cuts method is used most frequently on carburizing grades of steel to evaluate the control of case carbon content. Other methods of evaluation are usually adequate for medium-carbon and high-carbon steels that have been subjected to annealing, carbon restoration, or hardening.

Considerable doubt has been cast on the reliability of the data representing the first 0.03 to 0.1 mm (0.001 to 0.004 in.) cut from the surface. This reliability, however, is a function of the accuracy with which the test is performed and the care exercised in preparing and machining the test specimen.

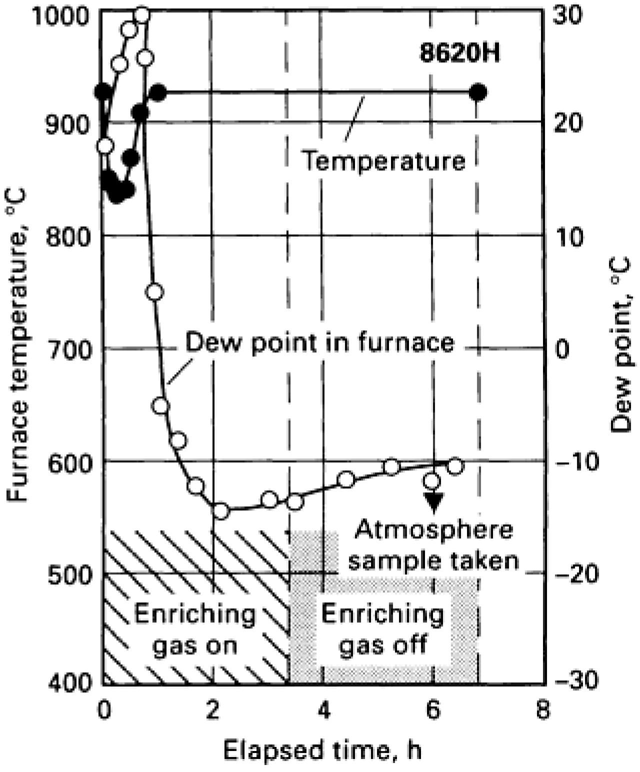
The test bar should be made of the same grade of steel as that of the workpieces. It should be accurately machined on centers to true cylindrical shape. The diameter should be such that the test bar section is representative of the critical region of the workpieces to be evaluated. The length of the test bar need only be sufficient to allow enough turnings for a carbon analysis and a check analysis.

The test bar is loaded into the furnace with the work load and is subjected to exactly the same cycle. If the work is slowly cooled from the furnace, the bars are:

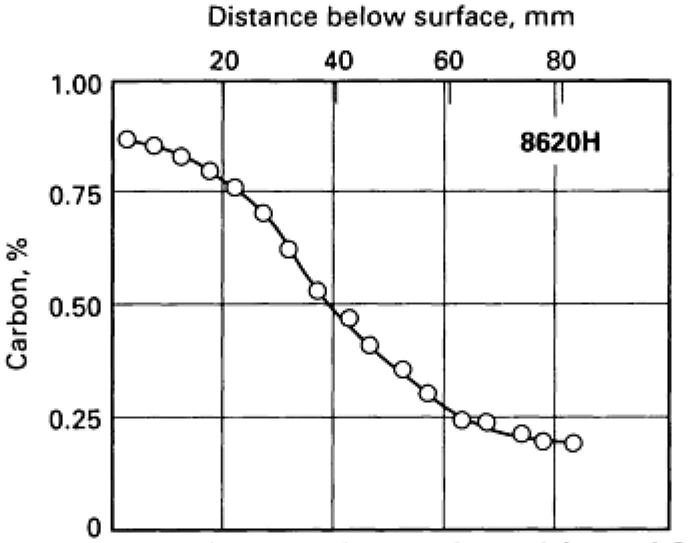
- Slowly cooled with the load
- Scrubbed with soap and water and rinsed with clean water
- Rinsed with benzene or ethyl alcohol to displace the water, and dried to prevent rust formation
- Lightly blasted with shot or grit
- Straightened to a 0.03 mm (0.001 in.) total indicator runout
- Scrubbed with soap and water and rinsed with clean water
- Rinsed with benzene or ethyl alcohol
- Machined

If the work is quenched at the end of the cycle and if the test bars are of a steel such as 1117 or 8620, the same sequence of operations can be followed except that the bars should be tempered at 600 °C (1100 °F), preferably in nitrogen, between the third and fourth steps of the procedure above.

Figure 1(a) shows the furnace temperature and atmosphere conditions employed in carburizing ring gears made of 8620H steel. Figure 1(b) indicates the resultant carbon gradient, as revealed by the analysis of consecutive cuts on the test bars that were carburized with the gears. The test bars were prepared from 28.5 mm ($1\frac{1}{8}$ in.) diam 8620H cold-drawn bar stock. The bar stock was cut to 250 mm (10 in.) lengths, which were centered and accurately machined to a nominal diameter of 25 mm (1 in.).



(a)



(b)

Fig. 1 (a) Furnace temperature and atmosphere conditions for carburizing and (b) resulting carbon gradient in 8620H steel. Conditions: Load: ring gears, 230 kg (510 lb) net, 390 kg (860 lb) gross. Furnace: electric, metallic-retort pit furnace. Carrier gas: endothermic gas at 2.8 m^3/h (100 ft^3/h) throughout the cycle, including 5 h and 59 min at temperature. Enriching gas: addition of 0.34 m^3/h (12 ft^3/h) of natural gas started when load was placed in furnace; flow of natural gas stopped after $2\frac{1}{2}$ h at temperature, or after 42% of at-temperature cycle. Generator dew point: -6 to -4 °C (22 to 25 °F) throughout the cycle. Heating-chamber pressure: 5.1 to 7.9 mm (0.20 to 0.31 in.) of water column. Carburizing temperature: 925 °C (1700 °F). Cooling method: Slowly cooled from 925 °C (1700 °F) in cooling pit. Atmosphere analysis near end of cycle: 20.8% CO, 0.4% CO_2, 34.0% H_2, 0% O_2, 0.8% CH_4

The consecutive-cuts method of evaluating the control of case carbon content provides an accurate means of determining the variations in case carbon composition that occur when different heat-treating cycles are used. In most instances, the details of these variations would be difficult to determine by any other conventional method of evaluating case carbon content.

The analysis of consecutive cuts provides an accurate method of determining the cycles to be used for carburizing, for continued checks on current cycles, and for determining whether simpler process-control methods are adequate. Variations in factors such as cycle time, gas flows, net and gross weights, loading method, and furnace condition can be evaluated. Because it provides information about the case on the finished workpiece, this method is useful for a final evaluation of all conventional types of control, such as atmosphere analysis, temperature cycle analysis, or the addition of enriching gas.

There are certain disadvantages of the consecutive-cuts method of evaluating carbon control. It is a slow analytical procedure. Information cannot be obtained until the particular workpieces represented have been processed; thus if results are not satisfactory, corrections cannot be made. Also, accuracy is required in machining and in analytical equipment and techniques.

Analysis of Shim Stock

Thin-gage shim stock can be used effectively to determine the carbon potential of an atmosphere. The success of this method is due to rapid through carburizing of the thin test strip, which eliminates carbon diffusion as a variable in the atmosphere evaluation. The accuracy of this test is adequate for application to the carbon control of commercial carburizing, carbon restoration, and carbonitriding.

In practice, a strip of annealed 1010 steel 32 by 75 by 0.1 to 0.15 mm ($1\frac{1}{4}$ by 3 by 0.004 to 0.006 in.) is weighed before and after 1 h of exposure to the furnace atmosphere. The gain in weight, as determined on an analytical balance, is used to calculate the carbon potential of the atmosphere. Thus:

$$\textit{Carbon}\ \text{potencial} = \left(\frac{\text{Gain in weight x 100}}{\text{Final weight}}\right) + \ \%\text{original carbon}$$

Total test time varies from $\frac{1}{2}$ to $1\frac{1}{2}$ h.

Figure 2 shows the carbon potential rod used in the shim stock test. Procedures for the exposure of shim stock to the furnace atmosphere are:

1. 1. Assembly of rod and test strip
2. 2. Attachment of rod to furnace wall in preparation for insertion of test strip into furnace atmosphere
3. 3. Insertion of test strip into furnace in unobstructed stream of furnace atmosphere above the work load. Test strip is exposed for 1 h
4. 4. Removal of test strip from furnace atmosphere. The same position indicated in step (b) is used for cooling the strip after it has been withdrawn from the furnace. Rod should be supported for a few minutes after withdrawal to avoid severe bending. Test strip is cooled for 15 min

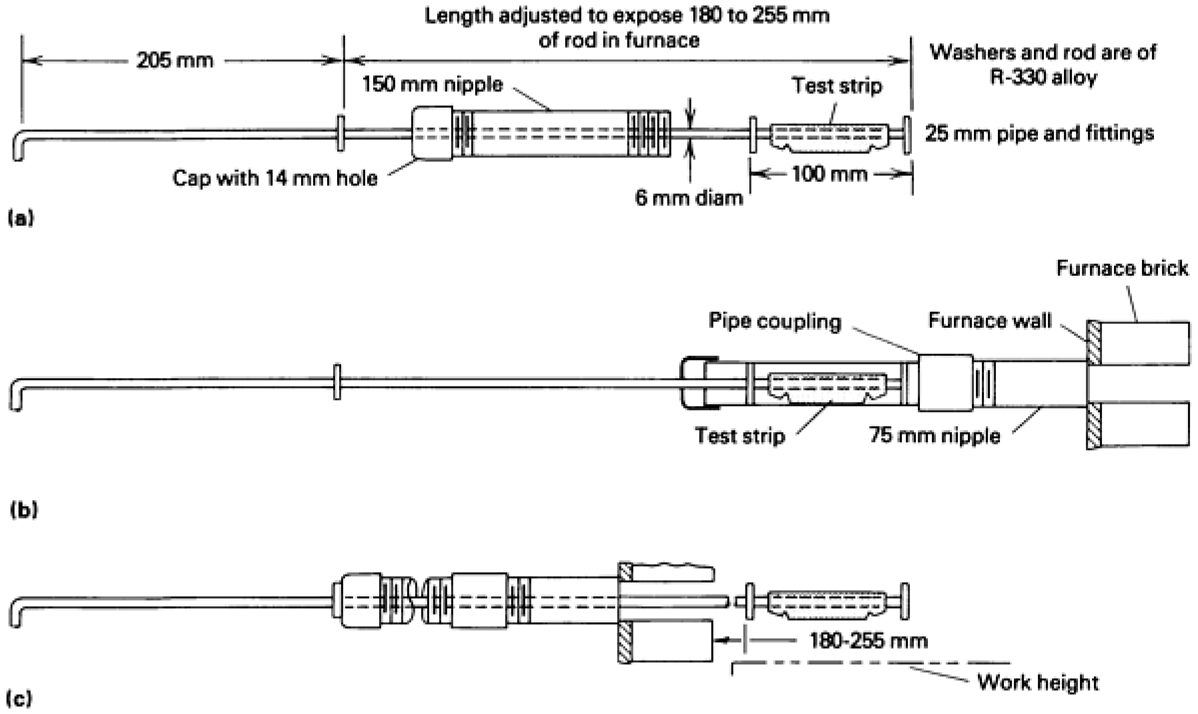


Fig. 2 Arrangements for exposing shim stock to furnace atmosphere for evaluation of carbon potential. (a) Assembly of test strip for determination of carbon potential. (b) Assembly of test strip on rod attached to furnace wall in preparation for insertion into furnace (same position used for cooling of test strip). (c) Test strip inserted into furnace above work in unobstructed stream of furnace atmosphere. (See text.)

Precautions to be taken in shim stock analysis are:

- For furnace operating temperatures of 815 °C (1500 °F) or lower, the exposure time should be increased to $1\frac{1}{2}$ h to ensure through carburizing of the testpiece
- To prevent oxidation of the test strip during cooling, the strip should be transferred from the furnace into the pipe nipple at a time when all furnace doors are closed
- The test strip should not be rolled or wrapped tightly around the carbon potential rod. This permits only partial exposure of the test strip, causing low results, and complicates removal of the strip for reweighing. Proper anchoring of the strip on the rod is accomplished by simply crimping the corners of the strip over the rod, leaving the center area open to the atmosphere
- In continuous furnaces, the carbon potential indicated by the test strip represents only the zone or area tested, not the entire furnace atmosphere
- The test strip should always be exposed to an unobstructed flow of furnace atmosphere. This is easily accomplished by placing the strip above the work load (Fig. 2c)
- A properly exposed and cooled strip containing 1.30% C or less should be clean and bright
- Slight oxide discoloration is caused by improper technique. The carbon content determined on such a strip would be slightly high because of the increase in weight due to the iron oxide
- A properly exposed and cooled strip containing about 1.40% C or more will have a dull, matte finish. Depending on actual carbon content, the steel surface may be coated with loose, dry carbon. This is a normal appearance caused by an atmosphere of high carbon potential. The surface carbon deposit should be wiped off before the shim stock is reweighed

The shim stock method permits a quick evaluation of atmosphere performance; unnecessary delays, such as the time required for completion of a carburizing cycle, are avoided. Generally, this test is supplemented by an analysis of test bars

carburized with the work for the entire furnace cycle. The correlation of strip carbon and surface carbon on parts is then established in order to arrive at a definite set of operating conditions.

The shim stock method determines the maximum carbon available in the atmosphere for batch or continuous furnaces. Generally, the atmosphere carbon is higher than the surface carbon of parts made of most SAE steels. Exceptions are steels that contain high percentages of one or more carbide-forming elements, such as 3310, 52100, and 9310. Parts made of these or equivalent steels form surface carbides and consequently have higher surface carbon than does shim stock.

This test is also applicable to carbonitriding atmospheres. Although the gain in weight is produced by both carbon and nitrogen, for all practical purposes it can be treated as though it were due to carbon only, permitting the same calculations as those used for carburizing atmospheres.

Shim stock exposed to furnace atmosphere may also be analyzed for carbon by combustion carbon analysis. This method eliminates the necessity for weighing the sample of shim stock before and after exposure.

Analysis of Rolled Wire

Rolled wire may also be used for measuring carbon potential. Wire is flattened into strip and is then used for determining carbon potential in much the same manner as shim stock is used, except that there are small differences in the design of the fixture on which the rolled wire is placed.

Spectrographic Analysis

Carbon content can be accurately determined by spectrographic analysis. This method makes use of a vacuum spectrometer, which permits the measurement of spectral lines in the ultraviolet region where air would ordinarily absorb much of the emitted radiation.

Spectrographic analysis is normally performed on flat test specimens that can be taper ground, step ground, or reground incrementally after each carbon determination. A very small amount of material is ground from the surface (to remove oxides). Successive cuts are made, and analyses are performed after each cut.

Special care must be taken to ensure that the depth corresponding to each carbon determination is measured accurately. Case depth determined on flat or round test specimens often differ from case depth determined directly on workpieces, because of differences in shape.

Whereas carbon determination by the combustion method provides an average carbon content for the amount of material removed by machining, spectrographic analysis determines the local carbon content of the specimen to a depth of 0.03 mm (0.001 in.) below the surface. Table 1 compares analyses performed on five samples of shim stock by the spectrographic and combustion methods.

Table 1 Carbon content of shim stock and workpiece surfaces as determined by spectrographic and combustion analyses

Sample number	Amount of carbon present, %		
	Spectrographic analysis	Combustion analysis	Workpiece surface (spectrographic analysis)
1	0.36	0.36	0.38
2	0.24	0.27	0.25

3	0.22	0.24	0.225
4	0.35	0.35	0.34
5	0.30	0.30	0.305

Note: Shim stock and workpieces were heat treated, in the same load, in a 915 mm (36 in.) continuous-belt furnace with an endothermic-based atmosphere (class, 301; dew point, -9 to -1 °C, or 15 to 30 °F).

Electromagnetic Testing

Two types of electromagnetic nondestructive tests have been used to evaluate the cases of case-hardened parts: One compares the magnetic properties of a part with those of a test standard, and the other measures coercive force, which is then converted to case depth through use of a calibration chart.

Magnetic-Comparator Testing

One electromagnetic test is performed by placing the part to be tested in an induction coil. A reference part of known electromagnetic response is placed in a second coil. Both parts are simultaneously subjected to identical electromagnetic fields, and their responses to these fields are compared by an electronic balancing circuit. Any imbalance between responses (indicated by a meter) is a function of the following properties of the test object: chemical composition, microstructure, case depth, surface flaws, residual stress, and work hardening.

Many electromagnetic instruments are capable of breaking down an electromagnetic response into inductive components, resistive components, third-harmonic amplitude, and phase differences. The user must correlate these variables with the property or properties to be evaluated.

Standards and Test Procedures. Electromagnetic (eddy current) testing can be used only as a comparison test; its accuracy and usefulness depend on the proper development of standards and test procedures. Acceptance and rejection standards are required for each part design to be evaluated. Once standards are developed and instrument settings are selected, production parts can be tested by comparison with the standards. Sufficient destructive testing must be carried out to produce the data required for the construction of a chart or graph by which meter readings can be converted to case depths with reasonable confidence. Periodic destructive testing should be carried out to reconfirm this correlation.

In a production situation involving many parts and wide differences in specified case depth, it is difficult and costly to establish standards for all parts. To eliminate this problem, a procedure has been developed in which a standard test specimen is processed with each heat. Case depth of the test specimen is determined by magnetic comparison. The standards for carburizing a testpiece are developed using the procedure described above, and these standards are correlated with actual parts by periodic destructive testing. The standard test specimen is made from a cold-finished bar of coarse-grained, silicon-killed 1018 modified steel with residual elements held to low levels. The testpiece is 11 mm ($\frac{7}{16}$ in.) square by 75 mm (3 in.) long. Testing of the standard specimen may yield results that are different from those obtained with actual parts, but once a correlation is established, the standard testpiece, rather than actual parts, may be used with reliability.

Effectiveness and Limitations. Test reliability for the determination of case depth is:

Error	mm	in.

Average error	0.10	0.004
Maximum error (3% of the time)	0.44	0.017
Minimum error (18% of the time)	0.00	0.000

The magnetic-comparator test will indicate whether a production lot is acceptable or of questionable quality. Destructive tests must then be conducted on questionable lots to determine which variables are out of specification and to assist in devising corrective measures.

Case depths of up to 5 mm (0.200 in.) may be measured. This method has been found to be more reliable for induction-hardened cases than for carburized cases. The chief variable that can adversely affect measurements is the case-to-core transition zone, which is much wider in carburized cases than in induction-hardened cases.

Coercive-Force Testing

A second type of electromagnetic instrument measures the coercive force of parts. A probe is placed on the part, and the coercive-force value is taken. The case depth is read from a calibration curve previously prepared by the destructive testing of samples with shallow and deep cases.

The equipment is easy to set up and use. Results can be correlated to the case depths of carburized or induction-hardened parts, usually of carbon steels. In some difficult applications, only a general trend of case depth can be given, but this is usually sufficient for production auditing. The test is extremely sensitive to core property variations accompanying abnormal quenching.

Coercive-force testing can be applied to cases up to about 20 mm (0.800 in.) deep. The instrument readings are not affected by minor differences in steel composition, but different calibration curves must be developed for different grades of carbon and alloy steels.

Case-Depth Variation

In commercial practice, case depth is controlled within certain tolerances, which depend on the intended service of the part, the type and condition of the carburizing furnace, the cycles employed, and the limitations of control equipment. The end use of the carburized part is the principal determinant of the acceptable range of case depth. Parts to be used in less-critical applications do not require close control of case depth, and the increased cost of ensuring close control would be unjustified.

The data shown in Fig. 3 provide a summary of the reproducibility of case depths within prescribed limits for test specimens and parts made of 8620 steel. Operating details are given in the descriptions that follow.

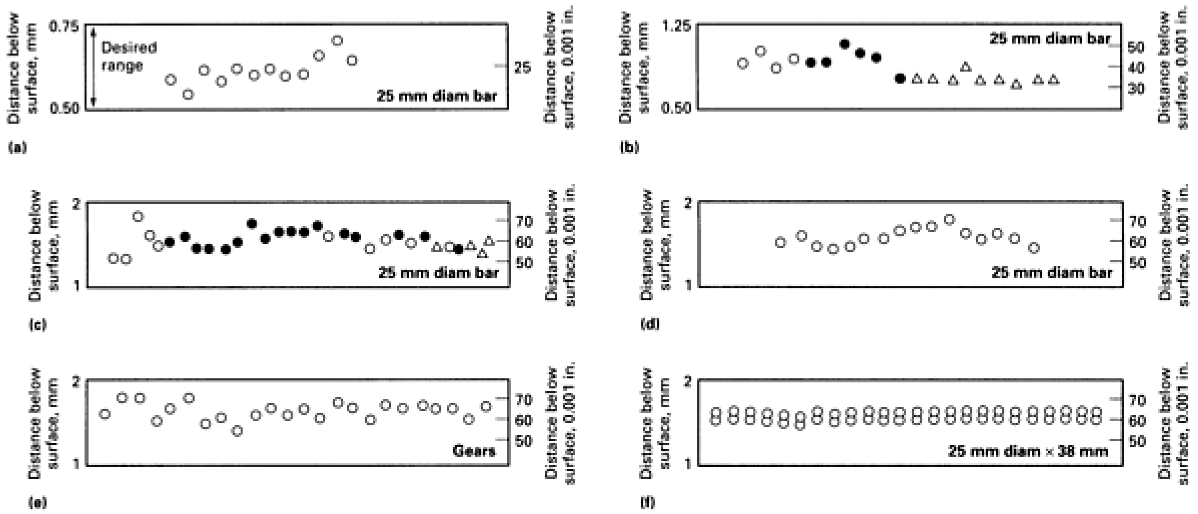


Fig. 3 Reproducibility of case depth in 8620 steel, using the criterion of depth to 0.40% C. Data points, representing individual heats, are plotted in chronological order (left to right). Data were collected in studies in two different plants. Legend for parts (b) and (c): d , furnace A; •, furnace B; V , furnace C. (See text.)

The case variation shown in Fig. 3(a) was determined from a carbon gradient curve secured by carburizing 25 mm (1 in.) rounds of 8620 steel with production parts at 925 °C (1700 °F) for $1\frac{3}{4}$ h in a horizontally loaded batch-type furnace, then reducing the temperature to 845 °C (1550 °F) before quenching in oil. A diffusion-type carburizing cycle was used. Dew point was -15 °C (5 °F) for the carburizing portions of the cycle at 925 °C (1700 °F), -12 °C (10 °F) for the diffusion portion at 925 °C, and -3 °C (27 °F) for the equalizing portion at 845 °C (1550 °F). The carburizing atmosphere was endothermic gas enriched with natural gas, without the addition of air.

After being quenched, the testpieces were tempered in lead at 650 °C (1200 °F) and then cleaned with a wire brush and liquid abrasive. The target depth to 0.40% C was 0.51 to 0.76 mm (0.020 to 0.030 in.). With 0.64 mm (0.025 in.) as the average, the distribution was:

Variation from average depth, mm (in.)	**Part distribution, %**
0.64 ± 0.03 (0.025 ± 0.001)	75
0.64 ± 0.05 (0.025 ± 0.002)	92
0.64 ± 0.08 (0.025 ± 0.003)	100

Testpieces similar to those described above were used to obtain case depth data (to 0.40% C) from three different batch-type furnaces using endothermic gas enriched with straight natural gas, without the addition of air. These data are summarized in Fig. 3(b). The loads were carburized at 925 °C (1700 °F), using a diffusion-type cycle. Dew point was

maintained at -15 °C (5 °F) for 3 h at 925 °C (1700 °F), at -12 °C (10 °F) for the diffusion portion of the cycle, and at -3 °C (27 °F) for 1 h at 845 °C (1550 °F) prior to quenching. The characteristics of the three different furnaces were:

Characteristics
Furnaces A and B
Size: 76 × 122 cm wide by 46 cm high (30 by 48 in. wide by 18 in. high)
Atmosphere control: dew cell; manual reset
Rated gross load: 68 kg (1500 lb)
Furnace C
Size: 91 by 183 cm by 61 cm high (36 by 72 in. by 24 in. high)
Atmosphere control: infrared analyzer controlling carbon dioxide; automatic reset
Rated gross load: 1588 kg (3500 lb)

The maximum variation recorded in 5 years was 0.91 to 1.19 mm; target, 1.02 mm (0.036 to 0.047 in.; target, 0.040 in.). The distribution of case depth was:

Variation from average depth, mm (in.)	**Part distribution, %**
1.016 ± 0.025 (0.040 ± 0.001)	32
1.016 ± 0.051 (0.040 ±0.002)	47
1.016 ± 0.076 (0.040 ± 0.003)	90
1.016 ± 0.102 (0.040 ± 0.004)	95

1.016 ± 0.178, -0.102 (0.040 ± 0.007, -0.004)	100

For a required case depth (to 0.40% C) of 1.40 to 1.78 mm (0.055 to 0.070 in.), the same three furnaces used to provide the data for Fig. 3(b) produced the results plotted in Fig. 3(c). The operation and means of testing were the same as those used for the shallower depths, except that the total cycle time at 925 °C (1700 °F) was 10.5 h. Total cycle time was 5 h with a dew point of -15 °C (5 °F) and 5 $\frac{1}{2}$ h with a dew point of -12 °C (10 °F). Equalizing time at 845 °C (1550 °F) was 1 h, and dew point was -3 °C (27 °F). Maximum case depth variation for 4 years was 1.422 to 1.676 mm (0.056 to 0.066 in.), with a distribution of:

Variation from average depth, mm (in.)	**Part distribution, %**
1.524 ± 0.025 (0.060 ± 0.001)	22
1.524 ± 0.051 (0.060 ± 0.002)	48
1.524 ± 0.076 (0.060 ± 0.003)	75
1.524 ± 0.102 (0.060 ± 0.004)	89
1.524 ± 0.127 (0.060 ± 0.005)	97
1.524 ± 0.152 (0.060 ± 0.006)	100

Reproducibility of Results

The data given in Fig. 4 correlate effective case depth to 50 HRC measured on the same gears in two different plants. Values were obtained by means of the hardness traverse method considered the most accurate method for measuring effective case depth. Nevertheless, several discrepancies in the results obtained at the two plants are apparent.

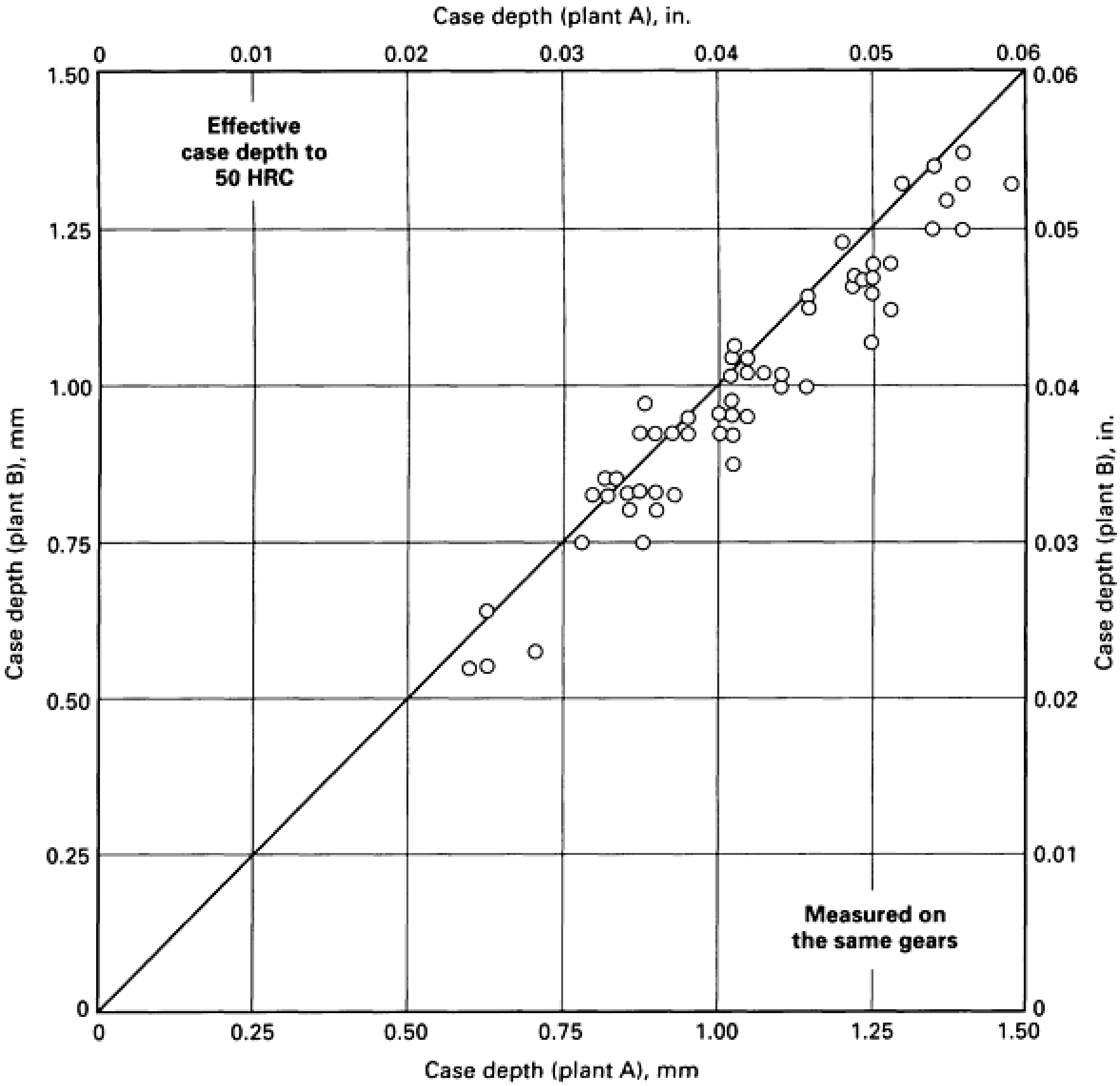


Fig. 4 Comparison of case depth measurements made on the same gears in two different plants

To compare hardness and microscopic methods of measuring case depth on the same specimens, carburized and hardened specimens of 8620 steel were prepared and submitted to five different heat-treating organizations for measurement by their laboratories. These specimens were prepared with reasonable care and were located within a short distance of one another during carburizing and hardening. All of the specimens were cut from the same bar. Each of the five laboratories that participated in the testing was asked to make all case depth measurements in accordance with identical industry standard procedures. The results are shown in Fig. 5.

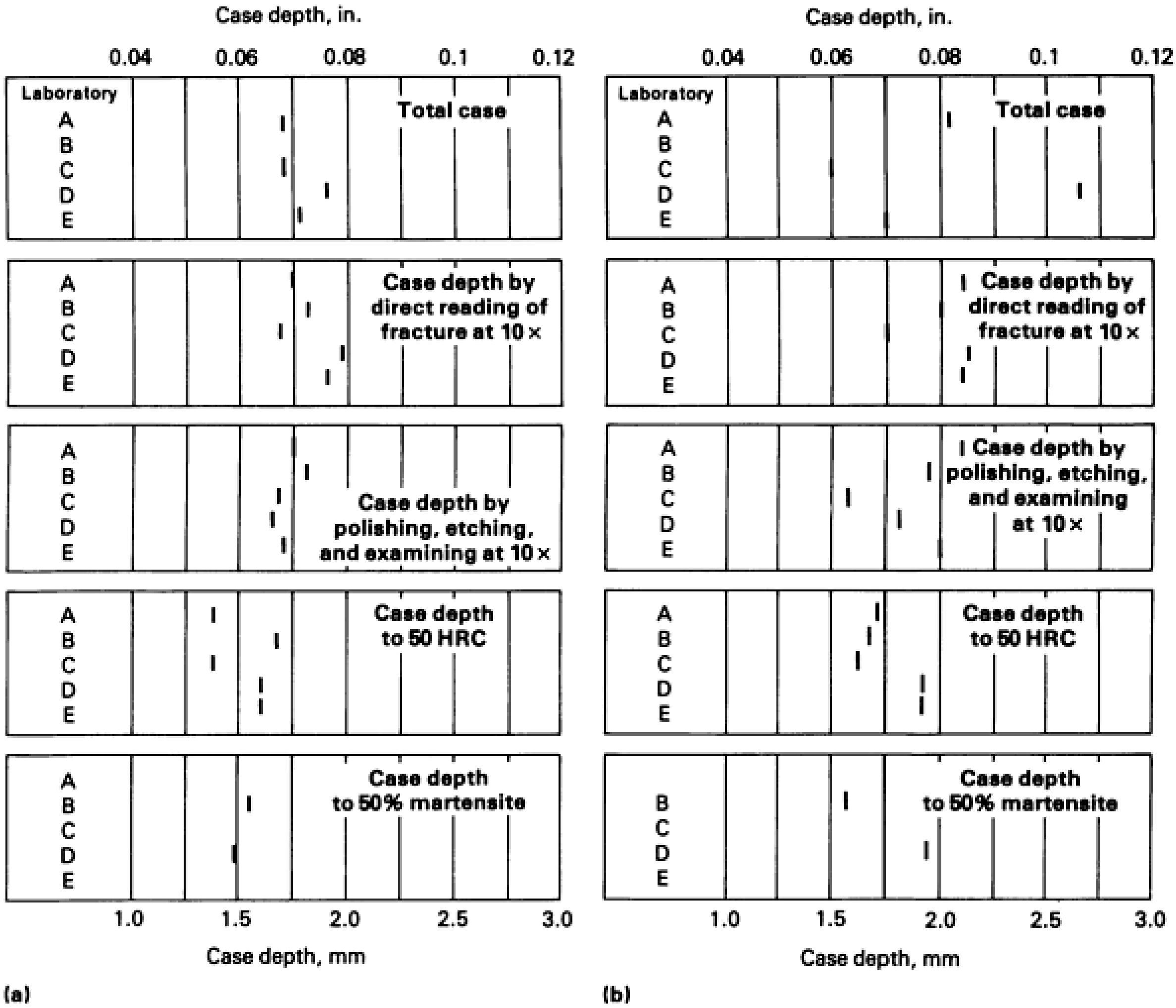


Fig. 5 Comparison of case depth measurements made on the same two samples of 8620 steel in five different laboratories. (a) Sample 1: 8620 with core hardness of 30 HRC and a surface carbon of 0.90%. (b) Sample 2: 8620 with core hardness of 40 HRC and a surface carbon of 0.90%

These measurements (all made by trained observers in qualified laboratories) diverge somewhat more widely than might be expected. They illustrate, perhaps in an exaggerated manner, the inherent lack of high precision in case depth measurements. With consultation among laboratories and a more precise definition of criteria, considerably closer agreement can be obtained, for instance, among different laboratories in the same multiple-plant organization, or between closely cooperating vendors and customers.

Carbon Concentration Gradients and Surface Carbon Content

The carbon concentration gradients of carburized parts are influenced by carburizing temperature, carburizing time, the type of cycle (various combinations of carburizing and diffusion times), the carbon potential of the furnace atmosphere, and the original composition of the steel.

The term carbon gradient not only encompasses the rate of change of carbon content with depth below the surface, but also alludes to the absolute value of carbon content in any layer other than the surface layer.

Carbon Gradients. Single-potential carburizing involves carburizing at a single temperature and constant atmosphere composition for the entire cycle. In some instances, single-potential carburizing is done to produce saturated austenite at the surface of the steel. Figure 6 shows the influence of carburizing temperature on the carbon gradient for single-potential carburizing of 1020 steel in a batch furnace. Comparable data are also given for 8620 steel carburized for $7\frac{1}{2}$ h

in an atmosphere containing 12% methane. Carburizing temperatures for both steels were 870, 900, and 925 °C (1600, 1650, and 1700 °F).

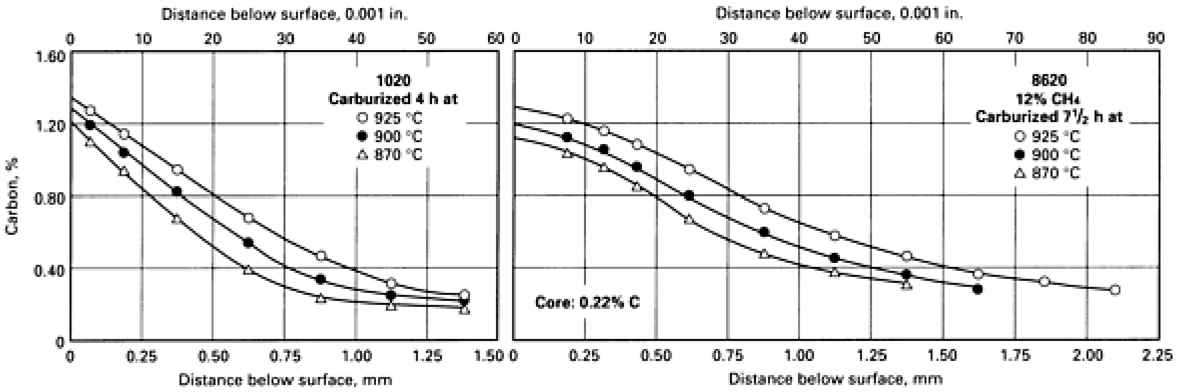


Fig. 6 Carbon gradients for 1020 and 8620 steels carburized at three temperatures. The 1020 steel was carburized in a batch furnace; the 8620 steel, in a recirculating pit furnace.

Figure 7 presents carbon gradient curves obtained in a batch furnace at a carbon potential corresponding to saturated austenite for four steels after carburizing for 4 h at 870 and 925 °C (1600 and 1700 °F). Typical influences of methane content, carbon potential, and time on the carbon gradient after single-potential carburizing of 1022 steel are shown in Fig. 8 and 9.

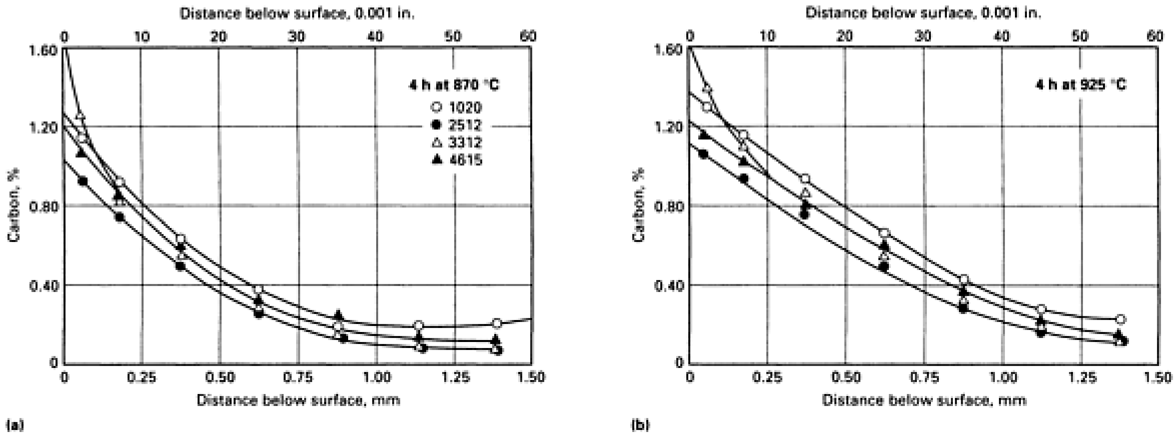


Fig. 7 Carbon gradients for four steels. (a) After carburizing for 4 h at 870 °C (1600 °F). (b) After carburizing for 4 h at 925 °C (1700 °F)

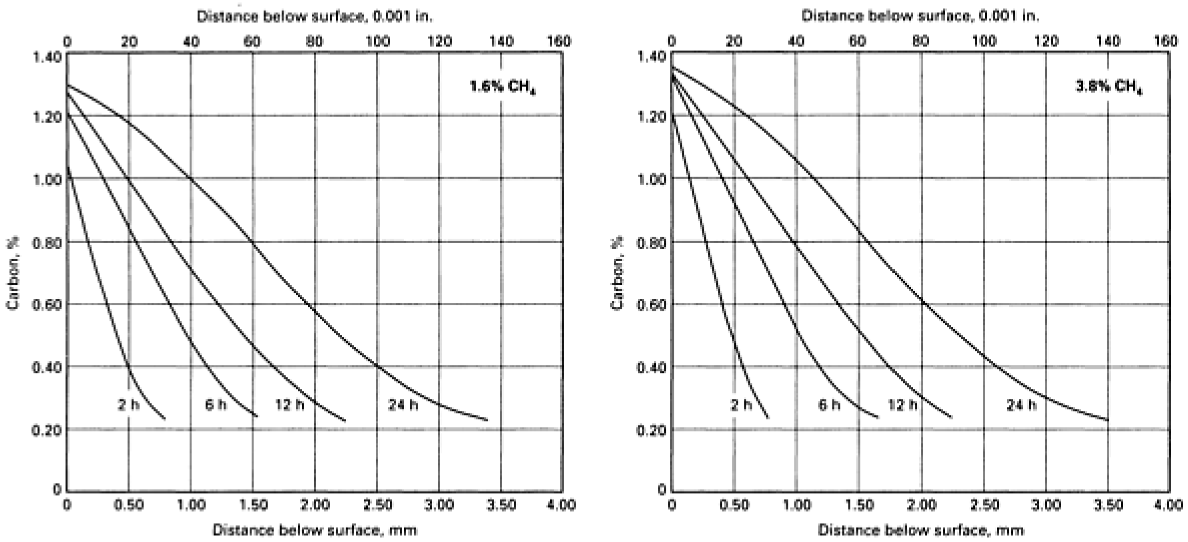


Fig. 8 Carbon gradients for carburized 1022 steel test bars carburized at 918 °C (1685 °F) in 20% CO-40% H_2 gas with 1.6 and 3.8% CH_4 added

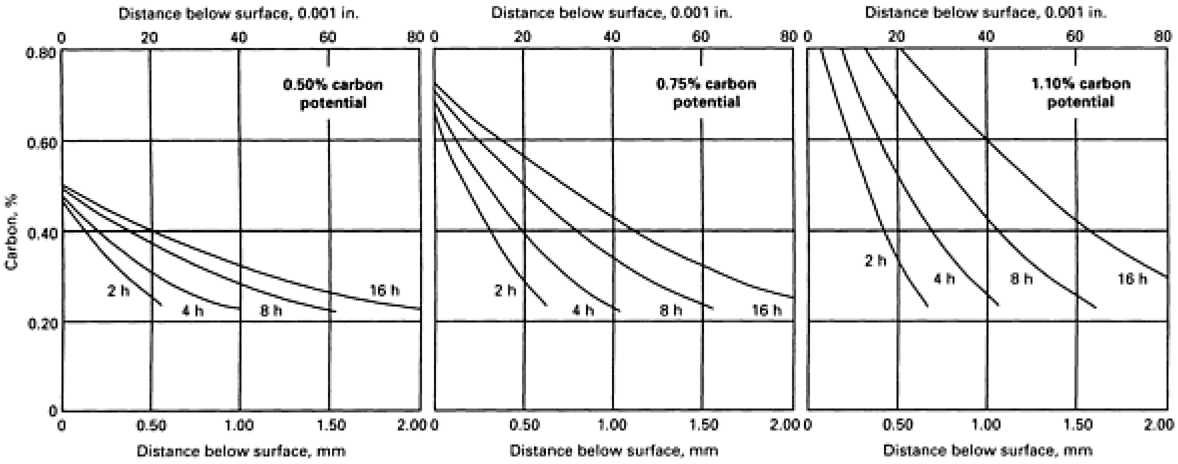


Fig. 9 Carbon gradients for carburized 1022 steel carburized at 918 °C (1685 °F) in 20% CO-40% H_2 gas containing enough H_2O to produce the carbon potentials shown

To develop optimum mechanical properties in the case, it is common practice to use carburizing cycles that consist of two or more combinations of temperature, time, and atmosphere composition (carbon potential). The main objective of using multiple-potential carburizing is to decrease the total cycle time.

The most widely used carburizing cycles are constant-temperature cycles starting with an atmosphere carbon potential that approaches the value for carbon saturation in austenite. Part way through the cycle, the flow of the enriching gas is reduced, which lowers the carbon potential of the atmosphere. During the remainder of the time at temperature, known as the diffusion cycle, the atmosphere is maintained at a carbon potential equal to the final desired surface carbon content. During the diffusion period, the surface layer is partly decarburized because it is in an environment of lower carbon activity. It must not be assumed that all of the carbon added during the carburizing cycle will be diffused inward during the diffusion cycle; most of it does diffuse inward, but some returns to the atmosphere.

Carbon gradients from multiple-potential carburizing are used for the twofold purpose of reducing the amount of retained austenite that would normally occur upon quenching, and increasing the depth of the effective case and making its

properties more uniform. The two examples that follow describe carbon gradients that are typical of those produced in continuous furnaces with zone control.

Example 1: Comparison of Carbon Gradients Produced with and without Zone Control

(Fig. 10). Two types of carburized cases were produced on 4027 steel by gas carburizing in the same continuous furnace using identical time-temperature cycles but different conditions of atmosphere control. For both cycles, total time in the furnace was 10.3 h, and the zone temperatures were 900, 925,925, and 845 °C (1650, 1700, 1700, and 1550 °F). The carbon gradients produced by the two cycles are shown in Fig. 10. One case was produced without zone control, that is, without regard to the fact that there is a high demand for carbon early in the carburizing cycle and a low demand during the final part of the cycle. A uniformly distributed mixture of carrier gas plus hydrocarbon gas was admitted continuously at various points along the length of the furnace. The ratio of carrier gas to hydrocarbon gas was high enough to ensure that only a minimum amount of soot would be deposited during the carburizing and cooling portions of the cycle. As can be seen from the curve labeled "Without zone control" in Fig. 10, the case had a high carbon content at the surface and a slightly concave curvature to the carbon gradient.

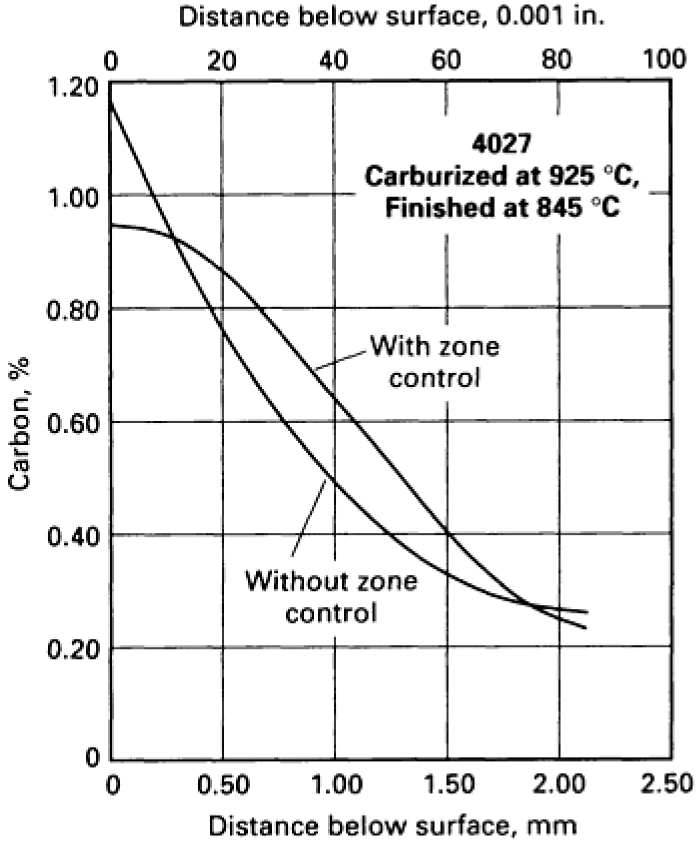


Fig. 10 Effect of zone control on carbon gradient for 4027 steel carburized in a continuous furnace (Example 1)

The other case (see curve labeled "With zone control" in Fig. 10) was produced under identical conditions, except for the distribution of the atmosphere within the furnace. Hydrocarbon gas was admitted only within the carburizing zones, with the greatest amount added in the first of these zones. The total amount of hydrocarbon gas was equal to that for the case produced without zone control. Carrier gas without enrichment was admitted to the furnace in the diffusion and cooling zones. The case had a lower surface carbon content and a greater effective depth than the case produced without zone control, and the carbon gradient curve was convex in the near-surface region of the case.

Example 2: Variation of Carbon Gradient with Processing Conditions in a Three-Zone Continuous Furnace under Manual Control

(Fig. 11). The carbon gradients shown in Fig. 11 are for 4815 steel that was carburized in a three-zone, continuous pusher furnace. Carbon potential was manually controlled. For all three cycles, the temperature in zones 1 and 2 was 920 °C (1690 °F), and the atmosphere was carrier gas enriched with methane; in zone 3, the temperature was 910 °C (1670 °F), and the atmosphere was carrier gas slightly diluted with air. The three cycles differed in the carbon potentials established in the third zone and in the time that parts were exposed in each of the three zones.

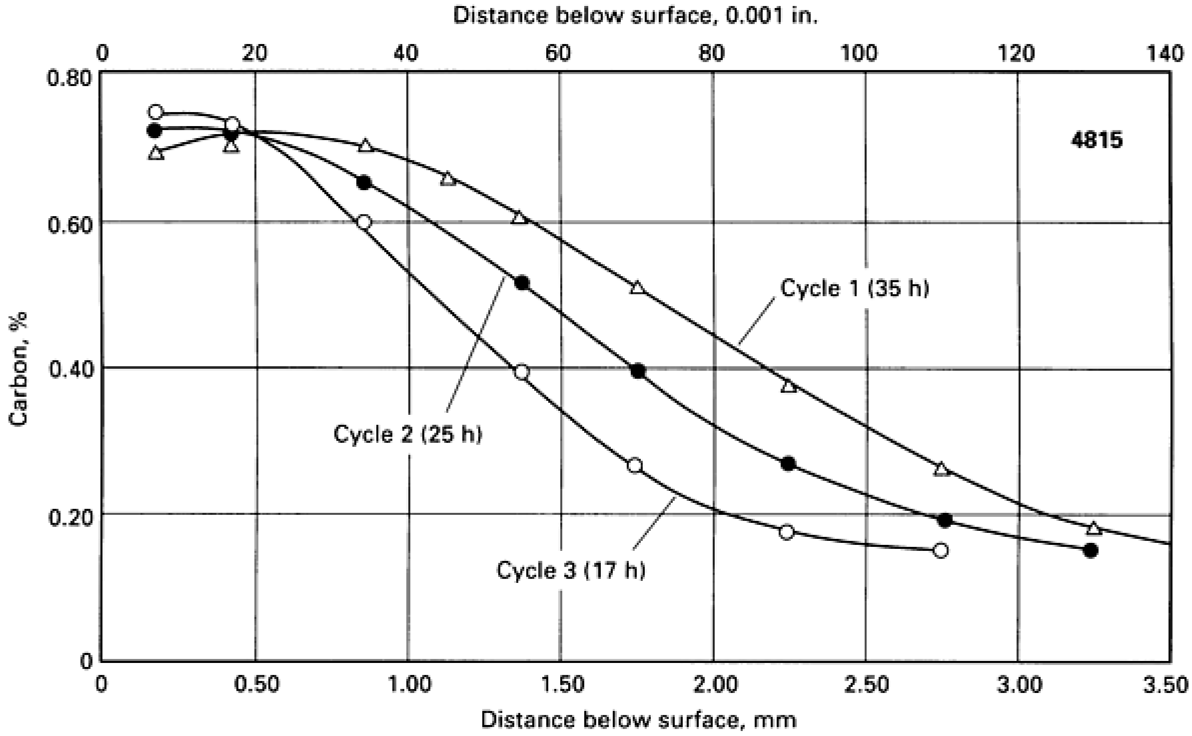


Fig. 11 Carbon gradients from three-zone, continuous pusher-type carburizing furnace with manual control of carbon potential (Example 2)

Cycle 1 was 35 h long, consisting of 8 h in zone 1 at 1.25% carbon potential, 14 h in zone 2 at 1.25% carbon potential, and 13 h in zone 3, where the carbon potential varied from 0.80% at the center of the zone to 0.55% at the discharge end. This cycle was designed to produce a total case depth of 2.8 mm (0.110 in.) at 0.25% C.

Cycle 2 was 25 h long, consisting of 6 h in zone 1 at 1.25% carbon potential, 10 h in zone 2 at 1.25% carbon potential, and 9 h in zone 3, where the carbon potential was 0.80% at the center and 0.60% at the discharge end. This cycle produced a total case depth of 2.3 mm (0.090 in.) at 0.25% C. The carbon gradient exhibited a slightly higher surface carbon content and a narrower zone of constant carbon content in the near-surface region than did the gradient resulting from cycle 1.

Cycle 3 consisted of 4 h in zone 1 and 7 h in zone 2, both at 1.25% carbon potential, plus 6 h in zone 3, where the carbon potential was 0.8% at the center and 0.75% at the discharge end, for a total carburizing-plus-diffusion time of 17 h. This cycle produced a total case depth to 0.25% C of 1.8 mm (0.070 in.). The carbon gradient showed a slightly higher surface carbon content than did either cycle 1 or 2 (Fig. 11) and a slightly shallower plateau of constant carbon content in the near-surface region of the case.

Surface Carbon Content. As indicated in Fig. 10, carbon potential control also affects surface carbon concentration. Surface carbon content has a pronounced effect on the properties of the steel and must be controlled for optimum results.

The amount of carbon in solution affects the amount of austenite that is retained after quenching, and the amount of retained austenite affects the hardness of the quenched case. The amount of austenite retained after quenching is determined by carbon potential, carburizing cycle, diffusion cycle, quenching temperature and rate, and steel composition.

Effect of Carbon Gradient on Case Properties. Carbon gradient is related to case hardness, as shown by the data in Fig. 12 for specimens of 1024 steel. The specimens were carburized for 2 $\frac{1}{4}$h at 900 °C (1650 °F) in an atmosphere containing 10% methane. They were oil quenched from 845 °C (1550 °F) and achieved a maximum surface hardness of about 62 HRC. However, a hardness of about 66 HRC was obtained at a depth of 0.25 mm (0.010 in.) below the surface, indicating the presence of some retained austenite at the surface. Retained austenite is frequently considered a normal constituent in the microstructure, corresponding to the hypereutectoid portion of the carbon gradient. Alloy steels are more likely to exhibit retained austenite than are carbon steels.

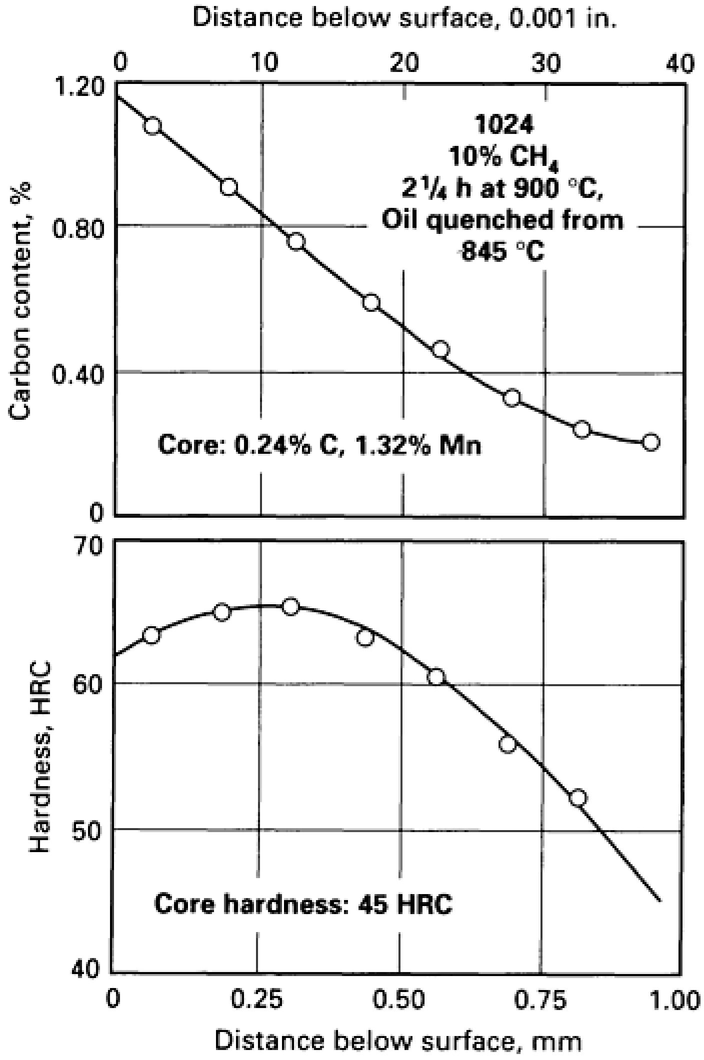


Fig. 12 Carbon and hardness gradients for 1024 steel carburized in a recirculating batch furnace under conditions that produced saturated austenite at the surface. The effect of retained austenite on surface hardness can be seen. Specimens were 25 mm (1 in.) in diameter by 150 mm (6 in.) long.

In many instances, finely dispersed retained austenite in amounts up to 30% is not detrimental to pitting-fatigue strength, whereas much lower amounts are often harmful if the austenite is not finely dispersed. However, small amounts of finely dispersed retained austenite apparently allow mating surfaces to conform at a slightly faster rate and to spread the load more evenly, thereby reducing local areas of high stress.

The effect of carbon content on pitting-fatigue strength has been the subject of controversy for many years. Undoubtedly other microstructural changes have clouded the issue. Rolling-contact fatigue tests have indicated that pitting-fatigue strength increases with increasing hardness in medium-carbon and high-carbon steels.

The effect of carbon content on resistance to wear and scuffing is too complicated to warrant a general conclusion. Excessive retained austenite permits surfaces to deform plastically under heavy loads, resulting in ripples, or "orange peel."

Low Surface Carbon. Most steels can be carburized by the carbon saturation-carbon diffusion type of cycle to produce surface carbon content well below saturation (for example, from 0.90 to 1.00% C). There is a strong preference in present carburizing practice for surface carbon concentrations of eutectoid composition or slightly higher. With the lean-alloy steels that are most often used, it is especially important to utilize the full hardenability of the steel. Maximum hardenability of the lean-alloy carburizing steels is obtained at carbon concentrations near eutectoid composition. The excess carbides formed at high carbon concentrations promote transformation to products other than martensite and may remove part of the carbide-forming elements from the austenite, thereby decreasing the effective hardenability.

Low carbon concentrations at the surface also permit direct quenching of work from the carburizing temperature, which is more economical than reheating before quenching. Direct quenching of carburized parts having high surface carbon concentrations favors the retention of austenite. Such austenite is undesirable because it lowers the indentation hardness of the case and promotes secondary hardening with the formation of untempered martensite, which may change the dimensions of the finished parts as well as embrittle them.

When surface carbon concentrations near eutectoid composition are desired, a multiple-manifold arrangement may be used by which part of the carrier gas and all of the hydrocarbon gas are introduced through ports at the front of the carburizing zone, where carbon demand is high. Only carrier gas is supplied to the other zones, and the carbon potential is adjusted to give the desired final surface carbon concentration.

Because, for a given carbon content of the core, the diffusion rate of carbon in austenite decreases with a lowering of surface carbon concentration, any "starvation" method of carburizing in which the workpiece surfaces are never carburized above the desired final value requires a longer cycle. Also, good recirculation of gases is essential. The atmosphere adjacent to the work quickly becomes depleted of carbon, and, if stagnant areas are allowed, excessively low surface carbon concentrations and shallow case depths will result on the work in these areas. This potential detriment to part quality is the chief reason why most continuous carburizing furnaces in use today are equipped with effective recirculating fans.

Variability in Surface Carbon. Statistical data relating to the control of surface carbon content are given in Fig. 13, 14, 15, and 16 for several plain carbon and low-alloy steels. These data represent practice in eight different plants and therefore involved several different types of furnaces, steel compositions, and "aim" carbon contents. Control varied from good to poor, as the graphs indicate.

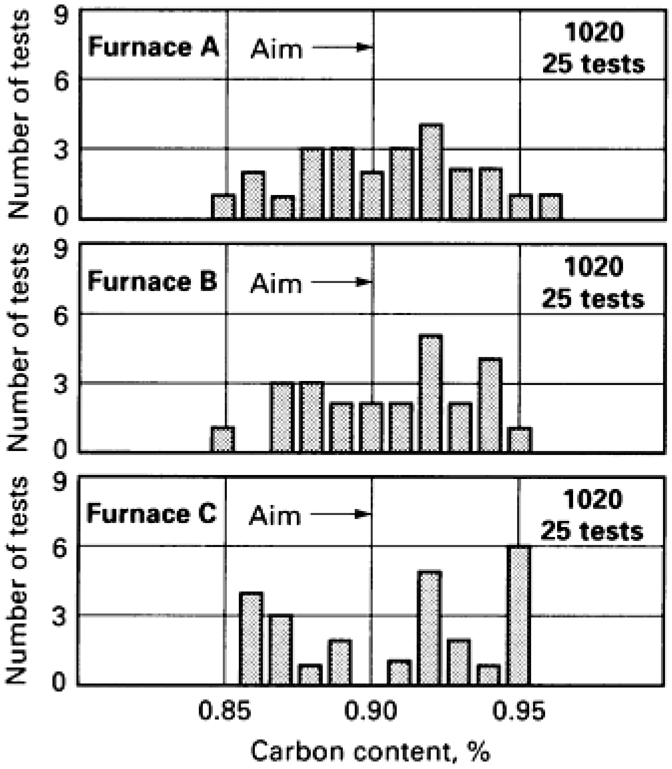
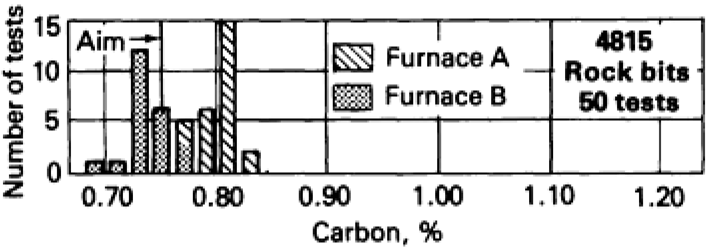
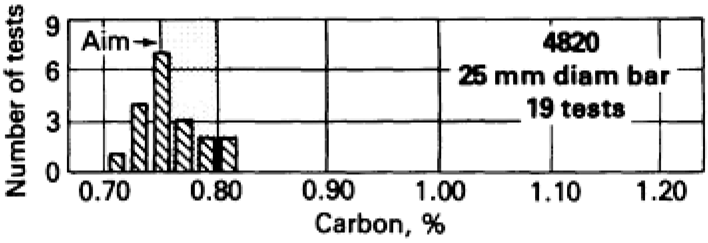


Fig. 13 Variation in carbon content 0.25 mm (0.010 in.) below the surface for 1020 steel carburized in three similar batch furnaces



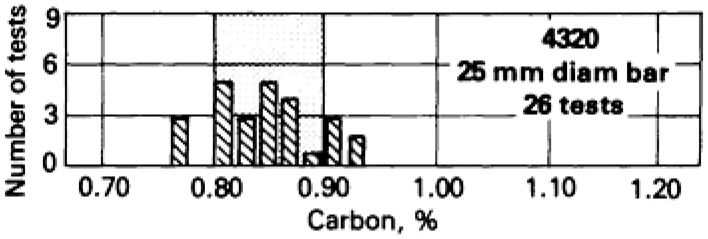
Aim
Furnace A
Furnace B
4815
Rock bits
50 tests
Number of tests
15
10
5
0
0.70
0.80
0.90
1.00
1.10
1.20
Carbon, %

(a)



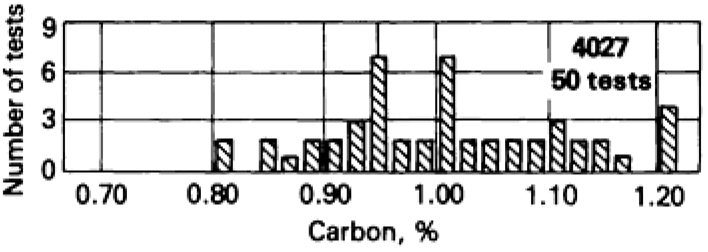
Aim
4820
25 mm diam bar
19 tests
Number of tests
9
6
3
0
0.70
0.80
0.90
1.00
1.10
1.20
Carbon, %

(b)



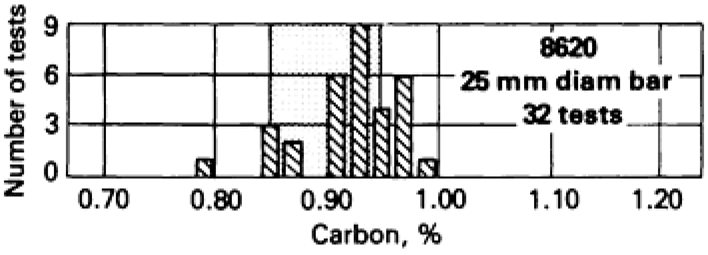
4320
25 mm diam bar
26 tests
Number of tests
9
6
3
0
0.70
0.80
0.90
1.00
1.10
1.20
Carbon, %

(c)



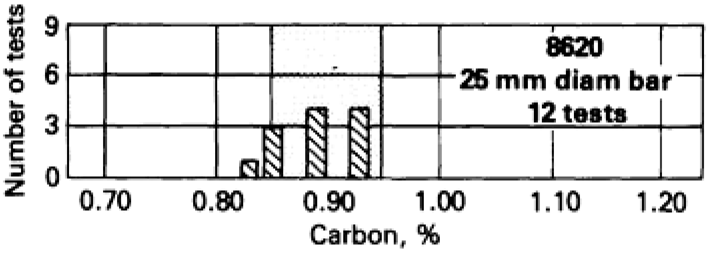
4027
50 tests
Number of tests
9
6
3
0
0.70
0.80
0.90
1.00
1.10
1.20
Carbon, %

(d)



8620
25 mm diam bar
32 tests
Number of tests
9
6
3
0
0.70
0.80
0.90
1.00
1.10
1.20
Carbon, %

(e)



8620
25 mm diam bar
12 tests
Number of tests
9
6
3
0
0.70
0.80
0.90
1.00
1.10
1.20
Carbon, %

(f)

Fig. 14 Variation in surface (or near-surface) carbon content for alloy steels carburized under different conditions. (See text.)

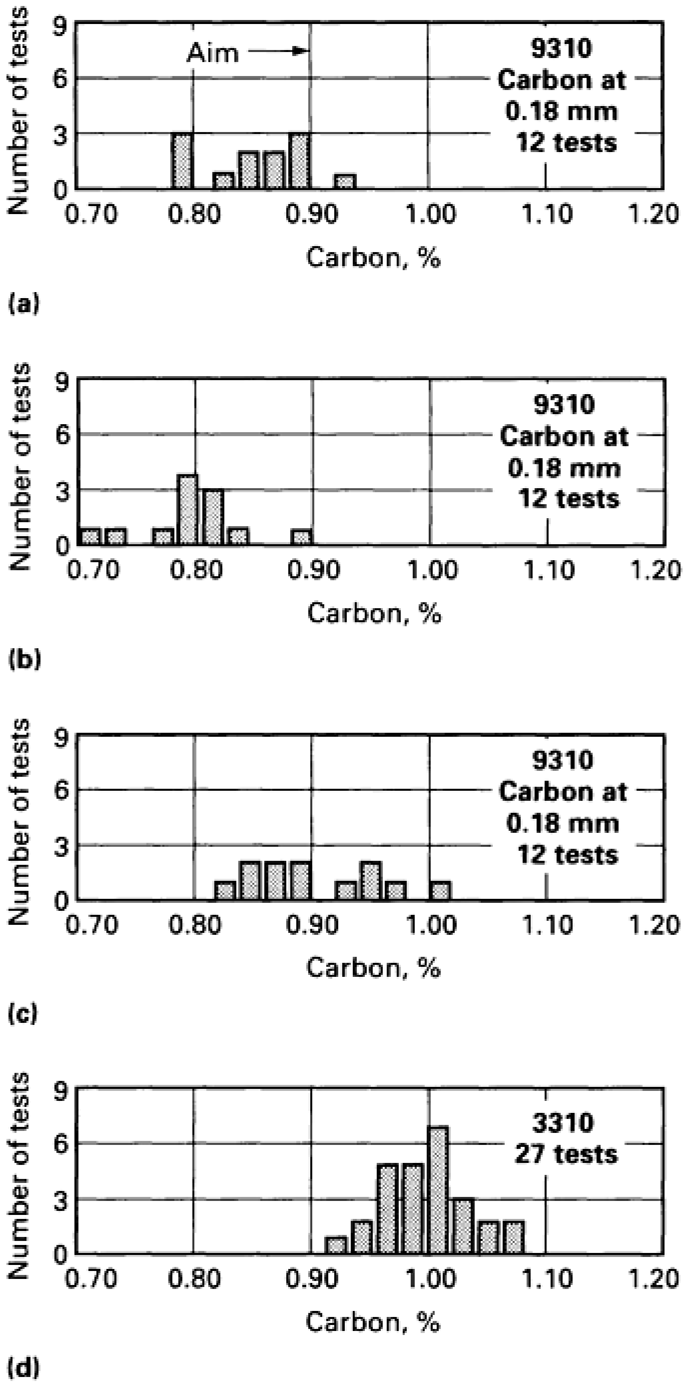
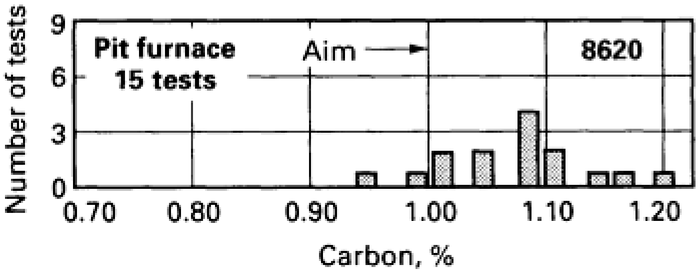
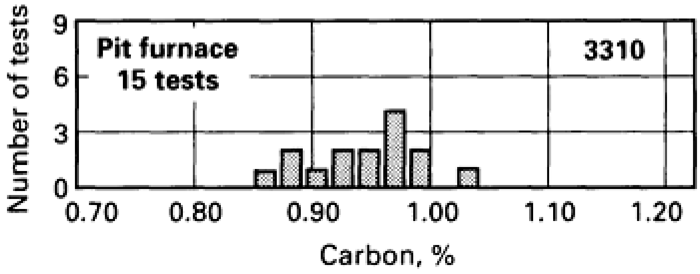


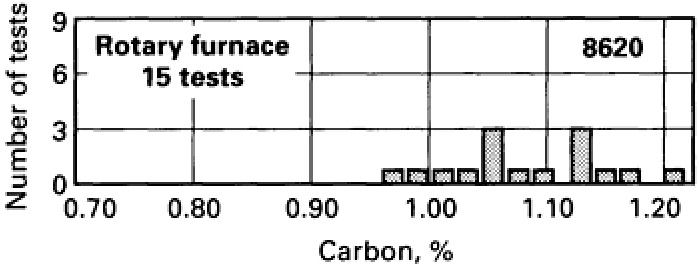
Fig. 15 Variation in surface (or near-surface) carbon content for 9310 and 3310 alloy steels carburized under different conditions. (See text.)


Pit furnace
15 tests
Aim
8620
Number of tests
9
6
3
0
0.70
0.80
0.90
1.00
1.10
1.20
Carbon, %

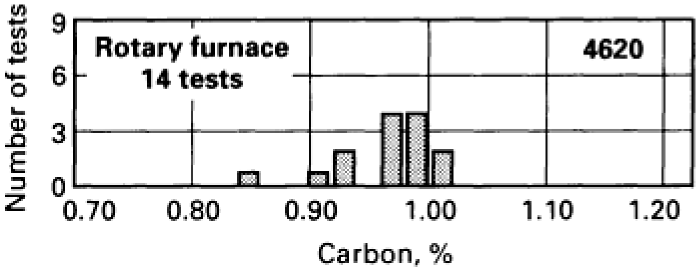
(a)


Pit furnace
15 tests
3310
Number of tests
9
6
3
0
0.70
0.80
0.90
1.00
1.10
1.20
Carbon, %

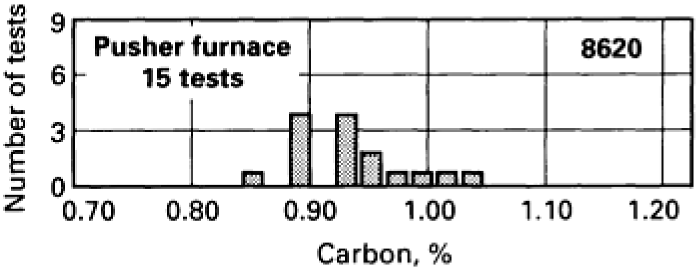
(b)


Rotary furnace
15 tests
8620
Number of tests
9
6
3
0
0.70
0.80
0.90
1.00
1.10
1.20
Carbon, %

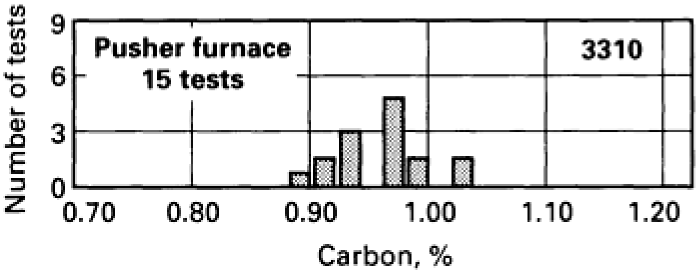
(c)


Rotary furnace
14 tests
4620
Number of tests
9
6
3
0
0.70
0.80
0.90
1.00
1.10
1.20
Carbon, %

(d)


Pusher furnace
15 tests
8620
Number of tests
9
6
3
0
0.70
0.80
0.90
1.00
1.10
1.20
Carbon, %

(e)


Pusher furnace
15 tests
3310
Number of tests
9
6
3
0
0.70
0.80
0.90
1.00
1.10
1.20
Carbon, %

(f)

Fig. 16 Variation in near-surface (0.13 to 0.25 mm, or 0.005 to 0.010 in.) carbon content for alloy steels carburized in different types of furnaces. (See text.)

The data summarized in Fig. 13 compare carbon concentrations 0.25 mm (0.010 in.) below the surface obtained in gas carburizing 25 batches in each of three similar batch furnaces. The 75 tests show a large majority of the concentrations to be within ±0.05% of the 0.90% C aim. Parts were carburized at 925 °C (1700 °F). The carbon potential was controlled through the dew point. A carrier gas with a dew point of 1.5 °C (35 °F) was enriched with natural gas to maintain a dew point of -5.5 °C (22 °F) in the furnace.

The data presented in Fig. 14(a) compare surface carbon content in rock bit cutters carburized in two pit furnaces to a desired carbon content of 0.75%. Furnaces were operated simultaneously, using the same carrier gas generator. Each furnace was about 1 m (3.3 ft) in diameter by 2 m (6.6 ft) deep and contained a load of about 1360 kg (3000 lb). A carburize-diffuse cycle was used. An automatic dew point controller was employed on the carrier gas generator but not on the furnace.

The results plotted in Fig. 14(b) show surface carbon contents (carbon content of the first 0.075 mm, or 0.003 in., cut) for 19 specimens of 4820 steel carburized along with loads of production parts in a two-row, pusher-type continuous furnace. The desired carbon content was 0.75 to 0.80%, with a specification of 0.70 to 0.90% carbon. All results were within specification, and most were within desired limits. Specimens were carburized at 925 °C (1700 °F) using a diffusion cycle, quenched from 815 °C (1500 °F) in oil at 60 °C (140 °F), tempered in lead at 620 °C (1150 °F) for 5 min, and cleaned with a wire brush, and liquid abrasive. The atmosphere at the charge end of the furnace was automatically controlled at a dew point of -15 °C (5 °F) and at the discharge end was controlled at a dew point of 3 °C (37 °F). Endothermic gas enriched with straight natural gas was used as the carburizing medium; air was added at the discharge end.

The data presented in Fig. 14(c) for 4320 steel bar specimens were obtained under the same carburizing and test conditions used for Fig. 14(b) for lengths of 4820 steel bar, except that the dew point was -1 °C (30 °F) at the discharge end and the specimens were tempered at 650 °C (1200 °F). The desired surface carbon content was 0.85 ±0.05%.

The results of 50 tests that represent variations in surface carbon content for continuous carburizing of 4027 steel are given in Fig. 14(d). These results were obtained over a period of 3 to 4 years. An automatic dew point controller was used.

The data given in Fig. 14(e) for 8620 steel bar specimens were obtained under the same carburizing and test conditions used for carburizing 4320 steel (Fig. 14c). The desired surface carbon content was 0.90 ±0.05%.

The data shown in Fig. 14(f) were based on the surface carbon content (the first 0.075 mm, or 0.003 in., depth of cut) of 25 mm (1 in.) rounds. The rounds were carburized with production parts in a horizontal batch furnace, quenched in oil from 845 °C (1550 °F), tempered in lead at 650 °C (1200 °F), and cleaned with a wire brush and liquid abrasive. The desired carbon content was 0.90 ± 0.05%. The carburizing medium was endothermic gas enriched with natural gas. No air was added. A dew point of -15 °C (5 °F) was used throughout the 925 °C (1700 °F) carburizing cycle, -12 °C (10 °F) for the diffusion cycle (also at 925 °C, or 1700 °F), and -3 °C (27 °F) for the 845 °C (1550 °F) cycle that preceded quenching.

The data in Fig. 15(a) represent carbon content at 0.18 mm (0.007 in.) below the surface. Actual surface carbon ranged from 0.85 to 1.03%. The steel was carburized in a batch-type furnace using a hot-wire analyzer for automatic atmosphere control. Actual case depth to 50 HRC was 1.10 to 1.32 mm (0.043 to 0.052 in.); required case depth was 1.15 to 1.25 mm (0.045 to 0.050 in.); total case depth ranged from 1.93 to 2.05 mm (0.076 to 0.081 in.).

The data summarized in Fig. 15(b) also represent carbon content at 0.18 mm below the surface. Actual surface carbon ranged from 0.84 to 1.19%. The steel was carburized in a batch-type furnace with manual atmosphere control. Actual case depth to 50 HRC was 0.38 to 0.58 mm (0.015 to 0.023 in.); required case depth was 0.38 to 0.64 mm (0.015 to 0.025 in.); total case depth ranged from 0.64 to 0.80 mm (0.025 to 0.031 in.).

Carburizing and test conditions for the data shown in Fig. 15(c) were the same as those for the data in Fig. 15(b). In this instance, surface carbon ranged from 0.89 to 1.48%, and case depth to 50 HRC was 0.64 to 0.94 mm (0.025 to 0.037 in.).

Specified case depth was 0.75 to 0.90 mm (0.030 to 0.035 in.); total depth ranged from 0.86 to 1.35 mm (0.034 to 0.053 in.). The same batch-type furnace was used to obtain the data for Fig. 15(a), 15(b), and 15(c).

The data shown in Fig. 15(d) represent surface carbon contents of 27 samples taken at 8-h intervals. Parts were carburized in trays in a continuous pusher furnace with dew point control of the atmosphere. Desired surface carbon was 1.0%.

The carbon concentration data for 8620 and 3310 steels that are shown in Fig. 16(a) and 16(b) were obtained on round-bar test specimens placed at several locations throughout each charge of production parts of the same steel composition. Specimens were carburized in a vertical pit furnace having a single circulating fan. The atmosphere was endothermic gas enriched with methane. The 8620 steel was carburized at 955 °C (1750 °F), without automatic atmosphere control, using a diffusion cycle in which only endothermic gas was introduced during the last third of the carburizing cycle. The 3310 steel was carburized at 925 °C (1700 °F), with automatic atmosphere control but no diffusion cycle.

Round bars were used to obtain the data shown for 8620 and 4620 steels in Fig. 16(c) and 16(d). Both steels were carburized at 955 °C (1750 °F) in a rotary retort furnace under an atmosphere of endothermic gas plus methane. A diffusion cycle, in which the methane was shut off for the last third of the carburizing cycle, was used for the 8620 steel. The 4620 steel was carburized without a diffusion cycle, and the carbon content ranged predominantly below the desired 1.0%. Results for the 8620 steel were largely above the desired carbon content.

The data in Fig. 16(e) and 16(f) for 8620 and 3310 steels were obtained from round test specimens distributed throughout loads in continuous pusher furnaces. The atmospheres were endothermic gas enriched with methane. The 8620 specimens were carburized at 925 °C (1700 °F) in a furnace with three fans, without automatic atmosphere control or a diffusion cycle. The 3310 specimens were carburized at 925 °C in a furnace equipped with two fans, with automatic atmosphere control but no diffusion cycle.

Surface carbon content may vary significantly as a function of location in the furnace. Figure 17 indicates a variation in surface carbon on 4620 steel bearing races from the tip to the bottom of the pit furnace used. The furnace was about 0.75 m (30 in.) in diameter by 0.90 m (36 in.) deep. An open load of races was carburized for 7 h in a natural gas atmosphere, and this step was followed by a $3\frac{1}{2}$-h diffusion cycle. Desired surface carbon was 1.00%. Each bar on the chart represents 14 heats of steel. It is apparent that in this instance surface carbon content was consistently higher in specimens carburized in the bottom portion of the furnace, possibly indicating a slightly higher operating temperature there.

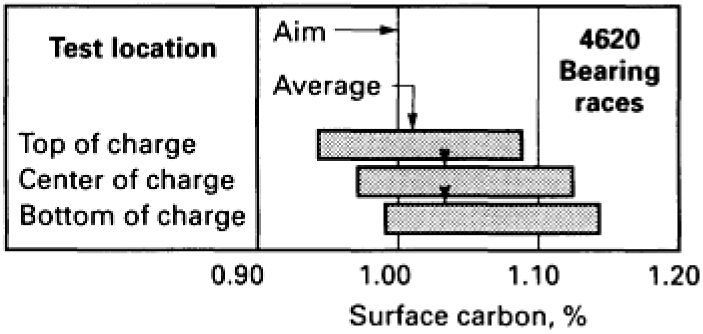


Fig. 17 Variation in surface carbon content with position in a pit furnace for 4620 steel bearing races

A horizontal batch furnace--operated as described for Fig. 3(b) and 3(c) except that, for a dew point of -12 °C (10 °F), diffusion time was 6 h--produced the distribution of case depth shown in Fig. 3(d) and tabulated as:

Variation from average depth,	Part distribution,

mm (in.)	%
1.5 ± 0.03 (0.061 ± 0.001)	31
1.5 ± 0.05 (0.061 ± 0.002)	50
1.5 ± 0.08 (0.061 ± 0.003)	63
1.5 ± 0.10 (0.061 ± 0.004)	81
1.5 ± 0.13 (0.061 ± 0.005)	100

In this instance, the target depth (to 0.040% C) was 1.4 to 1.8 mm (0.055 to 0.070 in.). Testpieces like those described for Fig. 3(a) were used to obtain the data.

A case depth of 1.4 to 1.8 mm (0.055 to 0.070 in.) (to 0.040% C) was specified for gears that were carburized at 925 °C (1700 °F) in a continuous furnace. The variation in case depth is likely to be greater in a continuous furnace than in a batch furnace, as indicated by results of 24 tests summarized in Fig. 3(e). These data were obtained from actual gears, one tested per week for 24 weeks.

Batch-type carburizing in the same plant that case hardened the gears produced case depths within an extremely close range, as indicated in Fig. 3(f). Case depths were determined by carburizing testpieces 25 mm (1 in.) in diameter by 38 mm (1 $\frac{1}{2}$ in.) in length along with 175 to 205 kg (390 to 450 lb) charges of gears, using dew point control. The testpieces were cut in half, polished, etched in nital, and then examined microscopically.

As indicated in the preceding discussion, the routine carburization of parts to a case depth variability not exceeding ±0.2 mm (±0.008 in.) is quite reasonable. This degree of maximum variation can be expected over long periods of time, provided that there is adequate process control, supplemented with frequent destructive examination (several times a week) of either actual parts or production control specimens from each furnace or integrated production line.

Carbon Restoration

Hot-worked steel products usually become more or less decarburized during heating for hot rolling, forging, extruding, and spinning. The depth of decarburization depends on the hot-working temperature, time at temperature, furnace atmosphere, reduction in area from bloom to finished size, and type of steel.

Decarburization may be corrected by carbon restoration, that is, by carburizing enough to restore the carbon content to value equal to the original or intended content. This is particularly important when the formed product must be quenched and tempered to develop high resistance to wear or fatigue. For instance, cold-heading stock intended for use in antifriction bearings or fasteners must be virtually free from decarburization. The micrographs in Fig. 18 show the restoration of carbon, in two stages, to decarburize 1035 steel heading stock.

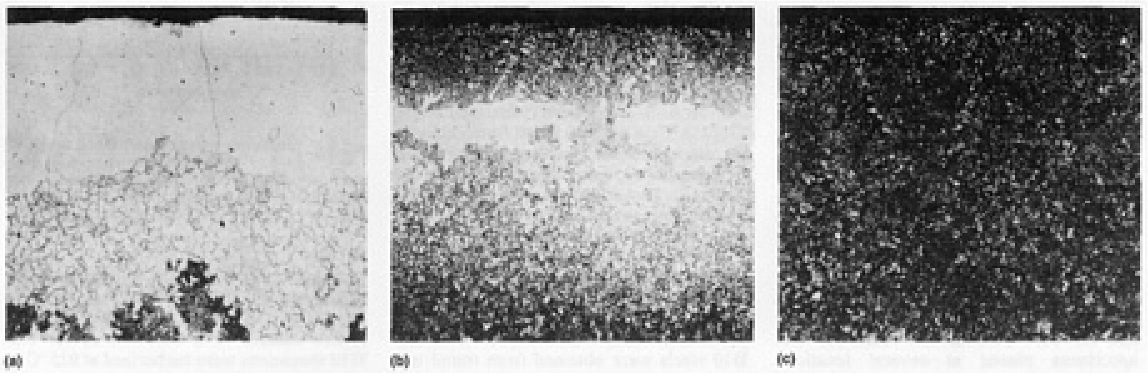


Fig. 18 Restoration of carbon in 1035 steel bar stock. (a) As-received steel with a carbon-free depth of 0.25 to 0.30 mm (0.010 to 0.012 in.); maximum affected depth, 0.38 to 0.64 mm (0.015 to 0.025 in.). (b) Same steel after carbon restoration at 850 °C (1560 °F) for 1 h followed by water quenching. (c) Same steel after carbon restoration at 850 °C (1560 °F) for 2 $\frac{1}{2}$ h followed by water quenching. All bar stock was 21.8 to 21.9 mm (0.859 to 0.862 in.) in diameter. All micrographs 100×

Four types of atmospheres are generally used for carbon restoration:

- Nitrogen-dissociated methanol
- Nitrogen enriched with hydrocarbon (usually, methane or propane)
- Dry, purified exothermic gas
- Endothermic gas

Of the four types, endothermic composition atmospheres are the best understood, the easiest to handle, and by far the most widely used in commercial practice. Nitrogen-methanol atmospheres can be considered direct replacements for generated endothermic gas because these two types of atmospheres have essentially the same composition.

When decarburization is shallow, surface carbon content can be corrected during the annealing or heat-treating cycle. For controlled carbon restoration, the annealing temperature must be above the control temperature for the steel being processed. If decarburization is deep, it may be necessary to use a higher temperature to obtain the necessary diffusion of carbon into the steel within practical time limits.

The process of restoring carbon can be applied to steels of low, medium, or high carbon content. Table 2 shows the treatment conditions used to restore carbon to four plain carbon steels of different carbon contents. The effectiveness of the treatment is also indicated. For control, both low-carbon and high-carbon shims were treated with these steels, and results for these shims are given as well. It can be seen that the low-carbon shims picked up carbon, whereas the high-carbon shims, with the exception of those treated along with the 1095 steel, lost carbon, indicating that equilibrium was established or closely approached.

Table 2 Effectiveness and conditions of carbon restoration for four plain carbon steels

Test cut number[(a)]	Amount of carbon present before and after treatment[(a)], %							
	1020[(b)]		1038		1070[(c)]		1095	
	Before	After	Before	After	Before	After	Before	After

1	0.11	0.20	0.12	0.37	0.16	0.66	0.16	1.04
2	0.19	0.18	0.08	0.34	0.49	0.63	0.62	1.02
3	0.18	0.18	0.17	0.36	0.63	0.62	0.82	0.95
4	0.16	0.19	0.27	0.37	0.69	0.65	0.94	0.95
5	0.18	0.18	0.33	0.39	0.71	0.65	1.00	0.95
6	0.17	0.19	0.39	0.38	0.72	0.68	1.00	1.01
7	0.16	0.19	0.39	0.39	0.72	0.70	1.02	1.01
8	. . .	. . .	. . .	. . .	0.72	0.70	1.03	1.01
Shim stock, 0.10% C[d]	0.10	0.25	0.10	0.40	0.10	0.70	0.10	1.16
Shim stock, 1.30% C[d]	1.30	0.25	1.30	0.42	1.30	0.68	1.30	1.81

Conditions of treatment	**1020[b]**	**1038**	**1070[c]**	**1095**
Restoration temperature, °C (°F)	870 (1600)	870 (1600)	870 (1600)	870 (1600)
Time, h	2	1	$2\frac{1}{2}$	3
Dew point, °C (°F)				
Furnace	20 (68)	7 (45)	-1 (30)	-4 (25)
Generator	23 (74)	-1 (30)	-9 (15)	-7 (20)
Atmosphere composition[e], %				
CO_2	1.1	0.9	0.2	0.2
O_2	0.0	0.0	0.0	0.0
H_2	36.6	38.5	40.6	40.6

CO	18.0	18.5	19.4	19.6
N_2	44.1	41.9	39.4	39.2
CH_4	. . .	0.2	. . .	0.4

(a) Carbon in steel determined by analysis of consecutive cuts: depth of cuts, 0.13 mm (0.005 in.).

(b) Represents four duplicate tests.

(c) Represents five duplicate tests.

(d) Treated for control.

(e) Analysis of atmosphere in furnace

Successful carbon restoration depends on (in order of importance):

- Composition of the furnace atmosphere
- Composition of the steel
- Processing temperature
- Surface condition of the material undergoing carbon restoration
- Type of furnace
- Furnace zone separation
- Atmosphere tightness of the furnace
- Distribution of the load
- Flow rate and degree of circulation of the furnace atmosphere

It is frequently expedient to control the dew point of an endothermic atmosphere by adding small amounts of air or methane to the furnace rather than adjusting the atmosphere generator. The addition of a small quantity of air increases the dew point, whereas the addition of methane decreases it. The addition of nitrogen to endothermic gas lowers CO_2, O_2, or dew point concentrations by *dilution.* This is seldom done, however, because the carburizing components of the endothermic gas (CO and H_2) are also diluted, resulting in a loss of carbon attainment rate and atmosphere control. If the CO content of an endothermic gas deviates widely from the normal 20% (±2%), adverse effects may be expected on carbon potential control where traditionally applied techniques are used (that is, C versus dew point, CO_2 content, and O_2 potential).

It is difficult to control the carbon potential of atmospheres so that reproducible carbon contents are developed in the surface of the part undergoing carbon restoration. A surface carbon level slightly below that of the base material is usually much less harmful than overcarburization, especially in fatigue applications. Consequently, if fatigue life is important to the serviceability of the part, it is best not to risk excessive carbon restoration.

The cost of restoring carbon to parts prior to final machining operations depends on such factors as the cost of the steel, the cost of carbon restoration, and the amount of final machining required. In general, if little or no machining is required for finishing a part, there may be an economic gain in restoring carbon. Conversely, if a part requires machining all over, which would remove most or all of the carbon-depleted area, carbon restoration may be unnecessary.

Quality Control

It is considered axiomatic that, to be effective and consistent, quality control for any facility must be properly conceived, formally documented, and rigorously followed. However, a single plan is not universally applicable; policies and procedures that work in one plant may be ineffective in another plant. The same is true of quality control for a carburizing facility.

Sampling Plans. Among commercial firms doing good-quality carburizing on a routine basis, the consensus is that only when samples are taken continually for destructive evaluation is it possible to ensure close control of case properties. The term samples may mean production parts, pieces of production parts, or specially designed test samples. Destructive examination usually means, as a minimum, etching a cross section and directly measuring case depth. In many instances the measurement of hardness gradient or examination of microstructure, or both, are also specified.

In one plant, where 44*xx* and 86*xx* steel gears of various sizes are carburized to a single set of requirements in tray-type, four-zone, continuous pusher furnaces, one gear is selected at random daily from each furnace line, after the direct-quench step. Quality is determined by taking microhardness measurements on a cross section through one of the teeth. Effective case depth to 50 HRC at the pitch line is reported, and the hardness profile is compared with that of previously produced gears. As an ongoing check, each part is tested with a mill bastard file immediately after quenching in oil to ensure that a file-hard case has been achieved.

In another plant, where a wide variety of gears is processed to various specifications and where both batch and continuous pusher furnaces are used, one sample part from each production lot is cut for destructive examination. Microstructure is observed, and effective case depth to 50 HRC is determined from a plot of microhardness (Knoop) versus depth. The operation of the furnaces is such that the type and size of gear are inconsequential. To evaluate furnace conditions, carbon gradients are measured for each furnace about every two to five working days. A standard carbon gradient bar is run along with production parts, the bar is step machined, and the carbon content of chips is determined spectrographically. For each plot of carbon gradient, the shape of the curve, case depth to 0.40% carbon, and surface carbon level are evaluated in relation to past performance.

In two other plants, part quality is evaluated by fracturing or cutting small standard test bars, etching the fractured or cut surfaces, and reading case depths with a Brinell glass. One of these plants uses test bars 11 mm square by 75 mm long (about $\frac{7}{16}$ in. square by 3 in. long) made of coarse-grained, cold-drawn, silicon-killed 1022 steel. In selecting test bar material, special narrow limits on composition, grain size, and hardenability are imposed so that normal heat-to-heat variations in response to heat treatment are minimized. In batch furnaces, at least one test bar is processed with each batch. (Sometimes, more than one is used, for example, in the tip, middle, and bottom trays of a load being carburized in a pit furnace.) In continuous furnaces, a test bar is placed in about every third tray in each row. In both plants, satisfactory case depths on carburized or carbonitrided test bars justify the release of parts into the normal production stream. If case depths on test bars are barely acceptable or are unsatisfactory, a sample part from the production lot is destructively examined and the decision to accept or reject the parts is based on the evaluation of this part.

Disposition of Rejected Parts. Experience and problem analyses have proved that nonconforming (rejected) parts must be handled by proper, strictly enforced procedures. Nonconforming parts must be identified so that they can be further investigated and then are reworked or discarded. It is extremely important that questionable parts be removed from the production area and placed in a quarantine area. Scrapped parts must be visibly mutilated to warn plant personnel against returning them to the process stream. Repairs should be made only with the knowledge of all departments concerned. Repaired components must be separated from the normal process stream until fully tested and proved to be of adequate quality.

The rejection of parts usually results from the failure of the furnace, generator, gas supply, or power. Fortunately, nonconforming components can often be reprocessed. Good preventive maintenance greatly minimizes such problems; an efficient shop produces only a small amount of scrap.

Defects and Distortion in Heat-Treated Parts

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Introduction

MOST OF THE PROBLEMS in heat-treated parts are attributed to faulty heat-treatment practices (such as overheating and burning, and nonuniform heating and quenching), deficiency in the grade of steels used, part defect, improper grinding, and/or poor part design. This article discusses overheating and burning, residual stresses, quench cracking, and distortion in some detail and offers some suggestions to combat them.

Most of these conditions result in a characteristic appearance of the treated parts that can be easily recognized by simple inspection. Some of these factors do not produce any distinguishing features in the semifinished or finished part. In particular, some of the visual evidence does not recognize the presence of overheating and burning and the development of residual stresses leading to distortion, quench cracking, and eventual failure of the heat-treated parts; metallurgical laboratory examination is needed to establish these problems that contribute significantly to the service performance of the part. Tool designers must also be aware of the problems and difficulties in manufacture, heat treatment, and use.

Overheating and Burning of Low-Alloy Steels

When low-alloy steels are preheated to high temperature (usually >1200 °C, or 2200 °F), prior to hot mechanical working (such as forging) for a long period, a deterioration in the room-temperature mechanical properties (particularly tensile ductility and impact strength or toughness) can be obtained after the steel has been given a final heat treatment (comprising reaustenitizing, quenching, and tempering) (Ref 1, 2, 3). Linked with the impaired mechanical properties is the appearance of intergranular matte facets on the normal ductile fracture surface of an impact specimen. This phenomenon is known as overheating and has been a matter of concern, especially in the case of steel forgings. Overheating has also been noticed in steel castings (due to variation in pouring temperature and effectiveness of the proprietary grain inoculants applied to the mold surface), in heavily ground parts, and in affected zones of welds (Ref 4). The usual practice is to reject the overheated products as being unsuitable for service.

It has now been established that overheating is essentially a reversible process caused by the solution of MnS particles in austenite during heating or reheating at high temperatures; the amount increases with temperature, and its subsequent reprecipitation during cooling occurs at intermediate rates as very fine (~0.5 μm) arrays of α-MnS particles on the austenite grain boundaries. On subsequent heat treatment the intergranular network of sulfides may provide a preferential, lower-energy fracture path in contrast to a normal transgranular fracture path. As a result, when impact loaded, a ductile intergranular fracture develops due to decohesion of the MnS/matrix interface and progress of microvoid coalescence. Figures 1 (a) and (b) show the usual appearance of the fracture surface at different magnifications (Ref 1).

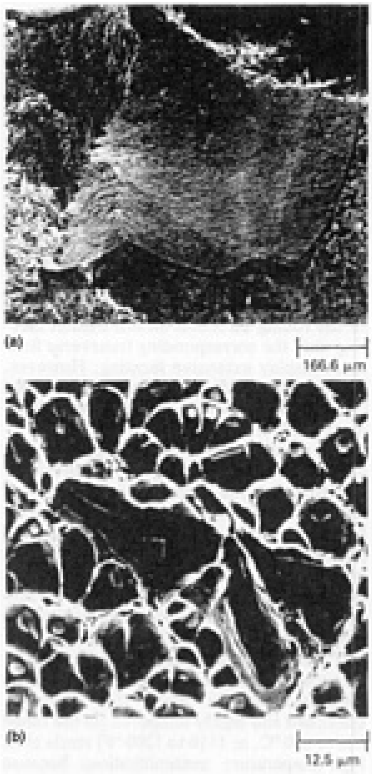

Fig. 1 Fracture surface of an impact loaded specimen. (a) Appearance of intergranular fracture of 4.25Ni-Cr-Mo steel containing 0.34% Mn and 0.008% S, in fully heat-treated condition but after cooling from 1400 °C (2550 °F) at 10 °C/min (20 °F/min). (b) Same specimen as in (a) but at higher magnification, showing ductile dimples nucleated by MnS particles precipitated at austenite grain boundaries. Courtesy of The Institute of Metals

When the low-alloy steel is preheated prior to hot working at too high a temperature (normally >1400 °C, or 2550 °F), local melting occurs at the austenite grain boundaries as a result of the segregation of phosphorus, sulfur, and carbon (Ref 5). During cooling, initially dendritic sulfides (probably type II-MnS) form within the phosphorus-rich austenite grain boundary, which then transforms to ferrite. This results in excessively weak boundaries. Subsequent heat treatment provides a very poor impact strength and almost completely intergranular fracture surface after impact failure. This phenomenon is termed burning. Burning thus occurs at a higher temperature than overheating. If this occurs during forging, the forging will often break during cooling or subsequent heat treatment (Ref 4).

Detection of Overheating

There are two basic methods for the determination of the occurrence of overheating, namely, fracture testing and metallography (or etch testing). Overheating may also be detected by a decrease in mechanical properties. But such changes are not very marked unless overheating temperature is high or overheating is too prolonged or severe; in some instances the mechanical properties do not change, even after the observation of extensive faceting. Usually the two methods mentioned above should be used in conjunction with some measure of toughness by impact or other testing in order to get a clear understanding of the degree and severity of overheating (Ref 2).

Fracture Testing. The direction of fracture testing is important in steels manufactured by conventional methods. It has been observed by some workers (Ref 6) that the longitudinal fracture test specimens parallel to the rolling direction do not exhibit faceting until the corresponding transverse fractures display extensive faceting. However, the testing direction in electroslag-refined (ESR) steels has been found to be insignificant (Ref 7).

The scanning electron microscope is considered to be the best and most convenient tool to detect the facets on the overheated fracture surfaces. These facets are characterized by small, well-defined, ductile dimples; each dimple is usually nucleated, presumably by fine arrays of inclusion particles: α-MnS particles (Fig. 1) in Mn-bearing steels (Ref 8, 9) or chromium sulfides in Mn-free steels (Ref 10, 11).

It is now well recognized that the fracture test specimen should always be tested in the toughest possible state (for example, quenched and highly tempered [in the range 600 to 650 °C, or 1110 to 1200 °F] steels after high-temperature austenitization) because this condition is most prone to overheating effects. Baker and Johnson (Ref 5) have suggested that an increased proportion of facets in the fracture specimens with increasing tempering temperature is attributed to the corresponding increase of the plastic zone size. In this case a slight amount of weakening will be sufficient to impart faceting because the grain boundary strength becomes lower (Ref 2). It should be noted that the existence of facets in the fractured specimens is not always associated with a lowering of impact strength (Ref 12).

Metallography (or Etch Testing). The most widely used etchant technique uses Austin's reagent (aqueous solution of 10% nitric and 10% sulfuric acids), ammonium persulfate, molten zinc chloride, saturated solution of picric acid at 60 °C (140 °F), and an electrolytic etch based on saturated aqueous ammonium nitrate. Table 1 shows the etching characteristics of overheated and burned steels (Ref 13). The etchant procedure with Austin's etchant is as follows: The sectioned specimen is etched for 30 s in the etchant, removed, washed off, and repeated three times. If the steel has been overheated, the original austenite grain boundaries will be preferentially attacked, and a black network of etch pits will be observed under the microscope (Ref 14). According to Preece and Nutting (Ref 13), the best results are obtained when ammonium nitrate etch is applied on the sectioned steel specimen in the fully heat-treated condition where this etchant preferentially attacks the matrix (original austenite grains), leaving the grain boundary unaffected (which appears as a white network). Bodimeade (Ref 15) concluded that all these etchants did not cope with mildly overheated low-sulfur steels. Table 2 is a summary of the results of potentiostatic etching techniques carried out by McLeod (Ref 12) using nitric-sulfuric, saturated aqueous picric acid (at 60 °C, or 140 °F), and ammonium nitrate etchants. He considered that when the suitable etching conditions were established, the potentiostatic etching method rendered more reliable and reproducible results as compared with the conventional etching techniques. However, the same problem with mildly overheated low-sulfur steels still persisted. Hence, the use of etch tests for low-sulfur low-alloy steels is not recommended for the detection of mild overheating.

Table 1 Etching characteristics of overheated and burned steels

Reagent	Method	Action on overheated steel	Action on burned steel
2.5% nitric acid in ethyl alcohol	Swab surface for 30 s	May produce grain contrast, but not indicative of overheating	White boundaries outlining preexisting austenite grains
Saturated aqueous solution of ammonium nitrate	Electrolytic, specimen anode, current density 1.0 A cm^{-2} (6.5 A $in.^{-2}$)	White boundaries outlining preexisting grains	Black boundaries outlining preexisting austenite grains
Aqueous 10% nitric acid + 10% sulfuric acid	Etch for 30 s, swab surface; repeat three times, then repolish lightly	Black boundaries outlining preexisting austenite grains	White boundaries outlining preexisting austenite grains
85% orthophosphoric acid (Fine's reagent)	Electrolytic, specimen anode, current density 0.15 A cm^{-2} (1.0 A $in.^{-2}$), etching time 15 min	Does not differentiate between overheated and nonoverheated steel	Attacks inclusions at grain boundaries
Oberhoffer's reagent	Swab surface for 30 s	Does not differentiate between overheated and nonoverheated steel	Shows phosphorus segregation at grain boundaries

Source: Ref 13

Table 2 Summary of potentiostatic etching experiments

Solution	Anodic loop voltage, mV	Observed effect	Best etching conditions		Comments
			Voltage,	Observed effect	

			mV		
Saturated aqueous ammonium nitrate	-400	Slight general etching	2200 (for 2 min)	Classic white boundaries on a dark background	Operates best in the transpassive region at >+1500 mV; time at any potential is important
					Underetching: random array of black pits
					Overetching: uniform black surface film
Aqueous 10% nitric acid + 10% sulfuric acid	200	Vigorous dissolution of specimen; formation of flaky black film	None	. . .	Most aggressive etchant of the three examined
	-250	Milder attack; large black pits in mildly etched matrix	About -250 (for 30 s)	Discontinuous array of grain-boundary pits and some random pits within grains	Polish lightly after etching to eliminate matrix etching effects
Saturated aqueous picric acid at 60 °C (140 °F)	100	No real, positive indication of overheating	None	. . .	Anodic loop very weak, necessitating long etching times because current density is very low; Teepol additions gave no improvement

Source: Ref 12

Detection and Effects of Burning

Burning is not commonly encountered. The two etchants (namely, nitric-sulfuric acid and ammonium nitrate solution) used for overheating can be successfully employed for detecting burning. When applied to burned steels, these etchants react in a manner opposite to that of overheated steels. Preece and Nutting (Ref 13) found ammonium nitrate solution to be the ideal reagent to detect this phenomenon. Other reagents are Stead's and Oberhoffer's reagents, which may also be used to check the burning effect. However, these etchants are unable to differentiate between overheated and nonoverheated steels.

Factors Affecting Overheating

The occurrence and severity of overheating depend principally on important factors, notably steel composition, temperature, cooling rate, and method of manufacture.

Composition. Sulfur is the constituent that greatly influences overheating. For steels with less than 0.002 wt% sulfur, overheating does not occur; this is because of the very low volume fraction of sulfides formed. However, the commercial production of such very-low-sulfur steels (for example, ESR steels) is expensive. Above this level of sulfur, the overheating onset temperature rises with the increasing amount of sulfur. It has now been explained that steels with low sulfur content (0.01 to 0.02%) are more prone to this defect than those with high sulfur content (>0.3%) because the transgranular strength is high, and therefore a small amount of grain-boundary sulfide precipitation is enough to induce intergranular failure (Ref 16). The phosphorus content has been regarded with the most concern in connection with burning. At constant phosphorus level, there is an increase in the overheating temperature with the increase of sulfur content, whereas the burning onset temperature decreases. Burning temperature is reduced with the increase in phosphorus content. At low sulfur contents, a wide gap between overheating and burning temperatures exists. For example, in the case of vacuum remelted steels, the temperature gap between the onset of overheating and burning is

~300 to 400 °C (~570 to 750 °F) and there is a remote possibility of burning occurring within the forging range, unless the overheating is severe (Ref 2). However, at high sulfur content the gap becomes narrow.

Temperature. To avoid overheating, care must be exercised in choosing a correct heating temperature so that uneven heating, flame impingement, and so forth, do not occur (Ref 3).

Cooling Rates. The cooling rate through the overheating range affects the size and dispersion of intergranular α-MnS particles. The intermediate cooling rate generally employed, 10 to 200 °C/min (20 to 360 °F/min), gives rise to maximum faceting as well as to the greatest loss in impact strength. However, slow and rapid cooling rates will suppress overheating. At very slow cooling rates, the sulfide particles become large, small in number, and more widely dispersed, and they have no more deleterious effects than the other inclusions already present. At rapid rates, the sulfide inclusions are too fine to produce any damaging effect (Ref 17).

Methods of Manufacture. Electroslag-remelted steels are less susceptible than vacuum-remelted steels, presumably due to the difference in oxygen level. Similarly, nickel steels are more prone to overheating. Vacuum-remelted steels have a lower overheating temperature than some comparable air-melted steels.

Prevention of Overheating and Burning

For preventing overheating of steels, a properly selected temperature should lie between a temperature low enough for the metal to be safe and high enough to be sufficiently plastic. The better the temperature control, the better the compromise.

Severe overheating can be reduced to mild overheating by soaking the steel at 1200 °C (2200 °F); with care, it may be removed completely. Hot working through the overheating range to a low finish temperature is also reported to remove the effects of overheating.

The alloying additions with a greater sulfide-forming tendency, such as calcium, zirconium, cerium (~0.3% of the melt), or mixed rare earth metals (in the form of misch metal containing 52% Ce, 25% La, and 12% Nd), have been shown to increase significantly both the overheating temperature and mechanical properties of the steel (for example, ductility and toughness). Provided that a high Ce/S ratio (>2) existed, a complete change in sulfide morphology occurred in low-alloy steels where the elongated MnS inclusion occurring in the untreated steel was totally replaced by small globular type-I rare earth sulfides and oxysulfides of high thermal stability even after austenitizing at 1400 °C (2550 °F) (Ref 2). This treatment does not show intergranular faceting. Burning can also be avoided in the same way by treating with calcium, zirconium, cerium, or mixed rare earth addition to form refractory, less-soluble sulfides.

Control of Cooling Rates. Control of cooling rates is not a practical method for large forgings because extremely slow cooling is prohibitively time consuming and causes excessive scaling and decarburization, and rapid quenching from high temperatures produces cracking and distortion of the parts (Ref 2).

Reclamation of Overheated Steel

Severely overheated steels can often be completely restored by any of the following heat treatments:

- Repeated normalizing (as many as six) starting at temperatures 50 to 100 °C (90 to 180 °F) higher than usual, followed by a standard normalizing treatment (Ref 2)
- Repeated oil-hardening and tempering treatments after prolonged soaking at 950 to 1150 °C (1740 to 2100 °F) in carburizing atmosphere. Rehardening more than three times is not advisable
- Soaking at 900 to 1150 °C (1650 to 2100 °F) for several hours. This causes growth of MnS particles by the Ostwald ripening process and results in an excessive scale formation and a loss of dimensional accuracy of the forgings

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Defects and Distortion in Heat-Treated Parts

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Residual Stresses

Heat treatment often causes stress- and strain-related problems such as residual stress, quench cracks, and deformation and/or distortion. The residual stress may be defined as the self-equilibrating internal or locked-in stress remaining within a body with no applied (external) force, external constraint, or temperature gradient (Ref 18, 19). There are two types of residual stresses:

- *Macro- or long-range residual stress* is a first-order stress that represents an average of body stresses over all the phases in polyphase materials. Macroresidual stresses act over large regions as compared to the grain size of the material. Traditionally, engineers consider only this type of residual stress when designing mechanical parts
- *Microresidual stress, also termed tesselated stress or short-range stress* is a second-order or texture stress, which is associated with lattice defects (such as vacancies, dislocations, and pile-up of dislocations) and fine precipitates (for example, martensite) (Ref 20, 21, 22). Microresidual is the average stress across one grain or part of the grain of the material. This information is indispensable in studying the essential behavior of material deformation

These two types of residual stresses may also be classified further as a tensile or compressive stress located near the surface or in the body of a material. This section focuses on the effects, development, control, and measurement of long-range residual stresses.

Effects of Residual Stress

The major effects of residual stress include dimensional changes and resistance to crack initiation. Dimensional changes occur when the residual stress (or a portion of it) in a body is eliminated. In terms of crack initiation, residual stresses can be either beneficial or detrimental, depending on whether the stress is tensile or compressive.

Compressive Residual Stress. Because residual stresses are algebraically summed with applied stresses, residual compressive stresses in the surface layers are generally helpful because the built-in compressive stresses can reduce the effects of imposed tensile stresses that may produce cracking or failure. Compressive stresses therefore contribute to the improvement of fatigue strength and resistance to stress-corrosion cracking in a part and an increase in the bending strength of brittle ceramics and glass (Ref 22).

Figure 2 shows that the endurance limit fatigue strength of selected steels increases with the surface residual compressive stress developed by specific heat treatment and surface processing. It is also apparent that, in the presence of high compressive stress, a poor microstructure in steel samples has a small influence on good endurance limit fatigue strength (Ref 23, 24, 25). These fatigue improvements are of great significance in components, particularly where stress raisers, such as notches, keyways, oil holes, and so forth, are highly desirable in the design of components (for example, crank-shafts, half-shafts, and so on) (Ref 26). Many fabrication methods have been developed to exploit this phenomenon. Prestressed parts (including shrink-fits, prestressed concrete, interference fits, bolted parts, coined holes, wire-wound concrete pipe), mechanical surface working processes (such as shot peening, surface roiling, lapping, and so on) of hardened ferrous and nonferrous alloys, and surface hardening treatments are widely used to produce residual compressive stresses at the component surface.

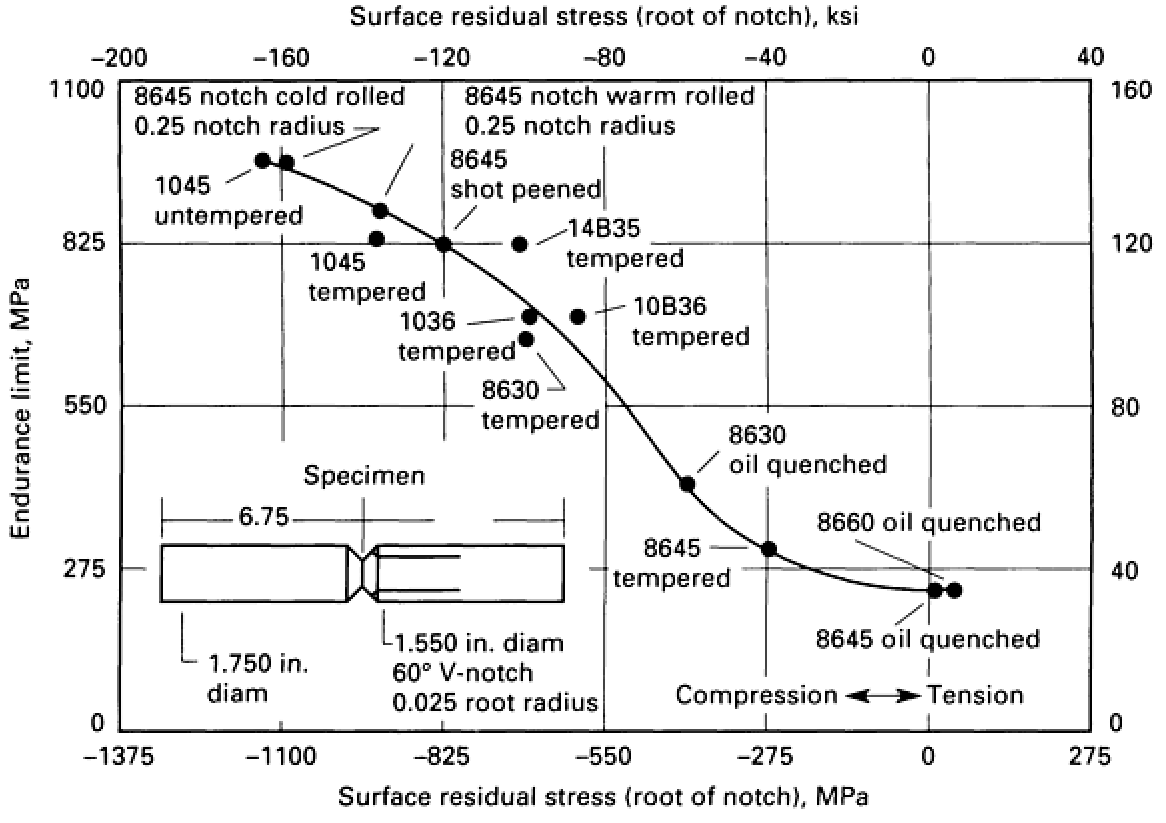

Fig. 2 Effect of surface residual stress on the endurance limit of selected steel. All samples were water quenched except as shown, and all specimen dimensions are given in inches. Source: Ref 23, 24

Residual tensile stresses at the surface of a part are usually undesirable because they can effectively increase the stress levels; may cause unpredicted stress-corrosion cracking (due to the combined effect of stress and environment), fatigue failure, quench cracking, and grinding checks at low external stresses; and tend to reduce fatigue life and strength of a part. In this case the extent of residual stresses may be closer or even larger than the strength of the material.

Residual tensile stresses in the interior of a component also may be damaging because of the existence and consequence of defects that serve as stress raisers in the interior part. The uncommon phenomenon of delayed cracking, in the absence of adverse environments and large applied stresses, has now been attributed to the action of residual stresses on minute defects in the material (Ref 26). For example, a 17.5 cm (6.9 in.) diam × 125 cm (49.2 in.) long steel shaft exploded into several pieces while lying free of any applied loads, on a laboratory floor. Under normal loading, it would have required a

tensile strength larger than 150 MPa (22 ksi) to rupture the shaft. Hence, the understanding of residual stress formation is very important, and this must be given due consideration in the manufacture and performance analysis of processed parts (Ref 26).

Development of Residual Stress in Processed Parts

Variations in stresses, temperature, and chemical species within the body during processing cause the production of macroresidual stresses. Various manufacturing processes such as forming, machining, heat treatment, shot peening, casting, welding, flame cutting, and plating render their characteristic residual stress pattern to processed parts. Table 3 lists a summary of compressive and tensile residual stresses at the surface of parts fabricated by common manufacturing processes.

Table 3 Summary of compressive and tensile residual stresses at the surface of the parts created by the common manufacturing processes

Compression at the surface
Surface working: shot peening, surface rolling, lapping, and so on
Rod or wire drawing with shallow penetration[(a)]
Rolling with shallow penetration[(a)]
Swaging with shallow penetration[(a)]
Tube sinking of the inner surface
Coining around holes
Plastic bending of the stretched side
Grinding under gentle conditions
Hammer peening
Quenching without phase transformation
Direct-hardening steel (not through-hardened)
Case-hardening steel
Induction and flame hardening
Prestressing

Ion exchange
Tension at the surface
Rod or wire drawing with deep penetration
Rolling with deep penetration
Swaging with deep penetration
Tube sinking of the outer surface
Plastic bending of the shortened side
Grinding: normal practice and abusive conditions
Direct-hardening steel (through-hardened)[(b)]
Decarburization of steel surface
Weldment (last portion to reach room temperature)
Machining: turning, milling
Built-up surface of shaft
Electrical discharge machining
Flame cutting

Source: Ref 22

(a) Shallow penetration refers to $\lesssim$1% reduction in area or thickness; deep penetration refers to $\gtrsim$1%.

(b) Depends on the efficiency of quenching medium.

In heat-treated parts, residual stresses may be classified as those caused by a thermal gradient alone, and a thermal gradient in combination with a structural change (phase transformation). When a steel part is quenched from the austenitizing temperature to room temperature, a residual stress pattern is established due to a combination of thermal gradient and local transformation-induced volume expansion.

Thermal contraction develops nonuniform thermal (or quenching) stress due to different rates of cooling experienced by the surface and interior of the steel part. Transformational volume expansion induces transformation stress arising from

the transformation of austenitc into martensite or other transformation products (Ref 27). Table 4 lists the changes in volume during the transformation of austenite into different structural constituents (Ref 28).

Table 4 Changes in volume during the transformation of austenite into different phases

Transformation	Change in volume, %, as a function of carbon content (% C)
Spheroidized pearlite $\rightarrow$ austenite	-4.64 + 2.21 × (% C)
Austenitc $\rightarrow$ martensite	4.64 - 0.53 × (% C)
Spheroidized pearlite $\rightarrow$ martensite	1.68 × (% C)
Austenite $\rightarrow$ lower bainite	4.64 - 1.43 × (% C)
Spheroidized pearlite $\rightarrow$ lower bainite	0.78 × (% C)
Austenite $\rightarrow$ upper bainite	4.64 - 2.21 × (% C)
Spheroidized pearlite $\rightarrow$ upper bainite	0

Source: Ref 4

Thermal Contraction. The relation between the thermal stress (σ_{th} during cooling and the corresponding temperature gradient in the component is given by:

$$\sigma_{th} = E \cdot \Delta T \cdot \alpha \quad \textbf{(Eq 1)}$$

where E is the modulus of elasticity, and α is the thermal coefficient of expansion of the material. It is thus apparent that thermal stresses are greatest for materials with high elastic modulus and coefficient of thermal expansion. Temperature gradient is also a function of thermal conductivity. Hence, it is quite unlikely to develop high-temperature gradients in good thermal conductors (for example, copper and aluminum), but it is much more likely in steel and titanium (Ref 29). Another term involving thermal conductivity, called thermal diffusivity (D_{th}), is sometimes used in context with temperature gradient. It is defined as $D_{th} = k/\rho c$, where k is the thermal conductivity, ρ is the density, and c is the specific heat. It is clear that low D_{th} (or k) promotes large temperature gradient or thermal contraction. It should be emphasized that large size of the part and high heating or cooling rates (severity) of quenching medium also augment temperature gradients leading to large thermal contraction.

Table 5 lists some of the relevant material properties that affect thermal and residual stresses (Ref 29).

Table 5 Relevant physical properties in the development of thermal stresses

Metal	Modulus of elasticity		Coefficient of expansion		Thermal conductivity	
	GPa	psi × 10^6	10^{-6}/K	10^{-6}/°F	W m^{-1} k^{-1}	Btu in./ft^2 · h · °F

Pure iron (ferrite)	206	30	12	7	80	555
Typical austenitic steel	200	29	18	10	15	100
Aluminum	71	10	23	13	201	1400
Copper	117	17	17	9	385	2670
Titanium	125	18	9	5	23	160

Source: Ref 29

Residual Stress Pattern Due to Thermal Contraction. Residual stress is developed during quenching of a hot solid part that involves thermal volume changes without solid-state phase transformation. This situation also exists when a steel part is cooled from a tempering temperature below the A_1. Figure 3 shows the development of longitudinal thermal and residual stresses in a 100 mm (4 in.) diam steel bar on water quenching from the austenitizing temperature, 850 °C (1560 °F) (Ref 30). At the start of cooling, the surface temperature *S* falls drastically as compared to the center temperature *C* (top left sketch of Fig. 3). At time *w,* the temperature difference between the surface and core is at a maximum of about 550 °C (1020 °F), corresponding to a thermal stress of 1200 MPa (80 tons/in.^{2}) due to linear differential contraction of about 0.6%, if relaxation does not take place. Under these conditions, tensile stresses are developed in the case with a maximum value of *a* (lower diagram), corresponding to time *w* in the upper diagram, and the core will contract, producing compressive stresses with a maximum of *b.* The combined effect of tensile and compressive stresses on the surface and core, respectively, will result in residual stresses as indicated by curve *C,* where a complete neutralization of stress will occur at some lower temperature *u.* Further decrease in temperature, therefore, produces longitudinal, compressive residual stresses at the surface and the tensile stresses at the core, as shown in the lower right-hand diagram of Fig. 3. Figure 4(a) is a schematic illustration of the distribution of residual stress over the diameter of a quenched bar due solely to thermal contraction in the longitudinal, tangential, and radial directions (Ref 19).

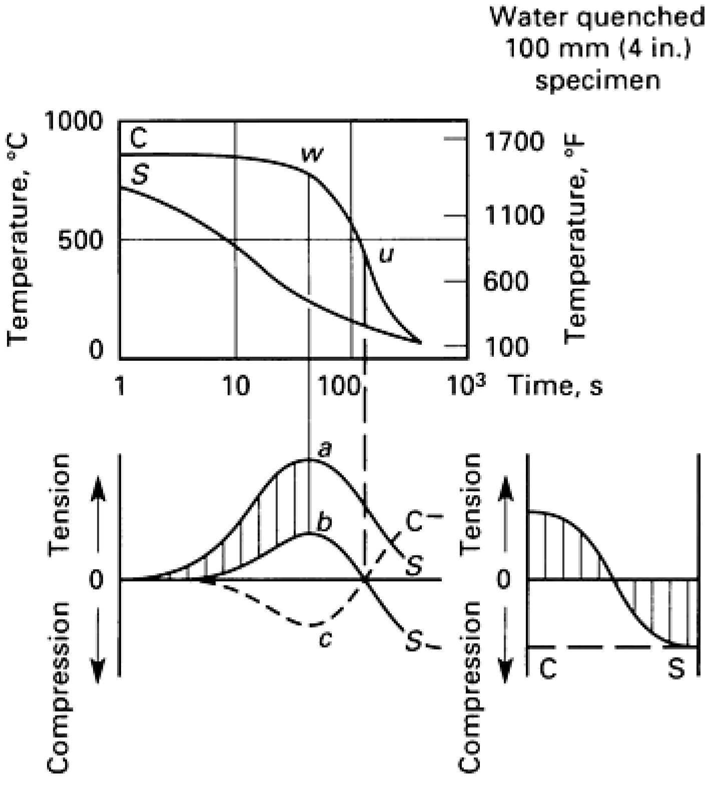

Fig. 3 Development of thermal and residual stresses in the longitudinal direction in a 100 mm (4 in.) diameter steel bar on water quenching from the austenitizing temperature, 850 °C (1560 °F). Transformation stresses are not taken into consideration. Source: Ref 30

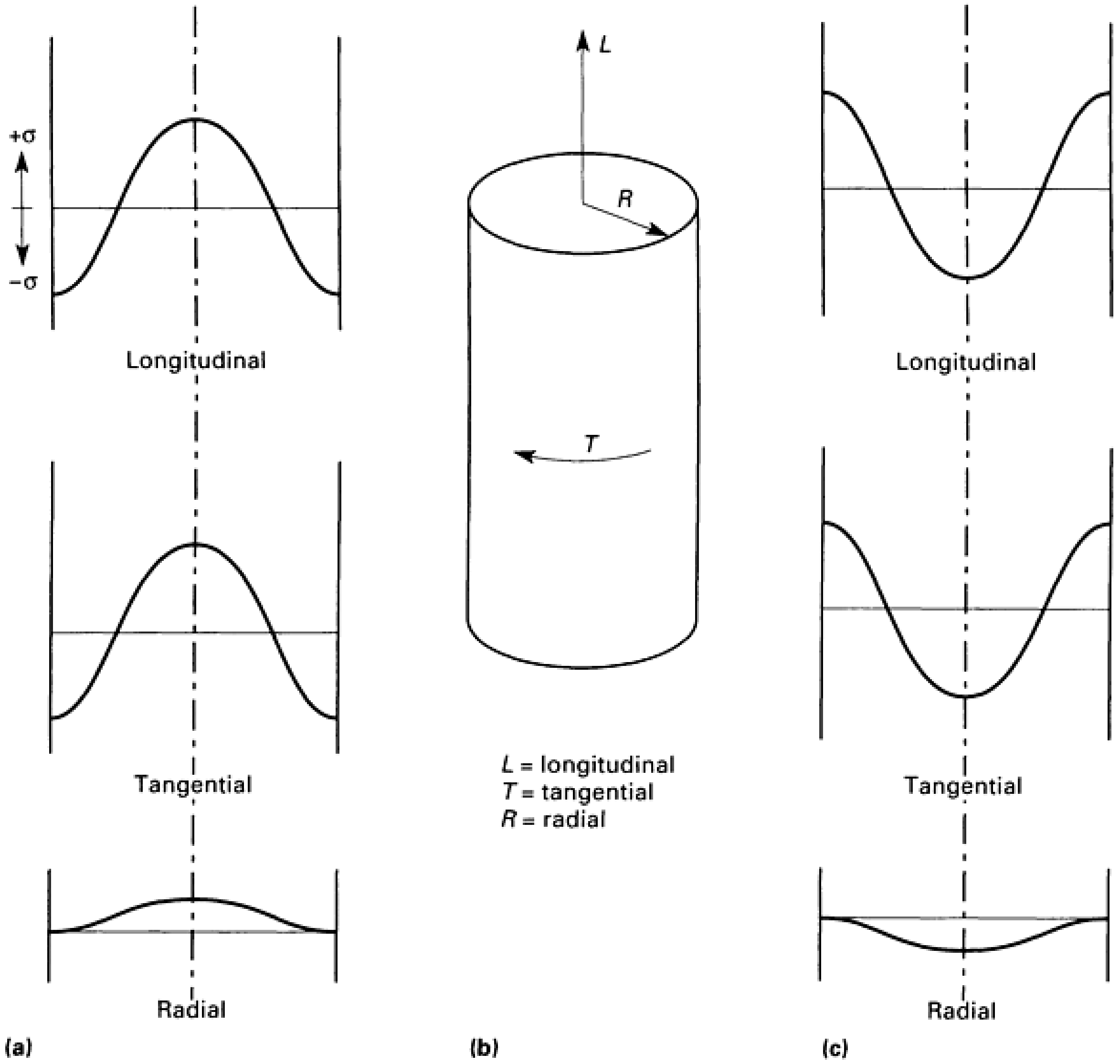

Fig. 4 Schematic illustration of the distribution of residual stress over the diameter of a quenched bar in the longitudinal, tangential, and radial directions due to (a) thermal contraction and (c) both thermal and transformational volume changes. (b) Schematic illustration of orientation of directions. Source: Ref 19

The maximum residual stress attained on quenching increases as the quenching temperature and quenching power of the coolant are increased. Tempered glass is made by utilizing quenching techniques in which glass is heated uniformly to the annealing temperature and then surface cooled rapidly by cold air blasts. This produces compressive surface stresses to counteract any tensile bending stress, if developed during loading of the glass, thereby increasing its load-carrying capacity (Ref 31).

Residual Stress Pattern Due to Thermal and Transformational Volume Changes (Ref 32). During quench hardening of a steel (or other hardenable alloy) part, hard martensite forms at the surface layers, associated with the volume expansion, whereas the remainder of the part is still hot and ductile austenite. Later, the remainder austenite transforms to martensite, but its volumetric expansion is restricted by the hardened surface layer. This restraint causes the central portion to be under compression with the outer surface under tension. Figure 4(c) illustrates the residual stress distribution over the diameter of a quenched bar showing volume expansion associated with phase transformation in the

longitudinal, tangential, and radial directions (Ref 19). At the same time during the final cooling of the interior, its contraction is hindered by the hardened surface layers. This restraint in contraction produces tensile stresses in the interior and compressive stresses at the outer surface. However, the situation as shown in Fig. 4(c) prevails, provided that the net volumetric expansion in the interior, after the surface has hardened, is larger than the remaining thermal contraction. In some particular conditions, these volumetric changes can produce sufficiently large residual stresses that can cause plastic deformation on cooling, leading to warping or distortion of the steel part. While plastic deformation appears to reduce the severity of quenching stresses, in most severe quenching the quenching stresses are so high that they do not get sufficiently released by plastic deformation. Consequently, the large residual stress remaining may reach or even exceed fracture stress of steel. This localized rupture or fracture is called quench cracking (Ref 32, 33).

It should be emphasized again that for a given grade of steel, both large size of the part and higher quenching speed contribute to the larger value of thermal contraction, as compared to the volumetric expansion, of martensite. In contrast, when the parts are thin and the quenching rate is not high, thermal contraction of the part subsequent to the hardening of the surface will be smaller than the volumetric expansion of martensite. Similarly, for a given quenching rate, the temperature gradients decrease with decreasing section thickness, and consequently the thermal component of the residual stress is also decreased (Ref 24).

Figure 5(a) shows the continuous cooling transformation diagram of DIN 22CrMo44 low-alloy steel exhibiting austenitic decomposition with the superimposed cooling curves of the surface and center in round bars of varying dimensions. If the large-diameter (100 mm, or 4 in.) bar is water quenched (that is, for slack quenching), martensitic transformation occurs at the surface, and pearlitic + bainitic transformations occur at the center, resulting in a residual stress pattern (top of Fig. 5) similar to that due solely to thermal stress (Fig. 4a). During the rapid quenching of the medium-size (30 mm, or 1.2 in.) bar diameter, the start of bainite transformation at the center coincides approximately with the transformation of martensite on the surface. This results in compressive stresses at both the surface and center, with tensile stresses in the intermediate region (middle of Fig. 5). When the smaller-diameter (10 mm, or 0.4 in.) bar is drastically quenched (for example, in brine), the entire bar transforms to martensite. This is associated with very little temperature variation between the surface and the center of the part. In this situation, tensile residual stress is developed at the surface and compressive stress at the center of the bar (bottom, Fig. 5) (Ref 34, 35).

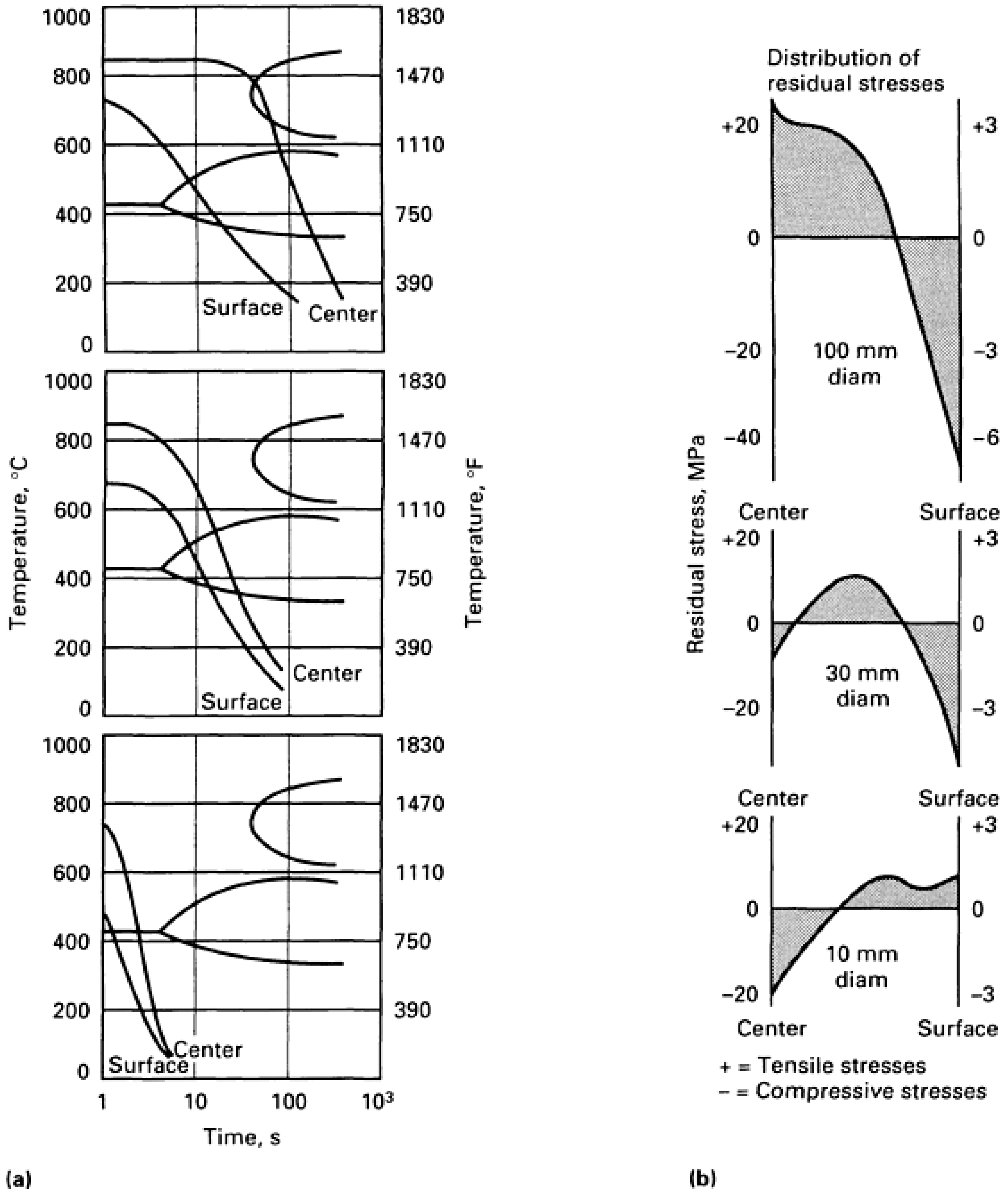

Fig. 5 (a) Continuous cooling transformation diagrams of DIN 22CrMo44 steel showing austenitic decomposition with the superimposed cooling curves of the surface and center during water quenching of round bars of varying dimensions. (b) The corresponding residual stress pattern developed because of thermal and transformational volume changes. Source: Ref 34, 35

Although the shallower hardening steels exhibit higher surface compressive stresses, deep hardening steels may develop moderately high surface compressive stresses with severe water quenching. When these deep hardening steels are through-hardened in a less efficient quenchant, they may exhibit surface tensile stresses (Ref 24, 31). Rose has pointed out the importance of transformations of core and surface before and after the stress reversal. According to him the tensile surface residual stress occurs when the core transforms after, and the surface transforms before, the stress reversal (Fig. 4c and bottom of Fig. 5), whereas compressive surface residual stress takes place when the core transforms before, and the surface transforms after, the stress reversal (top of Fig. 5). His analysis is capable of explaining complex stress patterns for various combinations of part sizes, quenching rate, and steel hardenability (Ref 21). However, the residual stress pattern in the hardened steels can be modified either with different transformation characteristics or during the tempering and finish-machining (after hardening) operations.

Residual Stress Pattern after Surface Hardening. In general, thermochemical and thermal surface-hardening treatments produce beneficial compressive residual stresses at the surface.

Carburized and Quenched Steels. When low-carbon steels are carburized and quenched, first the core transforms at high temperature (600 to 700 °C, or 1100 to 1300 °F) to ferrite and pearlite with the attendant relaxation of any transformation stresses. Later, the high-carbon case transforms to martensite at much lower temperature (less than 300 °C, or 570 °F), accompanied by volume expansion and under conditions of no (or minimum) stress relaxation. As a result, residual compressive stress is developed in the case with a maximum at the surface.

Large differences in carbon level between the case and the core determine the sequence of phase transformation on cooling after carburizing and the resultant development of compressive residual stress in the case. Likewise, compressive residual stress in the case increases as the core carbon content decreases. Increasing case depth reduces the contribution from the low-carbon core in the development of compressive stress in the case, thereby adversely affecting the fatigue properties (Ref 36).

In actual practice, a maximum compressive stress develops at some distance away from the surface (Fig. 6 and 7). This effect occurs because of the presence of retained austenite, the extent of which depends on steel composition, carbon content of the case, quenching temperature, and severity of quench. According to Koistinen (Ref 38) and Salonen (Ref 39) the peak compressive stress takes place at 50 to 60% of the total case depth corresponding to about 0.5 to 0.6% carbon level, which produces a low retained austenite content and martensite hardness around the maximum. Another factor that might influence this compressive residual stress profile is that the martensite formed in the lower-carbon regions of the case is of the lath type, which also affects the retained austenite content (Ref 20). The reversal sign of residual stress takes place at or near the case/core interface. Later, when Koistinen's theory was applied to the measured data, it appeared that the position of maximum compressive stress depends on severity of quenching, total case depth, steel hardenability, and so forth (Ref 21, 40). Figure 7 shows the details of generation of axial stress distribution of a carburized gear (made from deeper hardening steel) during quenching. In the early stages, the contour lines of equal stress were largely unaffected by the surface profile. Later a zone of high compressive stress distribution occurred in the central portion of the teeth, which remained until the end of the quench (Ref 37).

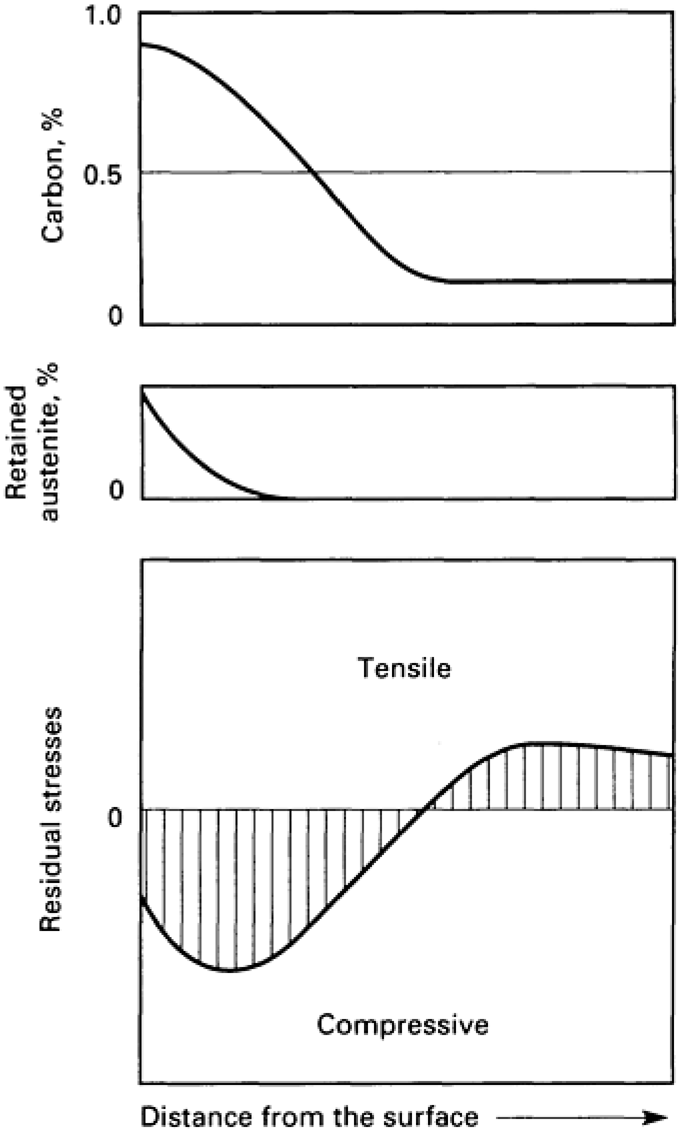

Fig. 6 Relationship between carbon content, retained austenite, and residual stress pattern. It shows the development of peak compressive stress some distance away from the surface. Source: Ref 20

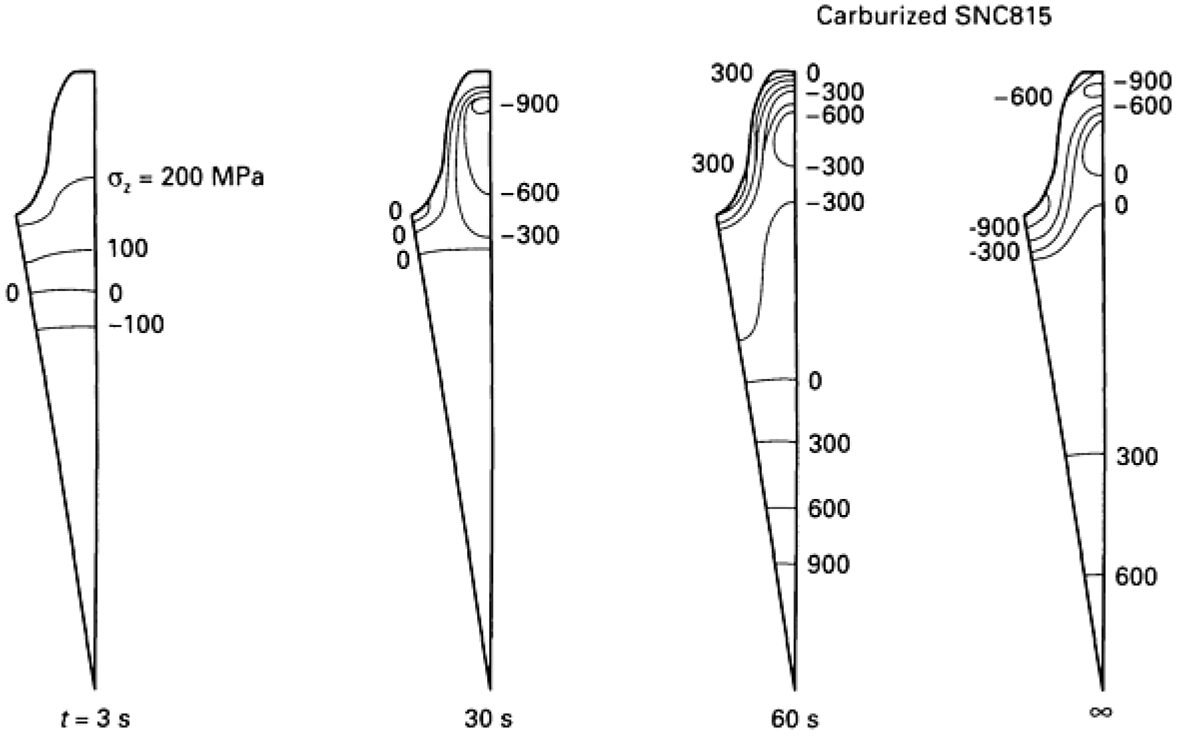

Fig. 7 Axial stress distribution (given in MPa) in carburized gear during quenching process. Source: Ref 37

In nitriding, like carburizing, a compressive residual stress is set up in the surface layers. High-temperature nitriding produces a little relaxation of stresses, whereas low-temperature nitriding imparts a maximum residual stress. In nitrocarburizing, improvement in residual surface compressive stress and fatigue strength depends on the hardness and depth of diffusion zone. These properties, in turn, decrease with increasing carbon and alloy content (that is, increased hardenability). During quenching, after nitrocarburizing, a (macro-) compressive residual stress is produced in the compound layer and gamma prime phase (Ref 41). When nitrocarburized parts are rapidly quenched, the above properties are further enhanced (Ref 42).

In borided steel processed at 900 °C (1650 °F), a high compressive residual stress is developed at the surface layers (Fig. 8), which consists of FeB and Fe_2B phases (Ref 43); this is attributed to the lower thermal expansion coefficient and the larger specific volume in a borided layer compared to that in a ferrite matrix (Ref 18, 43).

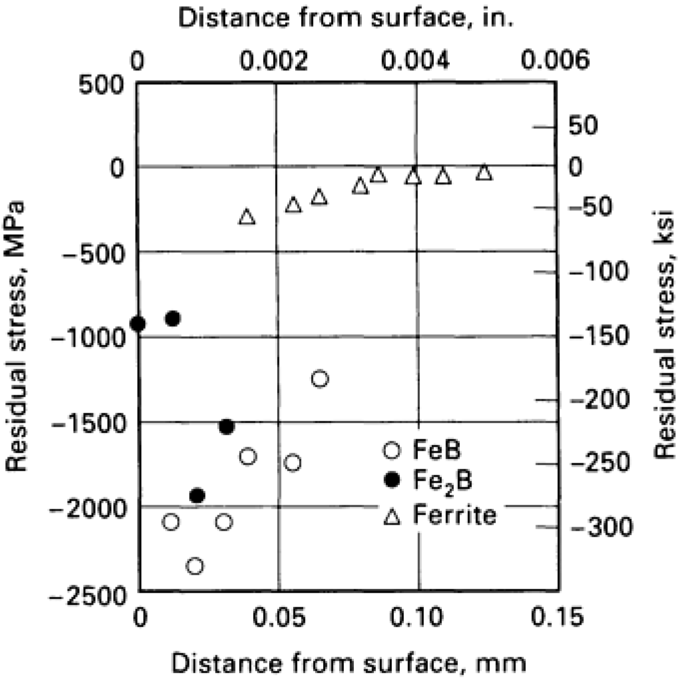

Fig. 8 Residual stress distribution of FeB and Fe_2B layers in borided steel processed at 900 °C (1650 °F). Source: Ref 18, 43

In an induction-hardened steel part, a compressive surface residual stress is produced when wear-resistant hard martensite (with slightly lower density) is formed on the surface of a section concurrently with volume expansion while nonhardened core remains essentially unchanged (Fig. 9) (Ref 44, 45). The magnitude of the compressive stress, which is affected by both thermal contraction and martensite formation, may be a considerable fraction of the yield strength, which permits the application of significantly higher stresses than could normally be possible in fatigue loading. As in the carburizing practice, the surface compressive residual stresses are usually found to increase, with depth below the surface (Ref 45) (Fig. 9, Ref 44). A fairly sharp transition to a tensile state takes place near the hardness drop-off between the case and unhardened surrounding material. With an increase in distance from the steep transition, the tensile condition gradually fades away toward zero stress (Ref 44). In induction hardening, an increase in hardenability changes the depth at which transition from compressive to tensile stress occurs. The increase in the rate of heating produces an increase in the maximum compressive and tensile residual stresses without affecting the mode of stress distribution (Ref 46).

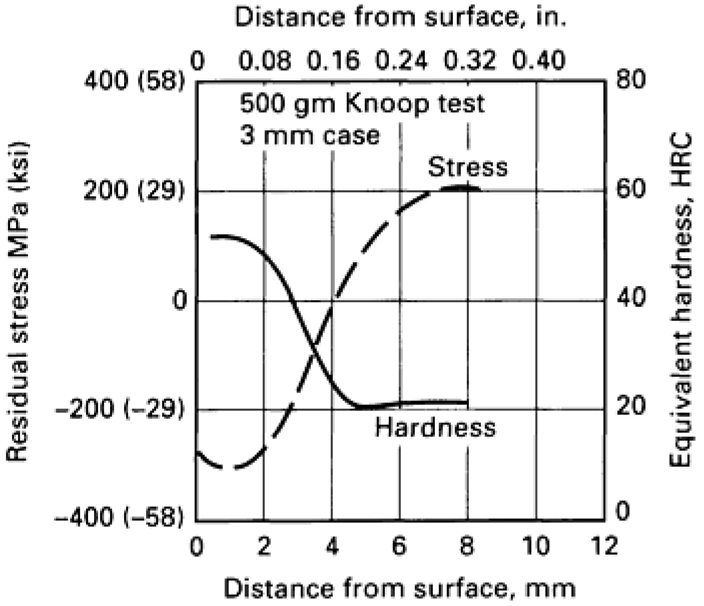

Fig. 9 A typical hardness and residual stress profile in induction-hardened (to 3 mm, or 0.12 in., case depth) and tempered (at 260 °C, or 500 °F) 1045 steel. Source: Ref 44

Residual Stress in Other Processing Steps. As welding progresses, the temperature distribution in the weldment becomes nonuniform and varying as a result of localized heating of the weldment by the welding heat source. During the welding cycle, comprising heating and cooling, complex strains develop in the weld metal and adjacent areas. As a result, appreciable residual stresses remain after the completion of welding. Since the weld metal and heat-affected zone contract on cooling (Fig. 10a), they are restrained by the cool adjacent part. This produces tensile residual stress in the weldment region and compressive residual stress in the surrounding base metal region (Fig. 10b).

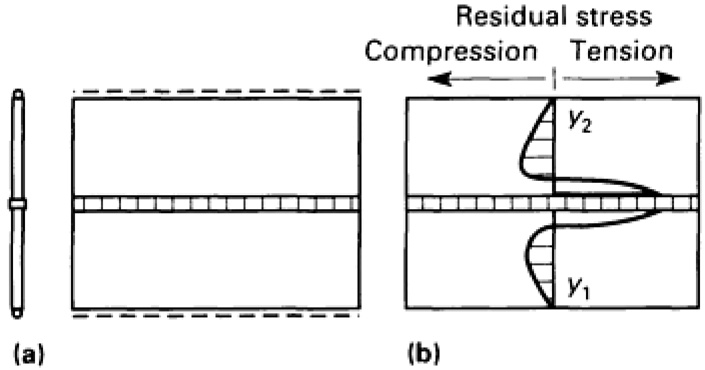

Fig. 10 (a) The transverse shrinkage occurring in butt weldments. (b) Longitudinal residual stress patterns in the weldment and surrounding regions. This also shows longitudinal shrinkage in a butt weld. Source: Ref 47

In general, a steep residual stress gradient is developed because of the steep tendency of the thermal gradient. This may, in turn, lead to hot cracking (between columnar grains) or severe center line cracking in the weld area (Ref 48). Catastrophic failures of welded bridges and all-welded ships are mostly attributed to the existence of large and dangerous tensile residual stress in them (Ref 49).

The grinding step in manufacturing is important, since it is always utilized to produce the finished surface. It has been shown that gentle surface grinding, using a soft sharp wheel and slow downfeed, produces compressive residual stress at the surface, whereas conventional (normal practice) and abrasive grinding result in surface tensile stresses of very high

magnitude (Fig. 11) (Ref 22, 50). However, the gentle grinding method is expensive from the viewpoint of operating time and wear of the wheel.

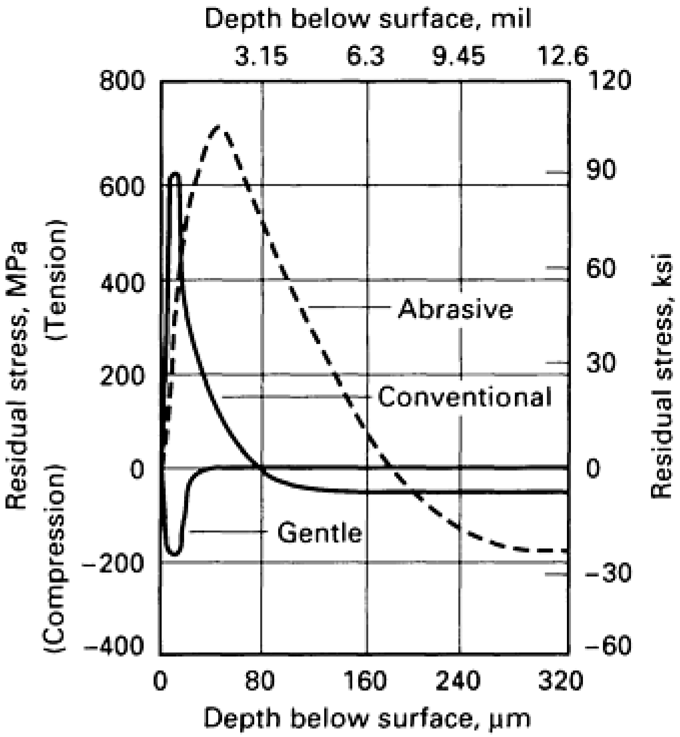

Fig. 11 Residual stress distribution after gentle, conventional, and abrasive grinding of hardened 4340 steel. Source: Ref 22

As a result of temperature gradient during cooling, castings develop compressive stresses at the surface and tensile stresses in the interior (Ref 22). However, transient temperature gradient and phase transformation occurring during the early stages of solidification and cooling of continuous steel castings in the mold may give rise to the development of harmful residual stresses leading to the formation of cracks (Ref 51).

Chemical processes such as electroplating, scale formation, and corrosion of metals can produce residual stresses due to coherency strains arising from the matching tendency of crystal structures of the outer surface product with the crystal structure of the adjacent layer (Ref 22). Residual stresses are also introduced when heat-treated parts are subjected to successive heating and cooling cycles during service conditions.

Residual Stress in the Heat-Treated Nonferrous Alloys. In nonferrous alloys, notably age-hardenable aluminum alloys, copper-beryllium alloys, certain nickel-base superalloys, and so on, a significant amount of thermal stress is generated during quenching prior to precipitation hardening. The quenching process in this condition does not invariably involve a phase change; rather, this is confined to the postquenching aging treatment. In other nonferrous alloys such as uranium and titanium alloys, the final structural condition is not obtained by a slow cool.

When high-strength titanium alloy is quenched from a solution annealing temperature of 850 to 1000 °C (1560 to 1830 °F), it develops large residual stress caused by poor thermal conductivity of titanium leading to high-temperature gradient. This problem can, however, be avoided by stress-relief annealing at 650 to 700 °C (1200 to 1290 °F), which produces a slight reduction in mechanical properties. When a high-strength aluminum age-hardening alloy is rapidly quenched from the solution temperature, high thermal and residual stresses are induced due to high coefficient of expansion of aluminum. Uphill quenching from liquid nitrogen temperature (-196 °C, or -320 °F) in a steam blast alleviates this problem. This induces stresses opposite in sign to those developed on water quenching from the solutionizing and cancels out their effect. This is followed by aging of the alloy in the conventional manner (Ref 29).

Fast polyalkylene glycol (PAG) quenching of solution-treated aluminum alloys tends to reduce residual stress levels because of its more uniform heat extraction rate (thermal shock is smaller, and thereby machining is less likely to produce

further distortion), thereby helping solve major and long-standing distortion problems among aluminum workpieces (Ref 52).

Control of Residual Stresses in Heat-Treated Parts

Table 6 lists some typical values of maximum residual stresses developed in the surface-hardened steels that have been reported in the literature (Ref 29). It is worth noting that there is a marked influence of tempering on the residual stress level. Tempering must be accomplished at about 150 °C (300 °F) to maintain 50 to 60% retention of the residual stress level obtained after quenching because a higher tempering temperature greatly reduces surface compressive stresses. However, a higher stress-relief temperature (~600 °C, or 1110 °F) is used for mechanically deformed components (for example, hot-rolled bars) or components with tensile surface residual stresses. Alternatively, serious residual tensile stresses may be avoided effectively by gentle grinding of the surface.

Table 6 A compiled summary of the maximum residual stresses in surface heat-treated steels

Steel	Heat treatment	Residual stress (longitudinal)	
		MPa	ksi
832M13 (type)	Carburized at 970 °C (1780 °F) to 1 mm (0.04 in.) case with 0.8% surface carbon		
	Direct-quenched	280	40.5
	Direct-quenched, -80 °C (-110 °F) subzero treatment	340	49.0
	Direct-quenched, -90 °C (-130 °F) subzero treatment, tempered	200	29.0
805A20	Carburized and quenched	240-340[a]	35.0-49.0
805A20	Carburized to 1.1-1.5 mm (0.043-0.06 in.) case at 920 °C (1690 °F), direct oil quench, no temper	190-230	27.5-33.5
805A17		400	58
805A17	Carburized to 1.1-1.5 mm (0.043-0.06 in.) case at 920 °C (1690 °F), direct oil quench, tempered 150 °C (300 °F)	150-200	22-29
897M39	Nitrided to case depth of about 0.5 mm (0.02 in.)	400-600	58.0-87.0
905M39		800-1000	116.0-145.0
Cold-rolled steel	Induction hardened, untempered	1000	145.0
	Induction hardened, tempered 200 °C (390 °F)	650	94.0

	Induction hardened, tempered 300 °C (570 °F)	350	51
	Induction hardened, tempered 400 °C (750 °F)	170	24.5

Source: Ref 29

(a) Immediately subsurface, that is, 0.05 mm (0.002 in.).

Measurement of Residual Stresses

There are two methods of measuring residual stresses: the destructive method, also called the dissection method, and the nondestructive methods comprising mainly x-ray diffraction, neutron diffraction, ultrasonic, and magnetic methods.

Destructive (or Dissection) Method. This method is old but reasonably accurate, practically nondestructive, uses well-established methods, and can be employed in confined situations at site (Ref 53). However, it is tedious, time consuming, and expensive (Ref 54). The other drawbacks are the destructive, or at best semidestructive nature of the method, and its ability to measure only the macroresidual stresses. The hole-drilling method is used extensively for measuring residual stresses, which depends on the dissection approach. It consists of the mounting of strain gages or a three-element strain-gage rosette on the surface and measurement of strains. Then a rigidly guided milling cutter is used to drill a small, straight, circular, perpendicular, and flat-bottomed hole not exceeding 3.2 mm (0.125 in.) at the center of the rosette and into the surface of the component being analyzed. Strain redistribution occurring at the surface in the surrounding area of the hole (resulting from the residual stress relief) is then measured with the previously installed strain gages. The residual stress is calculated at a large number of points in a surface from the strain measurements using the well-established method (Ref 22, 28). To minimize the introduction of spurious strains by the grinding operation, the rate of metal removal should be less than 3.125×10^{-4} m/s (1.23×10^{-2} in./s), and readings are recorded after 15 min of the end of the grinding process to ensure that any heat generated has been dissipated (Ref 55).

Nondestructive Methods. The main difficulty with the nondestructive methods is that measurements of crystallographic lattice parameters, ultrasonic velocities, or magnetization changes are made that are indirectly related to the residual stress. The above quantities are usually dependent on the stress and material parameters (such as metallurgical textures), which are difficult to quantify (Ref 54, 56).

The x-ray diffraction method is the well-established technique for measuring both macro- and microresidual stress nondestructively. In most instances, the x-ray diffraction method has been employed to provide quantitative values for residual stress profiles in surface or fully hardened components (Ref 57). This technique depends on the determination of lattice strains and the stress-induced differences in the lattice spacing. Macroresidual strain is measured from the shift of diffraction lines in the peak position using the so-called nonlinear $\text{Sin}^2 C$ method from which residual stress is calculated (Ref 57). For the measurement of microstrain the Voigt single-line method is applied (Ref 58). Precision in lattice strain measurement of the order of 0.2% is possible.

Portable x-ray diffraction equipment is now commercially available in various forms that allow stress measurement to be made very quickly (ranging from 4 to 30 s). The main drawbacks are that it cannot be applied to noncrystalline materials such as plastics, and it is only capable of measuring residual stresses of materials very close to the surface under examination. That is, the measurement is purely surface related (a depth of 0.01 mm, or 0.4 mil, is commonly quoted) (Ref 59).

Neutron radiography or diffraction, used for polycrystalline materials, has a much deeper penetration than x-rays, but has major safety problems and the disadvantage of being nonportable.

Ultrasonic method for evaluating residual stress involves ultrasonic stress birefringence or sonoelasticity; this depends upon the linear variation of the velocities of sound in a body (that is, ultrasonic waves) with the stress. This method has the potential for greater capability, versatility, and usefulness in the future (Ref 53, 56). However, this has the disadvantage, in common with the magnetic methods, that it requires transducers shaped to match the surface being inspected (Ref 60).

The magnetic method is based on the stress dependence of the Barkhausen noise amplitude. Each time an alternating magnetic field induced in a ferromagnetic material is reversed, it generates a burst of Barkhausen noise. The peak amplitude of the burst, as determined with an inductive coil near the surface of the component material, varies with the surface stress level. Since Barkhausen noise depends on composition, texture, and work hardening, it is necessary in each application to use calibrated standard (reference) samples with the same processing history and composition as the component being analyzed. This method is used to measure residual stresses well below the yield strength of the ferromagnetic materials. This method is rapid, and the measurements are made with the commercially available portable equipment. However, this method is limited to only ferromagnetic materials (Ref 56).

Thermal evaluation for residual stress analysis (TERSA) is a new nondestructive method that is in an experimental stage. It has the advantage that it is completely independent, remote, and noncontacting. It consists of merely directing a controlled amount of energy from a laser energy source into the volume of the material being inspected and then making a precise determination of changes in the resulting temperature rise by infrared radiometry. However, the working instrument will also require some form of display to enable visual examination to be made of any high-stressed regions (Ref 60).

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Quench Cracking

Anything that produces excessive quenching stress is the basic cause of cracking. Quench cracking is mostly intergranular, and its formation may be related to some of the same factors that cause intergranular fracture in overheated and burned steels. The main reasons for cracking in heat treatment are: part design, steel grades, part defects, heat-treating practice, and tempering practice (Ref 61).

Part Design. Features such as sharp corners, the number, location, and size of holes, deep keyways, splines, and abrupt changes in section thickness within a part (that is, badly unbalanced section) enhance the crack formation because while the one (thin) area is cooling quickly in the quenchant, the other (thick) area immediately adjacent to it is cooling very slowly. One solution to this problem is to change the material so that a less drastic quenchant (for example, oil) can be employed. An alternate solution is to prequench, that is, to cool it prior to the rest of the part. This will produce an interior of the hole or keyway that is residually stressed in compression, which is always desirable for better fatigue properties (Ref 61). The third solution is a design change, and the fourth is to use a milder quenchant.

Steel Grades. Sometimes this can be checked by means of a spark test, whereas at other times a chemical analysis must be made. In general, the carbon content of steel should not exceed the required level; otherwise, the risk of cracking will increase. The suggested average carbon contents for water, brine, and caustic quenching are given below:

Method	Shape	Carbon, %
Induction hardening	Complex	0.33
	Simple	0.50
Furnace hardening	Complex	0.30
	Simple	0.35
	Very simple, such as bar	0.40

A decrease in carbon content from 0.72 to 0.61% has been shown to slightly increase the thermal crack resistance of rimquenched railroad wheels (Ref 62).

Because of segregation of carbon and alloying elements, some steels are more prone than others to quench cracking. Among these steels, 4140H, 4145H, 4150H, and 1345H appear to be the worst. A good option is to replace the 4100 series with the 8600 series. An additional disadvantage with the use of 1345H steel is the manganese floating effect, which leads to very high manganese content in the steel rolled from the last ingot in the same heat. Similarly, dirty steels (that is, steels with more than 0.05% S, for example, AISI 1141 and 1144) are more susceptible to cracking than the low-sulfur grades. The reasons for this are that they are more segregated in alloying elements, the surface of this hot-rolled high-sulfur steel has a greater tendency to form seams, which act as stress raisers during quenching, and they are usually coarse grained (for better machinability), which increases brittleness and therefore promotes cracking. If these high-sulfur grades are replaced by calcium-treated steels or cold-finished leaded steels, this problem can be obviated (Ref 61).

Part Defects. Surface defect or weakness in the material may also cause cracking, for example, deep surface seams or nonmetallic stringers in both hot-rolled and cold-finished bars. Other defects are inclusions, stamp marks, and so forth. For large-seam depths, it is advisable to use turned bars or even magnetic particle inspection. The forging defects in small forgings, such as seams, laps, flash line, or shearing crack, as well as in heavy forgings, such as hydrogen flakes and internal ruptures, aggravate cracking. Similarly, some casting defects, for example, in water-cooled castings, promote cracking (Ref 50).

Heat-Treating Practice. Higher austenitizing temperatures increase the tendency toward quench cracking. Similarly, steels with coarser grain size are more prone to cracks than fine-grain steels because the latter possess more grain-boundary area to stop the movements of cracks, and grain boundaries help to absorb and redistribute residual stresses. An outstanding contributor to severe cracking is improper heat-treating practice, for example, nonuniform heating and nonuniform cooling of the component involved in the heat-treatment cycle. It is a good heat-treating practice to anneal alloy steels prior to the hardening treatment (or any other high-temperature treatment, for example, forging, welding, and so forth) because this produces grain-refined microstructure and relieves stresses (Ref 63).

Water-Hardening Steel. The water-hardening steels are most susceptible to cracks if they are not handled properly. Soft spots are most likely to occur in the water-hardening steels, especially where the tool is grabbed with tongs for quenching. Normally the cleaned surface shows adequate hardening and the scaled surface insufficient hardening, which can be examined with a file. Soft spots may occur from the use of fresh water, or water contaminated with oil or soap. Most large tools emerging from hardening operations contain some soft spots. However, accidental soft spots in the wrong place should be investigated, and steps must be taken to eliminate them.

Figure 12 shows the typical appearance of a thumbnail check as soft spot on chipping chisels, which occurs on the bit near the cutting edge. The cracks enclosing the soft spots should be avoided by switching to brine quench (Ref 64).

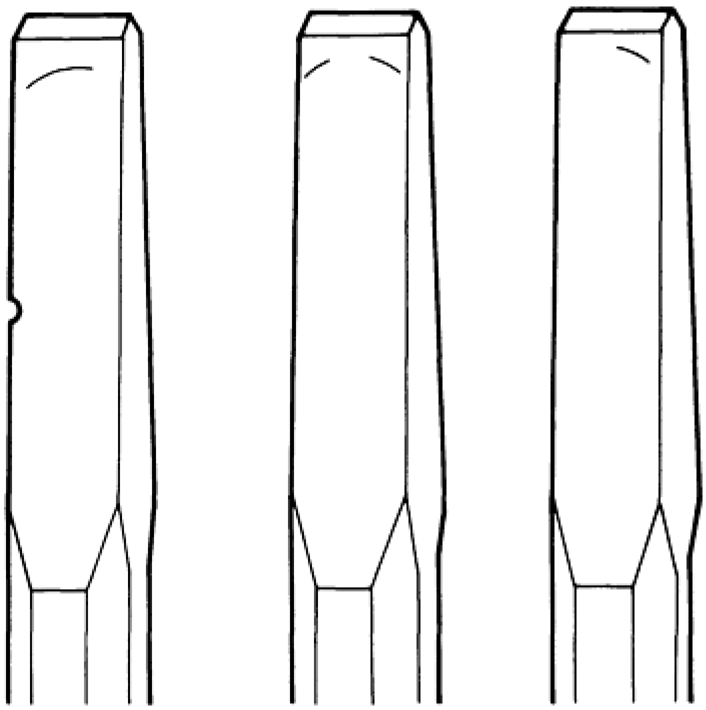

Fig. 12 Typical appearance of thumbnail check as soft spot on chipping chisel. Source Ref 64

Air-Hardening Steel. Similarly, when air hardening steels are improperly handled, they are likely to crack. For example, avoidance of tempering treatment or use of oil quenching in air-hardening steel can lead to cracking. However, the common practice in the treatment of air-hardening steels is initially to quench in oil until "black" (about 540 °C, or 1000 °F), followed by air cooling to 65 °C (150 °F) prior to tempering. As compared to air cooling right from the quenching temperature, this practice is totally safe and minimizes the formation of scale.

Polymer quenchants have found well-established use in the quenching of solution-treated aluminum alloys, hardening of plain carbon steels with less than 0.6% C, spring steels, boron steels, hardenable stainless steels, and all carburizing and alloy steels with section thickness greater than about 50 mm (2 in.), through-hardening and carburizing steel parts, and induction and flame-hardening treatments because of their numerous beneficial effects, including elimination of soft spots, distortion, and cracking problems associated with trace water contamination in quenching oils (Ref 65).

Agitation is an important parameter in polymer quenching applications both to ensure a uniform polymer film around the quench part and to provide a uniform heat extraction from the hot part to the adjacent area of quenchant by preventing a buildup of heat in the quench region.

Salt bath cooling of induction-hardened complex-shaped cast iron parts reduces danger of cracking, which is usually experienced when air cooling followed by hot-water quenching is used (Ref 66).

Decarburized Steel. Decarburization usually arises from insufficient protection as a result of plant failure (for example, defective furnace or container seals, defective valves), poor process control (for example, insufficient atmosphere-monitoring equipment, poor supervision), or the existence of decarburizing agents in the furnace atmosphere (for example, CO_2, water vapor, and H_2 in the Endogas (Ref 61, 67).

A partially decarburized surface on the part occurring during tool hardening also contributes to cracking because martensite transformation is completed therein well before the formation of martensite in the core. Decarburized surface on the tools has reduced hardness, which will lead to premature wear and scuffing. Partial decarburization must be avoided, especially on all deep-hardening steels, either by providing some type of protective atmosphere during the heating operation, stock removal by grinding, or carbon restoration process. In addition to protective atmosphere, salt baths, inert packs, or vacuum furnaces may be used to obtain the desired surface chemistry on the tools or dies. The fact

that the better and more consistent performance of the tools is observed after regrinding reveals the existence of partial decarburization remaining.

Carburized Alloy Steel. Two types of peculiar cracking phenomena prevail in the carburized and hardened case of the carburized alloy steels: microcracking and tip cracking. Microcracking of quenched steels are small cracks appearing across or alongside martensite plate (Fig. 13) (Ref 67) and the prior austenite grain boundaries (Ref 68). They form mostly on those quenched steel parts that contain chromium and/or molybdenum as the major alloying elements with or without nickel content and where the hardening is done by direct quenching.

Fig. 13 Microcracking in a Ni-Cr steel. Source: Ref 67

Microcracks are observed mostly in coarse-grained structures, such as large martensite plates. This is presumably because of more impingements of the larger plates of martensite by other large plates. Another cause of microcracking is the increased carbon content of martensite (that is, increased hardenability), which is a function of austenitizing temperature and/or time (Ref 67). This finding was established for 8620H steel, which has a higher austenitizing temperature prior to quenching where there is a greater tendency to microcrack (Ref 69). This problem can be avoided by selecting a steel with less hardenability (that is, with less austenitizing temperature). Another solution is to change the heat-treating cycle to carburizing, slow cooling to black temperature, reheating to, for example, 815 or 845 °C (1500 or 1550 °F), and quenching (Ref 61). Microcracking in case-hardened surfaces may be aggravated by the existence of hydrogen, which tends to absorb during carburizing. However, this hydrogen-enhanced microcracking can be eliminated by tempering the carburized parts at 150 °C (300 °F) immediately after quenching. Tempering exhibits an additional beneficial effect in that it has the ability to heal the microcracks due to the volume changes and associated plastic flow that develop during the first stage of tempering (Ref 70). No adverse report on the influence of microcracks on the mechanical properties has been noted; however, the controlling factors should be varied so as to keep the incidence of microcracks to a minimum (Ref 67).

Tip cracking refers to the cracking that appears in the teeth of carburized and quenched gears and runs partly or fully to the ends of the teeth in a direction parallel to the axis of the part. Many heat treaters have solved this problem to a great extent by decreasing the carbon content and case depth to the minimum acceptable design level or by copper plating the outer diameter of the gear blank prior to hobbing (Ref 66).

Nitrided Steels. The nitrided cases are very brittle. Consequently, cracking may occur in service prior to realizing any improved wear and galling resistance. This can be avoided by a proper tool design, for example, incorporating all section changes with a minimum radius of 3 mm (0.125 in.).

Tempering Practice. The longer the time the steel is kept at a temperature between room temperature and 100 °C (212 °F) after the complete transformation of martensite in the core, the more likely the occurrence of quench cracking. This arises from the volumetric expansion caused by isothermal transformation of retained austenite into martensite.

There are two tempering practices that lead to cracking problems: tempering too soon after quenching, that is, before the steel parts have transformed to martensite in hardening, and skin tempering, usually observed in heavy sections (≥50 mm, or 2 in., thick in plates and >75 mm, or 3 in., in diameter in round bars).

It is the normal practice to temper immediately after the quenching operations. In this case, some restraint must be exercised, especially for large sections (>75 mm, or 3 in.) in deep-hardening alloy steels. The reason is that the core has not yet completed its transformation to martensite with the expansion, whereas the surface and/or projections, such as flanges, begin to temper with shrinkage. This simultaneous volume change produces radial cracks. This problem can become severe if rapid heating practice (for example, induction, flame, lead, or molten salt bath) is used for tempering. Therefore, very large and very intricate tool steel parts should be removed from the quenching medium, and tempering should be started while they are slightly warm to hold comfortably in the bare hands (~60 °C, or 140 °F).

Skin tempering occurs in heavy section parts when the final hardness is >360 HB. This is due to insufficient tempering time and is usually determined when the surface hardness falls by 5 or more HRC points from the core hardness. This cracking often occurs several hours after the component has cooled from the tempering temperature and often runs through the entire cross section. This problem can be removed by retempering for 3 h at the original tempering temperature, which is associated with a change in hardness of 2 HRC points maximum (Ref 61).

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Distortion in Heat Treatment

Distortion can be defined as an irreversible and usually unpredictable dimensional change in the component during processing from heat treatment and from temperature variations and loading in service. The term dimensional change is used to denote changes in both size and shape (Ref 71). The heat-treatment distortion is therefore a term often used by engineers to describe an uncontrolled movement that has occurred in a component as a result of heat-treatment operation (Ref 72). Although it is recognized as one of the most difficult and troublesome problems confronting the heat treater and the heat-treatment industries on a daily basis, it is only in the simplest thermal heat-treatment methods that the mechanism of distortion is understood. Changes in size and shape of tool-steel parts may be either reversible or irreversible. Reversible changes, which are produced by applying stress in the elastic range or by temperature variation, neither induce stresses above the elastic limit nor cause changes in the metallurgical structure. In this situation, the initial dimensional values can be restored to their original state of stress or temperature.

Irreversible changes in size and shape of tool-steel parts are those that are caused by stresses in excess of the elastic limit or by changes in the metallurgical structure (for example, phase changes). These dimensional changes sometimes can be

corrected by mechanical processing to remove extra and unwanted material or to redistribute residual stresses or by heat treatment (annealing, tempering, or cold treatment).

When heat-treated parts suffer from distortion beyond the permissible limits, it may lead to scrapping of the article, rendering it useless for the service for which it was intended, or it may require necessary correction. Allowable distortion limits vary to a large extent, depending on service applications; in cases where very little distortion can be tolerated, specially desired tool steels are used. These steels possess metallurgical characteristics that minimize distortion.

Types of Distortion

Distortion is a general term that involves all irreversible dimensional change produced during heat-treatment operations. This can be classified into two categories: size distortion, which is the net change in specific volume between the parent and transformation product produced by phase transformation without a change in geometrical form, and shape distortion or warpage, which is a change in geometrical form or shape and is revealed by changes of curvature or curving, bending, twisting, and/or nonsymmetrical dimensional change without any volume change (Ref 72, 73). Usually both types of distortion occur during a heat-treatment cycle.

Dimensional Changes Caused by Changes in Metallurgical Structure during Heat Treatment. Various dimensional changes produced by a change in metallurgical structure during the heat-treatment cycle of tool steels are described below (Ref 74).

Heating (Austenitizing). When annealed steel is heated from room temperature, thermal expansion occurs continuously up to Ac_1, where the steel contracts as it transforms from body-centered cubic (bcc) ferrite to face-centered cubic (fcc) austenite. The extent of decrease in volumetric contraction is related to the increased carbon content in the steel composition (Table 4). Further heating expands the newly formed austenite.

Hardening. When austenite is cooled quickly, martensite forms; at intermediate cooling rates, bainite forms; and at slow cooling rates, pearlite precipitates. In all these transformation sequences, the magnitude of expansion increases with the decrease in carbon content in the austenite (Table 4). The volume increase is maximum when austenite transforms to martensite, intermediate with lower bainite, and is least with upper bainite and pearlite (Table 4). The volume increases associated with the transformation of austenite to martensite in 1 and 1.5% carbon steels are 4.1 and 3.84%, respectively; the volume increases involved in the transformation of austenite to pearlite in the same steels are 2.4 and 1.33% , respectively. Such volume increases are less in alloy steels and least in 2C-12Cr and A10 tool steels. It should be noted that plastic deformation (or strain) occurs during such transformations at stresses that are lower than the yield stress for the phases present (Ref 75). The occurrence of this plastic deformation, called the transformation plasticity effect, influences the development of stresses during the hardening of steel parts (Ref 76). During quenching from the austenite range, the steel contracts until the M_s temperature is reached, then expands during martensitic transformation; finally, thermal contraction occurs on further cooling to room temperature. As the hardening temperature increases, a greater amount of carbide goes into solution; consequently, both the grain size and the amount of retained austenite are increased. This also increases the hardenability of steel.

More trouble with distortion comes from the quenching or hardening operation than during heating for hardening, in which the faster the cooling rate (that is, the more severe the quenching), the greater the danger of distortion. When the milder quenchants are used, the extent of distortion is lessened. The severity of quenching thus influences the distortion of components.

The dependence of volume increase, particularly in tools of different dimensions, on grain size (or hardenability) is another important factor. Variations in volume during quenching of a fine-grained shallow-hardening steel in all but small sections is less than a coarse-grained deep-hardening steel of the same composition.

Tempering. Them is a certain correlation between the tempering temperature and volume change. Tempering reduces the volume of martensite but not adequately enough to equalize completely the prior volume increase as a result of martensitic transformation unless the components are completely softened. In low-alloy and plain (medium- and high-) carbon steels, during the first and third stages of tempering, a decrease in volume occurs that is associated with the decomposition of: high-carbon martensite into low-carbon martensite plus ϵ-carbide in the former stage, and aggregate of low-carbon martensite and ε-carbide into ferrite plus cementite in the latter stage. In the second stage, however, an increase in volume takes place (due to the decomposition of retained austenite into bainite) that tends to compensate for the early volume reduction. As the tempering temperature is increased further toward the A_1, more pronounced volume

reduction occurs. In some highly alloyed tool-steel compositions, the volume changes during martensite formation are less striking because of the large proportion of retained austenite and the resistance to tempering of alloy-rich martensite. These hardened steels show sharp increases both in hardness and volume between 500 and 600 °C (930 and 1110 °F) owing to the precipitation of very finely dispersed alloy carbides from the retained austenite. This produces a depleted matrix in alloy content, raising the M_s temperature of retained austenite. During cooling down from the tempering temperature, further transformation of retained austenite into martensite will occur with an additional increase in volume.

Size Distortion. Table 7 shows the typical volume percentages of microconstituents present in four different tool steels after their standard hardening treatments. Typical dimensional changes during hardening and tempering of several tool steels are given in Table 8. It is apparent here that some steels such as M3 and M41 high-speed steels show appreciable increase in size of about 0.2% after hardening and tempering between 540 and 595 °C (1000 and 1100 °F) to produce complete secondary hardening. Other types, such as A10, expand very little when hardened and tempered over the entire temperature range up to 595 °C (1100 °F). Excessive size changes in oil-hardening nonshrinkable tool steel is usually caused by lack of stress relief (when necessary), and hardening and/or tempering at the incorrect temperature. The golden rule is to learn to be suspicious of tools that are seriously off size in only one dimension. It is further noted that alloying addition in steels brings about a change in the specific volume of many microconstituents, but to a lesser extent than carbon (Ref 77). This table provides comparative data on size distortion in a variety of steels; however, this information cannot be used alone to predict shape distortion factor.

Table 7 Typical volume percentages of microconstituents existing in four different tool steels after their standard hardening treatments

Steel	Hardening treatment	As-quenched hardness, HRC	Martensite, vol%	Retained austenite, vol%	Undissolved carbides, vol%
W1	790 °C (1450 °F), 30 min; WQ	67.0	88.5	9	2.5
L3	845 °C (1550 °F), 30 min; OQ	66.5	90	7	3.0
M2	1225 °C (2235 °F), 6 min; OQ	64	71.5	20	8.5
D2	1040 °C (1900 °F), 30 min; AC	62	45	40	15

Note: WQ, water quenched; OQ, oil quenched; AC, air cooled.

Table 8 Typical dimensional changes during hardening and tempering of several tool steels

Tool steel	Hardening treatment			Total change in linear dimensions after quenching, %	Total change in linear dimensions, %, after tempering at										
	Temperature		Quenching medium												
	°C	°F			150 °C 300 °F	205 °C 400 °F	260 °C 500 °F	315 °C 600 °F	370 °C 700 °F	425 °C 800 °F	480 °C 900 °F	510 °C 950 °F	540 °C 1000 °F	565 °C 1050 °F	595 °C 1100 °F
O1	815	1500	Oil	0.22	0.17	0.16	0.18	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
O1	790	1450	Oil	0.18	0.09	0.12	0.13	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .

O6	790	1450	Oil	0.12	0.07	0.10	0.14	0.10	0.00	-0.05	-0.06	. . .	-0.07	. . .	. . .
A2	955	1750	Air	0.09	0.06	0.06	0.08	0.07	. . .	0.05	0.04	. . .	0.06	. . .	. . .
A10	790	1450	Air	0.04	0.00	0.00	0.08	0.08	0.01	0.01	0.02	. . .	0.01		0.02
D2	1010	1850	Air	0.06	0.03	0.03	0.02	0.00	. . .	-0.01	-0.02	. . .	0.06	. . .	. . .
D3	955	1750	Oil	0.07	0.04	0.02	0.01	-0.02	. . .	. . .	. . .	. . .	. . .	. . .	. . .
D4	1040	1900	Air	0.07	0.03	0.01	-0.01	-0.03	. . .	-0.4	-0.03	. . .	0.05	. . .	. . .
D5	1010	1850	Air	0.07	0.03	0.02	0.01	0.00	. . .	0.3	0.03	. . .	0.05	. . .	. . .
H11	1010	1850	Air	0.11	0.06	0.07	0.08	0.08	. . .	0.3	0.01	. . .	0.12	. . .	. . .
H13	1010	1850	Air	-0.01	. . .	. . .	. . .	. . .	. . .	. . .	0.00	. . .	0.06	. . .	. . .
M2	1210	2210	Oil	-0.02	. . .	. . .	. . .	. . .	. . .	. . .	. . .	-0.06	0.10	0.14	0.16
M41	1210	2210	Oil	-0.16	. . .	. . .	. . .	. . .	. . .	. . .	. . .	-0.17	0.08	0.21	0.23

Shape Distortion or Warpage. This is sometimes called straightness or angularity change. It is found particularly in nonsymmetrical components during heat treatment. From the practical viewpoints, warpage in water- or oil-hardening steels is normally of greater magnitude than is size distortion and is more of a problem because it is usually not predictable. This is caused by the sum effect of more than one of these factors:

- Rapid heating (or overheating), drastic (or careless) quenching, or nonuniform heating and cooling causes severe shape distortion. Slow heating as well as preheating of the parts prior to heating to the austenitizing temperature yields the most satisfactory result. Rapid quenching produces thermal and mechanical stresses associated with the martensitic transformation. In the case of low- and high-hardenability steels, respectively, this problem becomes severe or very small
- Residual stresses present in the component before heat treating. These arise from machining, grinding, straightening, welding, casting, spinning, forging, and rolling operations, which will also furnish a marked contribution to the shape change (Ref 78)
- Applied stress causing plastic deformation. Sagging and creep of the components occur during heat treatment as a result of improper support of components or warped hearth in the hardening furnace. Hence, large, long, and complex-shaped parts must be properly supported at critical positions to avoid sagging or preferably are hung with the long axis on the vertical
- Nonuniform agitation/quenching or non-uniform circulation of quenchant around a part results in an assortment of cooling rates that creates shape distortion (Ref 79). Uneven hardening, with the formation of soft spots, increases warpage. Similarly, an increase in case depth, particularly uneven case depths in

case-hardening steels, increases warpage on quenching (Ref 80)

- Tight (that is, thin and highly adherent) scale and decarburization, at least in certain areas. Tight scale is usually a problem encountered in forgings hardened from direct-fired gas furnaces having high-pressure burners. Quenching in areas with tight scale is extremely retarded compared to the areas where the scale comes off. This produces soft spots, and, in some cases, severe unpredicted distortion. Some heat treaters coat the components with a scale-loosening chemical prior to their entry into the furnace (Ref 79). Similarly, the areas beneath the decarburized surface do not harden as completely as the areas below the nondecarburized surface. The decarburized layer also varies in depth and produces an inconsistent softer region as compared to the region with full carbon. All these factors can cause a condition of unbalanced stresses with resultant distortion (Ref 79)
- Long parts with small cross sections ($>L = 5d$ for water quenching, $>L = 8d$ for oil quenching, and $>L = 10d$ for austempering, where L is the length of the part, and d is its diameter or thickness)
- Thin parts with larger areas ($>A = 50t$, where A is the area of the part, and t is its thickness)
- Unevenness of, or greater variation in, section

Examples of Distortion

Ring Die. Quenching of ring die through the bore produces the reduction in bore diameter as a result of formation of martensite, associated with the increased volume. In other words, metal in the bore is upset by shrinkage of the surrounding metal and is short when it cools (Ref 24). However, allover quenching causes the outside diameter to increase and the bore diameter to increase or decrease, depending upon precise dimensions of the part. When the outside diameter of the steel part is induction- or flame-hardened (with water quench), it causes the part to shrink in outer diameter (Ref 63). These are the examples of the effect of mode of quenching on distortion (Ref 81).

Thin die (with respect to wall thickness) is likely to increase in bore diameter, decrease in outside diameter, and decrease in thickness when the faces are hardened. If the die has a very small hole, insufficient quenching of the bore may enlarge the hole diameter because the body of die moves with the outside hardened portion.

Bore of Finished Gear. Similarly, the bore of a finished gear might turn oval or change to such an extent that the shaft cannot be fitted by the allowances that have been provided. Even a simple shape such as a diaphragm or orifice plate may, after heat treatment, lose its flatness in such a way that it may become unusable.

Production of Long Pins. In the case of the production of long pins (250 mm long × 6 mm diameter, or 10 × $\frac{1}{4}$ in.) made from medium-alloy steel, it was found, after conventional hardening, that when mounted between centers, the maximum swing was over 5 mm (0.20 in.). However, the camber could be reduced to within acceptable limits by martempering, intense or press quenching.

Hardening and Annealing of Long Bar. When a 1% carbon steel bar, 300 mm long (or more) × 25 mm diameter (12 in. long, or more, × 1 in. diameter), is water quenched vertically from 780 °C (1435 °F), the bar increases both in diameter and volume but decreases in length. When such bars are annealed or austenitized, they will sag badly between the widely spaced supports. Hence, they should be supported along their entire length in order to avoid distortion.

Hardening of Half-Round Files. Files are usually made from hypereutectoid steel containing 0.5% chromium. Files are heated to 760 °C (1400 °F) in an electric furnace after being surface coated with powdered wheat, charcoal, and ferrocyanide to prevent decarburization. They are then quenched vertically in a water tank. On their removal from the tank, the files appear like the proverbial dog's tail. The flat side has curved down, the camber becomes excessive, and the files can no longer be used in service. One practical solution is to give the files a reverse camber prior to quenching. The dead flat files could, however, be made possible, and the judgment with regard to the actual camber needed depends upon the length and the slenderness of the recut files (Ref 82).

Similarly, when a long slender shear knife is heat treated, it tends to curve like a dog's tail, unless special precautions are taken.

Hardening of Chisels (Ref 63). Chisels about 460 mm (18 in.) long and made from 13 mm (0.5 in.) AISI 6150 bar steel are austenitized at 900 °C (1650 °F) for 1.5 h and quenched in oil at 180 °C (360 °F) by standing in the vertical position with chisel point down in special baskets that allow stacking of two 13 mm (0.5 in.) round chisels per 650 mm^2

($1\ in.^2$) hole. Subsequently, hardened chisels are tempered between 205 and 215 °C (400 and 420 °F) for 1.5 h. These heat-treated parts show 55 to 57 HRC hardness but are warped. The reasons for this distortion are:

- The portion of the bar that touches the basket cools slowly, producing uneven contraction and thermal stress
- The martensite formation is delayed on the inner or abutting side of the bar, causing unequal expansion during transformation. This distortion can be eliminated or minimized by loading the parts in the screen-basket in such a way that stacking arrangement permits sufficient space between each part and by slightly decreasing the austenitizing temperature (Ref 62). Distortion can also be minimized by austempering the part, provided that the carbon content is on the high side of specification to produce the lower bainitic structure of 55 to 57 HRC. If higher yield stress is not warranted, only chisel ends need hardening and subsequent tempering (Ref 63)

Hardening of a Two-Pounder Shot. The hardness of a two-pounder shot was specified at 60 HRC on the nose and 35 HRC at the base. A differential hardening technique was performed on the shot made of a Ni-Cr-Mo steel. This technique consisted of quenching the shot in the ice-cold water by its immersion in a tank up to the shoulder, followed by drawing out the water from the tank at a stipulated rate until the water line reached the base of the nose. The final step involved withdrawing the shot from the tank when completely cold. The back end was then softened by heating in a lead bath after initial tempering. The first few shots hardened in this way were observed to split vertically across the nose. The failure was, however, avoided by withdrawal of the shot before attaining ice-cold temperature and its subsequent immersion in warm water (Ref 82).

Hardening of a Burnishing Wheel. In the manufacture of railway axles, the gearing surface on which the axle rests in the housing has to be given a high burnishing polish employing a circular pressure tool that is made of 1.2C-1.5Cr steel. For satisfactory results, the hardness of the tool surface should be about 60 HRC. It has been found that the tool usually cracks before its withdrawal from the cold-water quenching bath. This problem may, however, be avoided by quenching the tool in water for 10 s prior to transferring it to an oil bath for finish quenching. Time quenching can be judiciously applied for many heat treatment problems of distortion or cracking. Stress-relieving treatment after the use of the tool for some time may also enhance its performance life. As indicated above, martempering is also one of the solutions for this problem (Ref 81).

Hardening of Case-Carburized Mild Steel. If oil-hardening steels are not available for making a component, mild steel parts are carburized and water quenched to obtain the desired hardness, possibly resulting in excessive distortion, which is very difficult to straighten without cracking.

Hardening of Carburized Low-Carbon Steel Rollers. The best course of quenching carburized En32 steel rollers (25 mm diam × ≥600 mm long, or 1 in. diam × ≥2 ft long), employed in textile printing, is to roll them down skids into water-quenching tanks because this produces less warpage than when quenched slowly with the bar either in vertical, horizontal, or inclined positions. These are the procedures adopted for hardening of cylinders with length considerably greater than the diameter.

Hardening of Helix Gears. The distortion of the helical gears made of IS 20MnCr1 grade steel (similar to AISI 5120) used as the third speed gear in the gear box of Tata trucks is an unavoidable natural consequence of the hardening process after carburizing. This type of distortion is linked with increased length and decreased diameter and occasionally increased helical angle (Ref 83). If the extent of distortion can be controlled, a constant correction to the helix angle can be imparted in the soft-stage manufacturing (machining) prior to heat treatment so that this correction can compensate for the distorted angle and may result in a gear with desired helix angle. Thus a constant magnitude of distortion without minimization is assured in every job of every batch of production in commercial manufacturing. However, the residual stress system and metallurgical properties such as core strength, case depth, surface hardness, proper microhardness in the surface regions, and so forth, are assured (Ref 84). Similarly, when heavy-duty tooth gear is gas carburized and quenched to harden the surface layer, the diameter and tooth span increase and tapering and bending also occur.

Nitriding of Screw. A rolling mill screw, after liquid nitriding, may also show a small decrease in length, which causes pitch errors in the screws (Ref 83).

Induction and Flame Hardening of Spur Gears. Spur gears, after induction and flame hardening, exhibit increased circular pitch, the error being maximum for the tooth groove quenched first. Similarly, in line-heating process, the thin plate undergoes convex bending and the thick plate concave bending (Ref 83).

Precautions

Inadequate support during the heat-treatment cycle, poorly designed jigs and quenching fixtures, or incorrect loading of the parts may cause distortion (Ref 73). In general, plain-carbon and low-alloy steels have such a low yield strength at the hardening temperature that the parts are capable of distorting under their own weight. Every care, therefore, must be taken to ensure that parts are carefully supported or suspended during heating; long parts are preferably heated in a vertical furnace or with the length in the vertical plane (Ref 85). They should be quenched in the vertical position with vertical agitation of the quenchants. Also, it must be remembered that many tool steels are spoiled by failure to provide enough support when they are taken out from the furnace for quenching. Thus, every precaution is taken to ensure that parts are adequately supported during entire heat treatment by employing well-designed jigs, fixtures, and so on.

Other precautions to minimize distortion include:

- Tool steels should be heated to hardening temperature slowly, or in steps, and uniformly. Hot salt baths are used to render fast, uniform heat input
- It is best to heat small sections to the lower region of the recommended hardening temperature range and to heat large sections at the higher temperature range. Overheating by employing too high a temperature or too long a heating time must be avoided
- It is a good practice to protect the surface of the component from decarburization (by packing it in cast iron chips or using a vacuum furnace, for example). If a separate preheating furnace is not available, the part can be put in a cold furnace, after which the temperature is raised to proper preheating temperature and kept at that temperature to attain uniform heating throughout, prior to proceeding to the hardening temperature (Ref 86)
- With the slower cooling rate, which is consistent with good hardening practice, a lower thermal gradient will be developed, thereby producing less distortion
- Thus rapid heating and cooling rates of irregularly shaped parts must be avoided
- Proper selection of quenchant with desirable quenching properties and adequate agitation during hardening must be provided

Methods of Preventing Distortion (Ref 82, 87)

Straightening is one method to remove or minimize distortion. Since straightening (after hardening) can largely relieve the desirable residual compressive stresses (in plain-carbon and low-alloy steels) that may cause breakage, it would be better to accomplish this before the steel cools below the M_s temperature, that is, when the steel is in the metastable austenitic state (Ref 35). This temperature is above 260 °C (500 °F) for most tool steels and is preferably about 400 °C (750 °F) for long shear knives, which are usually made of 2C-12Cr steel. Warping on parts such as shafts and spindles can be corrected by straightening during or after hardening, followed by grinding to size (Ref 84). Mostly high-alloy steels are straightened after hardening due to the higher percentage of retained austenite and their comparatively low yield stress. Straightening also can be accomplished during the tempering process (Ref 35). However, straightening of hardened parts with higher strength will cause a loss of fatigue properties and possibly initiation of cracks at the surface. Hence, straightening after the hardening treatment must be very carefully controlled and should be followed by a low-temperature tempering treatment.

The case-hardened (for example, nitrided, carburized) parts can be straightened to a very large extent as a result of their lower core hardness. Nitrided parts may be straightened at 400 °C (750 °F) (Ref 35).

Support and Restraint Fixtures. Fixtures for holding finished parts or assemblies during heat treatment may be either support or restraint type. For alloys that are subjected to very rapid cooling from the solution-treatment temperature, it is common practice to use minimum fixturing during solution treatment and to control dimensional relations by using restraining fixture during aging. Support fixtures are used when restraint type is not needed or when the part itself renders adequate self restraint. Long narrow parts are very easily fixtured by hanging vertically. Asymmetrical parts may be supported by placing on a tray of sand or a ceramic casting formed to the shape of the part (Ref 64). Restraint fixtures may require machined grooves, plugs, or clamps. Some straightening of parts can be accomplished in

aging fixtures by forcing and clamping slightly distorted parts into the fixture. The threaded fasteners for clamping should not be used because they are difficult to remove after heat treatment. It is preferable to use a slotted bar held in place by a wedge (Ref 64). The bore of a hub, the most important dimension in the hardening of thin spur gears, can be mechanically plugged to prevent the reduction of the bore and keep the out-of-roundness close to tolerance limits. When hardening large hollows, either restraining bands on the outside during tempering or articulated fillers serve the same purpose.

Quenching Fixtures. When water quenching or oil quenching is essential, distortion can be minimal by employing properly designed quenching fixtures that forcibly prevent the steel from distorting (Ref 88). Figure 14 shows a typical impingement-type quenching fixture. The requirements essential for the better design of this type of fixture are as follows (Ref 79):

- There must be an accurate positioning of the part in the fixture. Whenever possible, round bars should be rotated during quenching to level out variations in jet pressure around the part
- There should be an unhindered flow of quenchant through the sufficiently large holes (3.3 to 6.4 mm, or 0.13 to 0.25 in. in diameter). Jets as large as 12.25 mm (0.50 in.) in diameter may be employed with furnace-heated heavy sections (for example, plates). A large portion of the excess quenchant with these large jets is for the removal of scale (Ref 89)
- Spacing between the holes should be reasonably wide (for example, 4*d*, where *d* is the hole diameter)
- For oil-quenching fixtures, the facility to submerge the part is required to reduce fumes and flashing
- There must be the provision for efficient cleaning of the holes
- A facility must be available to drain out the hot quenchant for effective quenching performance with cold quenchant

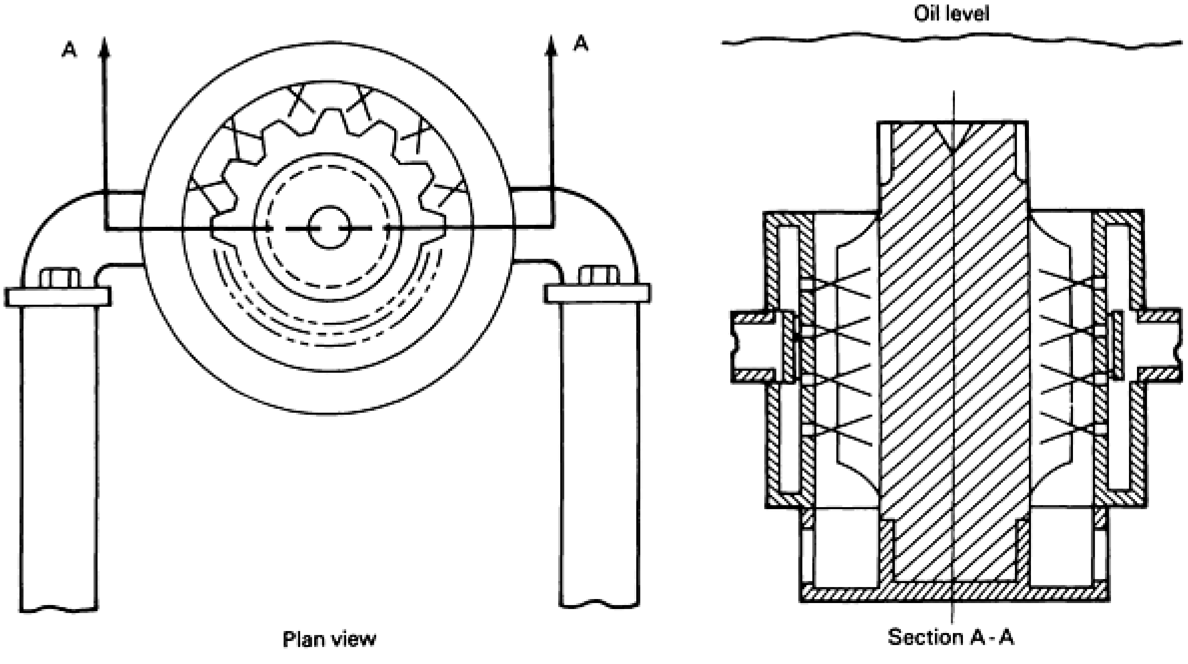

Fig. 14 A typical impingement-type quenching fixture. Source: Ref 80

Pressure quenching is the most efficient method of cooling parts from elevated temperature by using a combination of high pressure (such as 5 MPa, or 5 atm) and turbulent gas flow throughout the entire surface area of the workload (Ref 90). This is economical and fast, provides even cooling, offers a unique design and minimum distortion and improved metallurgical qualities. As a result of these beneficial effects this is suited to quench large-diameter tooling for the aluminum extrusion industry; quench larger-diameter carburized gear, larger fasteners, and precision gears to be jigged vertically; harden high-speed steel tools (such as saw blades, dies, and other parts with edge configuration) and 718 jet engine compressor blades (Ref 90). This is also employed to quench (vacuum processed) large sections of titanium alloy castings for aircraft applications (Ref 91). Figure 15 is a pressure-quench module that may be attached to vacuum-sealed quenched and continuous-vacuum furnace as a replacement for the oil-quench section.

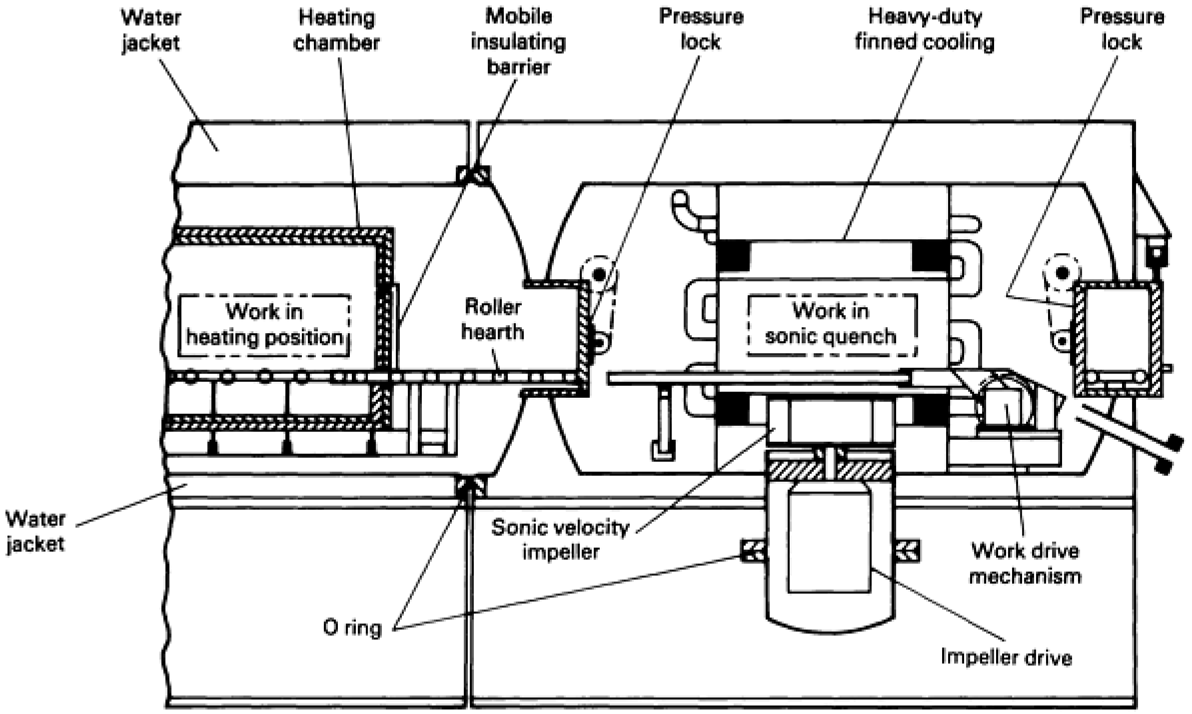

Fig. 15 Pressure-quench module for attachment into standard vacuum-sealed quenched and continuous vacuum furnaces. Source: Ref 90

Press quenching is widely employed in preventing and controlling quench distortion in components where the geometry renders them particularly prone to distortion (Ref 92). For example, flat circular diaphragms of spring steel used in the control or measurement of pressure are press quenched between two copper blocks, which cannot be accomplished by direct quenching (Ref 80).

Rolling Die Quenching. A rolling die quench machine can provide uniform water quenching with minimal distortion for large-production runs. When a heated part is placed on the rollers, the die closes and the rolls turn. This removes any distortion incurred during heating. According to manufacturers of rolling die quench machines, symmetrical parts with the following straightness can be achieved in production:

$$TIR = K\frac{l}{d} \qquad \text{(Eq 2)}$$

where *TIR* is the total indicator reading of straightness, *l* is the length (in.), *d* is the diameter (in.), and K is the constant = 10^{-4}.

For minimum yield strength requirements of 310 MPa (45 ksi), air-hardened or normalized parts with negligible distortion can be produced (Ref 79).

Stress Relieving. The presence of residual stresses in the parts caused by cold working, drawing, extrusion, forging, welding, machining, or heading operations greatly increases the tendency of distortion. However, these residual stresses can be relieved by subcritical annealing or normalizing treatment just before the final machining operation, which decreases the distortion to an appreciable extent. This is of special importance for intricate parts with closed dimensional tolerances (Ref 80). Stress reduction is necessary to avoid distortion during hardening and to avoid cracking resulting from the combination of residual stress to the thermal stress produced during heating to the hardening temperature. In the event that stress relieving is not performed after heat treatment, large distortions of the part can be removed by heavy grinding. However, the drawbacks of this operation are: possible elimination of most, if not all, of the hardened case of the carburized and hardened part; and danger of burning and crack formation on the surface layers. Hence, it is customary to stress relieve plain carbon or low-alloy steel parts at a temperature of 550 to 650 °C (1020 to 1200 °F) (for 1 to 2 h),

hot-worked and high-speed steels at 600 to 750 °C (1110 to 1380 °F), and the heavily machined or large parts at 650 °C (1200 °F) (for 4 h) prior to final machining and heat-treatment operations. Subresonant stress relieving may also be employed to neutralize thermally induced stress without changing the mechanical properties or the shape of the component. These components include: large workpieces, premachined or finish-machined structural or tubular, nonferrous, hardened, nonsymmetrical or varying section thickness, stationary, or assembled. However, this does not work on copper-rich alloys and the edges of burned plates (Ref 93).

Control of Distortion

In order to remove or minimize distortion, the modern trend is to shift from water-quenching practice to milder quenching, for example, oil quenching, polymer quenching, martempering, austempering, or even air-hardening practice. Milder quenchants produce slower and more uniform cooling of the parts, which drastically reduces the potential distortion. Other strategies of controlling distortion for age-hardening aluminum, beryllium, and other alloys include: alloy and temper selection, fixturing, age-hardening temperatures, proper machining, and stamping operations (Ref 94). The fewer the number of reheats applied to components in case-hardening steels following carburizing, the smaller is the distortion on the finished part. When top priority is given to minimum distortion, it is desirable to make the parts from oil-hardening steels with a controlled grain size and to harden them by martempering direct from carburizing. Presently polyalkylene glycol-base quenchants, such as UCON quenchants HT and HT-NN, are variously used for direct quenching from the forging treatment, continuous cast quenching, and usual hardening of forged and cast steels and cast iron. In this case boiling does not take place at the component surface but rather at the external surface of the deposited polymer film. More uniform cooling occurs, and thermal stresses are released. Because of the lower boiling point and high thermal conductivity, UCON quenchants act through the martensite zone more rapidly than oil (Ref 95).

Distortion during ferritic nitrocarburizing is minimal because of low treatment temperature and the absence of subsequent phase transformations (Ref 66). There are many methods of reducing distortion in induction-hardened components; these methods are usually found by experience with variables such as the hardening temperature and the type and temperature of quenching medium employed. Methods of reducing distortion in induction-hardened parts include: the hardening of small spindles held vertically in jigs; the plug-quenching of gears to prevent the bores from closing in; the flattening of cams by clamping them together during tempering; and the selective hardening of complex shapes (Ref 96).

As a replacement of medium- or slow-quenching oils, UCON quenchants E and E-NN can be readily used in induction- and flame-hardening operations, both in spray and immersion types, for high-carbon and most alloy steels and traditional hardening of cast iron and cast or forged steels of complex geometry with better distortion-reduction properties. Agitation of quenchant should be carried out by motor-driven stirrers to move the medium with respect to the part being quenched or by pumps that force the medium through the appropriate orifice. Alternatively, the parts are moved through the medium, and for some applications, spray quenchant is recommended. Water additives are sometimes employed in salt baths to increase heat extraction (Ref 64).

Ultrasonic quenching is also effective in controlling distortion, which involves the introduction of ultrasonic energy (waves with a frequency of 25 kHz) in the quenching bath. This breaks down the vapor film that surrounds the part in the initial stages of water or oil quenching (Ref 86).

Distortion after Heat Treatment

Straightening. When every possible case has been employed to minimize distortion, it may still be essential to straighten after heat treatment, which has already been discussed.

Grinding after Heat Treatment. In the case of carburized or nitrided parts, the metallurgist and designer, together with the production engineer, must collaborate regarding the amount to be removed by grinding after heat treatment. This grinding allowance must be taken into account when determining the initial dimensions and also when specification for the case depth is to be applied.

Distortion may also occur after heat treatment, with time, owing to the completion of any unfinished transformation or the effect of increased temperature during grinding. For example, fully hardened components such as blade shears may be damaged by characteristic crazing pattern because of heavy and careless grinding. Local overheating results in the transformation of undecomposed austenite, and the accompanying changes in volume produce sufficient stresses to cause cracking and developing of a crazing pattern.

Dimensional Stability. To achieve dimensional stabilization or stability (that is, retention of their exact size and shape) over long periods, which is a vital requirement for gages and test blocks, the amount of retained austenite in heat-treated parts must be reduced because retained austenite slowly transforms and produces distortion when the material is kept at room temperature, heated, or subjected to stress. Dimensional stabilization also reduces internal (residual) stress, which causes distortion in service.

Stabilization can be obtained by multiple tempering (with prolonged tempering times); the first tempering reduces internal stress and facilitates its transformation to martensite on cooling. The second and third retempering reduce the internal stress produced during the transformation of retained austenite.

It is the usual practice to carry out a single or repeated cold treatment after the initial tempering treatment. In cold treatment, the part is cooled below the M_f, which will cause the retained austenite to transform to martensite; the extent of transformation depends on whether the tool part is untempered or first tempered. Cold treatment is normally accomplished in a refrigerator at a temperature of -70 to -95 °C (-100 to -140 °F). Tools must be retempered immediately after return to room temperature following cold treatment in order to reduce internal stress and increase the toughness of the fresh martensite. Finally, they are ground to size. It may be pointed out that vibratory techniques are being used more frequently to achieve dimensional stability but do not offer any metallurgical benefits (Ref 80).

Distortion and Its Control in Heat-Treated Aluminum Alloys

The high levels of residual stress and distortion that are produced in the water-quenched aluminum extrusion and forgings (such as 2000, 6000, and 7000 series) and aluminum castings can be reduced 60 to 100% by using proper selection of polyalkylene glycol quenchant or polyvinyl pyrrolidone 90 concentration (for example, 25% solutions for wrought alloys, 20 to 30% UCON quenchant A for thicknesses up to 25 mm (1 in.), and 17 to 22% for larger than 25 mm (1 in.) section thicknesses in casting alloys) with sufficient agitation, lower bath temperature, proper fixture (throughout solutionizing, quenching, and age-hardening treatments), and straightening (in the as-quenched state after taking out from the fixture) procedure. The initial cost of these polymer solutions as a replacement to the conventional hot-water quenching method is easily compensated for by other advantages such as reduced scrap, reduced machining (compared to two machining operations required--one before and another after heat treatment--in the conventional water-quenching method), and increased fatigue life as a result of reduced convective heat transfer or film coefficient between the part and the quenchant, more uniform quench, precise control of quench rates, and improved heat-transfer qualities from the deposition of liquid organic polymer on the surface of the part being quenched (Ref 97, 98, 99). This method costs less, therefore saves time and allows easy shaping, bending, and twisting of the parts without establishing residual stresses. Such parts as leading edge wing skins, spars, and bulkheads are used in the aerospace industries (Ref 96).

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Importance of Design

The wrong design of the tool material may result in the establishment of nonuniform heating and cooling of the components, which produces overload and/or internal stresses leading to distortion and failure during or after hardening. Correct consideration at the design stage plays an important role in lessening the distortion and danger of cracking. The basic principle of successful design is to plan shapes that will minimize the temperature gradient through the part during quenching. Fundamental rules such as maintaining a simple, uniform, regular, and symmetrical section with comparatively few shape changes, ensuring small and smooth cross-sectional size changes, and using large radii are still too frequently overlooked at the design stage. Thus, successful heat treatment demands a rational design that avoids sharp corners as well as sudden and undue changes of section.

It is often possible for tool designers to compensate for size distortion. For example, in preparing precision hobs for gear cutting, dimensional accuracy must be kept within very close tolerances. On linear longitudinal growth, it is the general practice to go out-of-round in the following high-speed steel bars as much as 0.3% in M1 type, 0.2% in M2 type, and 0.15% in T1 type during heat treatment. These data will alter slightly with changes in design of the hobs, but essentially the growth in tungsten-base high-speed steel is lower than that of the molybdenum-base high-speed steel (M1 and M2). This does not require any difficulty if the growth is compensated for and if the steel is consistent in its growth (Ref 87).

The distortion produced in the surface hardening of long shafts by the scanning method can be a great problem if the equipment is not in very good condition. Due consideration must be given so that locating centers run concentrically, in line and at the appropriate speed; the coil must be accurately aligned, and the quench must be correctly designed with sufficient number of holes of suitable size and angle. For long shafts with a relatively small diameter (for example, half-shafts, which are likely to distort), the use of hydraulically operated restraining rolls usually overcomes this (Ref 100).

The designer should bear in mind the following rules while designing a die or machine part that is to be heat treated:

- Distribution of the material should be as uniform as possible
- Provide fillets (large radii) at the base of keyways, cutter teeth, and gear teeth to avoid stress concentration; semicircular keyways, which permit the use of round-cornered keyways, are the right

choices. Ideally, drives using involute splines are preferred over keyways

- Avoid abrupt changes of section; in other words, provide smooth changes of section
- Large holes (such as drawing or cutting openings in die rings or plates) must be centrally located from the outer contour. In some cases holes are drilled through the heaviest section of the tool in order to help fairly balance the weight of the section rather than to unbalance it (Ref 64). Deep blind holes should always be avoided because they cause nonuniform quenching. If this is not possible, the hole can be ground in after hardening. Drilled hole junctions in a steel part should be avoided because they enhance very high and undesirable cooling conditions. The problem with these cross holes is to get sufficient quenchant into them. The inside surface of the holes tends to be in a state of high tensile stress, usually leading to cracking, at least with water quenching. As a minimum, the corner at the junction of the holes with outer diameter of the part should be given a generous radius to better distribute the tensile stress (Ref 90). Similarly, grooves and keyways in highly stressed areas should be avoided, or, if possible, they should be located in low-stressed areas of the part. Alternatively, fixtures should be used that make it possible for the hole or the inside of the groove to be quenched in the beginning or more rapidly than the rest of the part (Ref 24)
- Round off all the holes, corners, and outer edges
- If sharp corners are unavoidable, provide relief notches in place of sharp edges
- The insertion of identification marks on the hardened component is recommended, preferably after hardening with tools having well-rounded edges and minimum deformation (shallow penetration depth), and at positions far away from the high-stress concentration zones (reentrant angles, bends, and so on) (Ref 101)
- Large intricate dies should be made up in sections, which frequently simplifies heat treatment (Ref 64)

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Statistical Process Control of Heat-Treating Operations

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Introduction

AS DEMAND FOR INCREASED QUALITY and documentation is felt by heat treaters, the subject of automatic collection and use of process information in a statistical process control/statistical quality control (SPC/SQC) format becomes increasingly critical. Data acquisition and documentation 10 years ago meant a chart recorder for temperature and a log sheet for the operator's dew-point readings. Today, it more than likely means a computer system tied into key points on the heat-treating equipment with the objective of logging important information for later review or perhaps being taken into account in real time.

Traditional versus Statistical Control

When man first heat treated a sword made from an iron carbon alloy, he learned that it was necessary to heat it until it glowed red and then plunge it into water. He further learned that the resulting product was often very brittle but could be made more usable by heating it again, this time to a much lower temperature. This small body of knowledge was enough process control to produce many useful products for many years.

Initially, it was noticed that if certain temperature ranges were used in certain circumstances, products of better quality would result and the idea of controlling temperature was born. Much later it was discovered that control of the carbon content of the material was important. Modern science was now controlling the properties of the end product.

If the tools used for process control in heat treating today are viewed against this backdrop, our current position on the evolutionary ladder can be pinpointed:

- *Step 1:* Rudimentary process knowledge from direct observation
- *Step 2:* Understanding of certain obvious influences from experimentation
- *Step 3:* Manual control of obvious influences like temperature
- *Step 4:* Automatic control of these obvious influences
- *Step 5:* Documentation of continued variation in process results, using statistical techniques to manually identify special problems
- *Step 6:* Use results of statistics and enhanced process understanding to gain control of the less obvious influences
- *Step 7:* Control the process from a theoretically complete model, taking into account all possible influences to produce a near-perfect product every time

The state of the art is currently at Step 5, the application of statistics in the search for problems. The jump to Step 6 is being made in some manufacturing disciplines using a new technique called "design of experiments." This is a complex statistical approach that may incorporate artificial learning into data regression-based computer programs. A program of this type will direct the human operator to perform experiment after experiment with a process in order to gain insight into any possible effects, direct or synergistic, that an entire list of possible process parameters might have. A process model initialized with known theory, but ultimately based on derived statistics, will emerge that can be used to indicate those parameters that will make significant contributions and should therefore be subject to automatic control.

A model such as this could be used to bake a better cake, for example. The model might direct the operator to make a cake with 1 egg the first time, 0.5 eggs the second, and 1.5 eggs the third. It would then ask for quantified results as to the measured quality of each of the experimental cakes. The model might conclude by saying that the optimum cake must be made with between 1.1 and 1.2 eggs, along with similar odd amounts of all the other applicable ingredients. It might even conclude that no salt is necessary in a cake because the statistics did not bear out importance of this item.

Basic SPC/SPQ Nomenclature

The purpose of this article is to provide a practical discussion of the application of SQC techniques to heat-treating operations and for that reason many of the applicable definitions and equations are not used but can be found by the reader in other reference materials on this subject. However, it is felt that the following minimum basic definitions and equations are necessary to be presented here for a better understanding of the text.

- *Accuracy versus precision:* Accuracy is measured by the extent to which the measured average of a group of readings, regardless of how widely the readings are dispersed, agrees with the true value of the unit being measured. Precision is the repeatability of the measurement (how much dispersion exists between readings) regardless of how close the readings are to the true value (or how accurate the readings are)
- *Gage repeatability and reproducibility study* (*GR & R*): A study conducted on measurement devices to determine the precision and accuracy of the device. Results are expressed as an R & R index
- *Process:* Any specific combination of machines, tools, methods, materials, and/or people employed to attain specific output in a product or a service. A change in any one of the constituents results in a new process
- *Process capability:* Refers to the reproducibility of a process over a long time period during which

normal changes in workers, material, and other conditions are encountered

- *Quality:* Product features which are free from deficiencies and thus meet the needs of the customer and provide product satisfaction
- *Statistical process control:* The application of statistical techniques for measuring and analyzing the variation in processes
- *Statistical quality control:* The application of statistical techniques for measuring and improving the quality of processes and products. Statistical quality control includes statistical process control, diagnostic tools, sampling plans, and other statistical techniques
- *C_p index:* Stands for capability of process, and is the ratio of the specification tolerance to six standard deviations (6σ). C_p is a measure of the dispersion of data only
- *C_{pk} index:* A measure of both dispersion and centeredness of the data as follows:

$$C_{pk} - \textit{the} \text{ lesser of: } \frac{\text{USL - mean}}{3s} \textit{ or } \frac{\textit{mean} \text{ - LSL}}{3s}$$

where USL is the upper specification limit, and LSL is the lower specification limit

Use of Statistical Control in Heat Treating. In the last few years, it has become commonplace to see heat treaters tracking the results of their most critical processing with SPC techniques. The most commonly examined parameters include hardness, case depth, and distortion, although many others are tracked as well. Unfortunately, it has also become commonplace to observe these very same heat treaters failing to use these techniques for anything more than supplying required after-the-fact documentation on treated parts. It seems that the promise of statistical process control and its roll in the revitalization of manufacturing quality in heat treatment is not being fulfilled.

It is important to understand that any SPC program is a means, not an end. Statistical process control is a tool to audit a process and help distinguish controllable variables from uncontrollable variables. It also provides a means for quantitatively measuring the level quality of a process. Statistical process control alone does nothing to improve the process. Continual improvement of the heat-treating process is the real goal and this comes from actions taken by people. Statistical process control is utilized as a tool to direct those actions.

Simply installing an SPC system on a dilapidated furnace does not improve the performance of the furnace. SPC alerts the furnace operator to the fact that, statistically, a problem does exist and requires investigators to determine which variables are causing excessive variations to occur. Statistical process control does not tell *what* is wrong, only that, statistically, excessive variation is present and this condition should be investigated to determine the assignable cause.

SPC versus SQC. It is necessary to make a distinction between statistical process control and its relative, statistical quality control. The latter is what most heat treatment shops are really using when histograms, mean/range charts, and capability indices are calculated for the variation in attained results (for example, hardness, case depth, and so on) in the processing of a given component.

Because statistical quality control is an after-the-fact tool, its best use is in the control of continuous processing where trends can be noticed and corrected before significant damage occurs. Processes such as large volume induction hardening (see the article "Induction Heat Treating of Steel" in this Volume) and continuous carburizing have been substantially improved with SQC charting techniques.

In batch processing, however, statistical quality control is of little value in preventing problems because at least one entire load of parts will be adversely affected before a problem can even be noticed. Even if the problem is caught after one load, the proposed solution cannot be tested without committing yet another load. Statistical quality control can be very helpful in batch or short run type (set-up dominated) processes by using it to analyze set-up variables. If the process is then set up to optimal set-up parameters (as determined by experimentation or evaluation of part outputs), meeting parts specifications will necessarily result.

Statistical Process Control. The idea behind true statistical process control is that the results of a process can be guaranteed if none of the relevant process parameters are allowed to stray outside of previously established control limits.

The long standing problem in applying statistical process control to heat treatment has been finding methods to quantify and measure process parameters that are of known importance (outside of the obvious ones). Many SPC programs are based upon charting controlled parameters such as temperature, atmosphere carbon potential, quenchant temperature, and so on. While this approach is certainly not incorrect, it does often lead to a situation where a deviation in an SQC chart (results) commonly cannot be attributed to any special cause deviation in a corresponding SPC chart (processing parameters), because all the things being charted are controlled variables that by design will not normally change.

Processing Methods Considerations

Repeatability is a key issue when considering how to improve a heat treatment process. The more process variables that can be controlled within specific known limits from part to part, furnace load to furnace load, and day to day, the more repeatable the process results will be.

Continuous Operations. The continuous types of heat treatment equipment (that is, rotary retort, pusher carburizers, belt furnaces, and so on) offer the most straightforward approach to applying SQC and SPC techniques to improve process performance.

Because a high volume of work pieces is involved, there is adequate opportunity to perform in-process sampling of key product characteristics. Negative outcomes can be predicted before they take their full course. Also, special causes are often more identifiable because process variables are steadier in continuous processes than in batch-type processes.

Single Part Treatments. With induction and flame heat treating, parts are typically processed one at a time. Using part evaluation techniques to predict negative results becomes difficult and impractical. Thus, the focus must shift to statistical process control and the identification, monitoring, and controlling of the process variables to ensure repeatability of the results.

Electric power, flame temperature, scan speed, coil dimension, part positioning, and quenchant temperature are some variables that need to be considered. Trending of process variables can be used to determine special causes.

Batch Operations. Batch-type furnaces usually offer the opportunity to do a significant amount of sampling and analysis within a load. However, all this does is develop a degree of confidence on the results of the entire load. The process variables must be monitored and analyzed to ensure that the process is under control and there is repeatability from load to load and from day to day. This is especially true when each load is different in terms of part geometry, material and/or specification, which is the norm in commercial heat treating.

Process Deterioration

A fact of life in any heat-treating process is that the equipment gradually succumbs to the wear and tear of constant operation, thus the process inevitably gets worse with time. The challenge is to counter this natural deterioration with corrective action before out-of-specification parts are produced.

SPC techniques can be utilized to measure furnace performance and address process deterioration in heat treating. By monitoring key process variables and/or key process outputs, preferably in on-line fashion, trends can be spotted and action taken before nonconforming product is produced.

Key process variables may mean not only controllable variables, but also uncontrollable and secondary variables.

Uncontrollable Process Variables. Examples of uncontrollable variables that are useful in the monitoring of a heat-treating process are:

- *Quench transfer time:* Although this is not a controllable variable in most furnace systems, it is often a critical parameter in terms of producing good parts. It may be beneficial to monitor and analyze transfer time in order to get an early warning of the deterioration of the transfer mechanism. One method for verification of sufficiently fast transfer time is to compare the maximum allowable transfer time for a successful process to the actual transfer time which would trigger an alarm if the maximum were exceeded. This automatic control method would then flag suspect loads or parts resulting from either a mechanical failure or equipment function deterioration

- *Temperature recovery time:* By measuring and analyzing the time it takes for a batch furnace to reach setpoint temperature (with a standard load weight or empty), trends can be picked up that would indicate a loss in furnace performance. These out of control trends as plotted on an SPC chart would then trigger an investigation to determine the cause of the condition (for example, damaged insulation, poor door seals, heating system malfunction, and so on)
- *Quench temperature rise:* Although a quench system may be controlled within a specific range (that is, 30 to 65 °C, or 90 to 150 °F), it may be important to know how the temperature cycles from quench to quench. This would give a macroanalysis of the entire quenching system and give warnings of failed, or impaired, agitation and/or quenchant cooling. Over-loading of the furnace could also be indicated

Secondary process variables are those that are caused by the deterioration of control loops. Examples are of secondary variables:

- *Fuel consumption:* By monitoring gas or electric consumption for a standardized furnace cycle and loading (could be empty), diminished performance in the heating system can be detected
- *Additive atmosphere gas:* By monitoring and trending the amount of natural gas (or propane) addition required to control a specific carbon potential setpoint, the deterioration of furnace atmosphere integrity can be detected

Process and Product Capabilities

Capability studies are conducted on all types of manufacturing processes to determine the statistical variation of a product with respect to a measured characteristic. For heat-treating processes, characteristics frequently measured are hardness and case depth. Because these metallurgical characteristics are sometimes difficult to define, specifications may initially need to be clarified with regard to the exact test scales or test methods to be used and the critical locations where these tests are to be made before a capability study is conducted. Process results for many metallurgical and heat-treating processes are dependent on material-related characteristics such as hardenability, material chemistry, and/or part geometry that also make the process test results sensitive to those variables.

After the metallurgical requirements are clearly established, a basic process capability study may be conducted. Care should be taken so that the parts tested are from the loading locations representing the extremes in process variability. A good guideline for test sample locations is to use those loading locations prescribed for temperature uniformity surveys in specification MIL-H-6875.

For continuous processes, it is important to collect the samples over a sufficiently long period of time in order to reflect process heating power fluctuations or other process abnormalities that could be time dependent.

The use of normal probability paper for data representation and plotting is highly recommended. If the data does not plot as a straight line indicating a normal distribution, a metallurgical or process-related reason for this skewness should be apparent or be determined. An example of a capability study of an atmosphere harden and temper operation for automotive seat belt parts made from SAE 4037 steel is shown in Fig. 1 and Fig. 2.

MIDLAND METAL TREATING, INC.

VARIABLE DISTRIBUTION ANALYSIS

CUSTOMER ABC COMPANY		INSPECTOR: J.D.	DATE: 7/15/90	ACTUAL RANGE
W.O.	SAMPLE SIZE: 25	SPECIFICATION: ROCKWELL "C" 32 - 39		34 -37.5
P.O.	AQL %:	PART NUMBER: 1234567		MEAN 35.7

ROCKWELL "C"	FREQUENCY 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	f	ACCUM. f	ACCUM %
32																									
32.5																									
33																									
33.5																									
34	X																						1	1	4
34.5	X	X																					2	3	12
35	X	X	X	X																			4	7	28
35.5	X	X																					2	9	36
36	X	X	X	X	X	X	X	X															8	17	68
36.5	X																						1	18	72
37	X	X	X	X	X																		5	23	88
37.5	X	X																					2	25	100
38																									
38.5																									
39																									

Fig. 1 Final hardness distribution analysis for a typical quench and temper operation

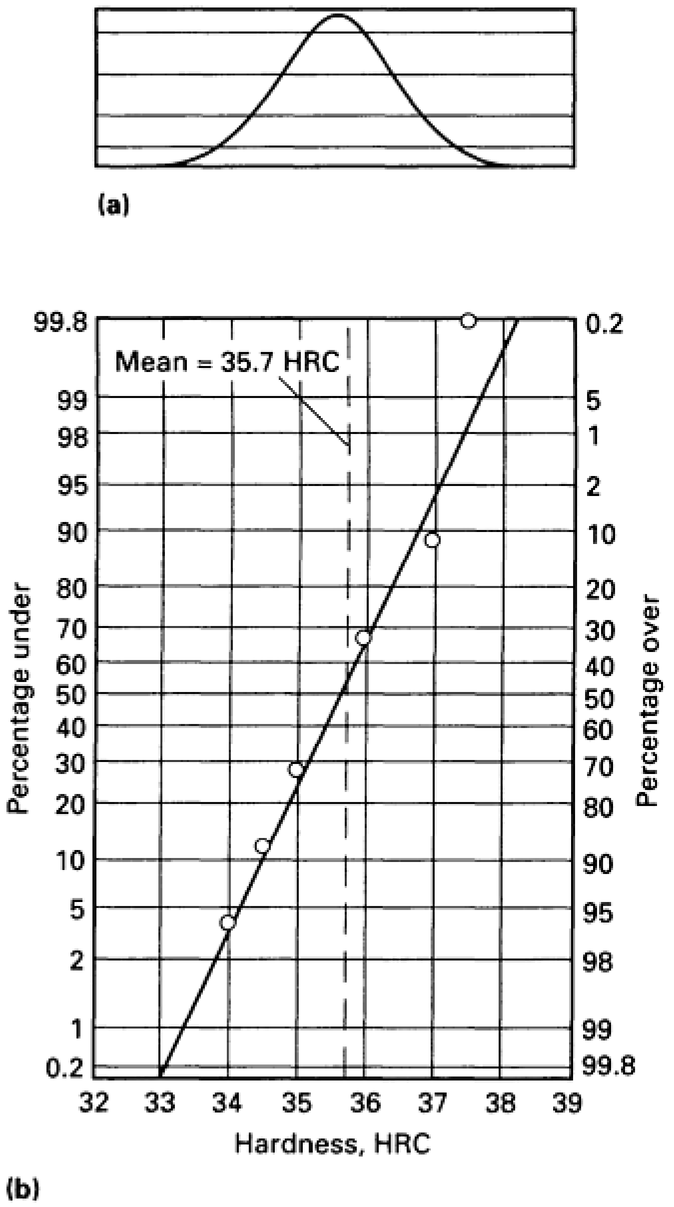

Fig. 2 Normal probability plot of data from Fig. 1. (a) Frequency distribution. (b) Distribution analysis sheet. Specification, mean = 35 HRC; range = 7 HRC. Results, mean = 35.7 HRC, 6σ = 5.5 HRC, C_p = 1.27. Action, adjust temper to adjust mean to 35 HRC

As can be seen in Fig. 3, the overall process capabilities results are the result of many contributing factors:

- *Base material contributions:* Unique material characteristics, material defects, and hardenability differences. These can vary from lot to lot and also between materials
- *Part-related contributions:* Part geometry and section size variations
- *Process-related contributions:* Temperature uniformity as affected by process control and mass effects, time control, atmosphere control, and cooling method (as determined by uniformity and average severity)
- *Evaluation method contribution:* Standards accuracy and testing method accuracy

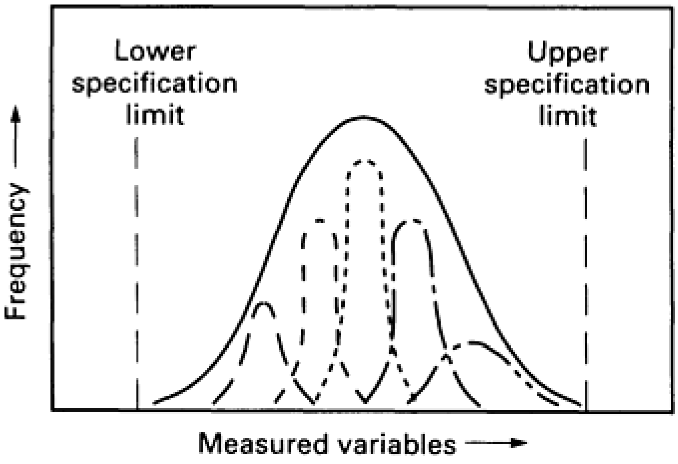

Fig. 3 Factors contributing to overall heat-treating process result variations

Thus, to successfully use the process capability study as a dynamic tool to refine and narrow process variability, the following three steps should be used in conjunction with process capability studies:

Step No. 1:

- Identify critical control variables and their relative contributions to process attribute variations (this can be done by process modeling techniques)
- Measure process inputs with corresponding process output results
- Document process control procedures

Step No. 2:

- Modify control procedures, manufacturing procedures, or equipment in order to reduce process variability

Step No. 3:

- Remeasure process capability (as in Step No. 1 above) to ascertain the effectiveness of the changes

The overall heat-treating process variability result may be characterized as being comprised of the following factors (they may be classified into four categories) and the accompanying sources of the undesirable background signals (intrinsic or extrinsic noise):

- Base material related (intrinsic noise)
- Part configuration and manufacture related (intrinsic noise)
- Process related (extrinsic noise)
- Evaluation method related (extrinsic noise)

By using properly standardized test coupons as the basis of a process capability study, we can separate out the variability due to intrinsic noise factors and arrive at the inherent process capability. However, in practice, we will still have these contributions in the process and this should be kept in mind. Additionally, a GR & R study may be performed on the evaluation method to determine the contribution of these factors to variability.

Base Material Considerations

Cast irons are probably the best example of a material where test results (that is, hardness) can be a function of the hardness testing scale used. This sensitivity of hardness value to the testing method and the hardness scale used is because the different phases present in the workpiece vary significantly in hardness. This same effect exists in other materials which are heat treated (see Fig. 4).

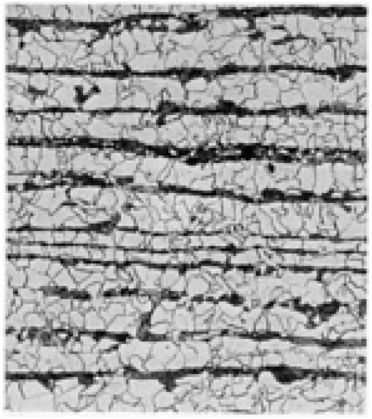

Fig. 4 Microstructure of hot-rolled AISI 1022 steel showing severe banding. Bands of pearlite (dark) and ferrite were caused by segregation of carbon and other elements during solidification and later decomposition of austenite. Etched in nital. 250×

Another type of problem that can influence testing results which are not the direct result of processing is "banding." Many steels, particularly a resulfurized one such as AISI 1100 or 1200 series, exhibit banding or microalloy segregation. The bands exist prior to heat treatment and the ferrite-rich and pearlite-rich areas run in bands across the longitudinal rolling direction of the bar stock from which parts are made.

It has been found that this condition can result in a 4 to 10 point of Rockwell C hardness variation after hardening between these bands of different chemical composition. This problem is greatest when the bands are widest and the heat treatment times are very short, such as for induction hardening processes.

Decarburization. Surface carbon reduction to a greater or lesser degree exists on most steels having more than 0.30% C. This defect results from basic steel manufacturing and if not removed in the part manufacturing process prior to heat treatment can influence the surface hardness of parts after induction, flame, or direct hardening processes that may not be capable of correcting the surface decarburization condition. However, it should be recognized that many heat-treating processes can also cause this same problem. It is thus important for one to have characterized the incoming product to be processed so that the controllable incoming material variability can be isolated and corrected independently from the product variations due to the process.

Material Variations. Before applying statistical control techniques to monitor process or product uniformity, it is important to understand how the raw material uniformity is controlled prior to heat treat processing. That is, whether or not the incoming material is identified and kept separate by heat numbers in the case of steel or by batch number in the case of cast materials.

Part-Related Contribution

Each part evaluated by statistical means after heat treat processing can have other unique features such as section size variation, geometry, and/or surface finishes which can affect the test results obtained.

Use of Test Coupons. Test coupons can be used to provide an accurate heat-treating process evaluation if one is only interested in measuring changes or variations in the process. Test coupons must be carefully designed to be an effective statistical process control tool. They must be:

- Properly selected for size, shape, and material that can be directly correlated to the material and parts configuration being processed
- Prepared in sufficient quantity (same heat of steel) and quality to eliminate or minimize the material uniformity variable from the processing variation

By using statistical quality control with test coupons in conjunction with statistical quality control on heat treated parts, product variations attributed to process only variations may be identified and controlled.

Example 1: Use of 10 000 Test Pins Measuring 64 mm (2 $\frac{1}{2}$ in.) Long by up to 17.8 mm (0.700 in.) OD Made from a Single Heat of 8620H Steel Used to Monitor the Carburizing and Hardening Operations of 5- to 8-Pitch Gears.

Test pins were used to monitor carburizing and hardening processing for 5- to 8-pitch gears made mostly from 8620H steel. This procedure is used to monitor the *process variation* in carburizing of surface hardness, effective case depth, and core hardness. The diameter chosen for the test pin is based on the gear tooth thickness and the fact that the test pin center cooling rate would be on the steeper portion of the Jominy hardenability curve. This means that monitoring the center core hardness on test pins is an indirect measurement of quench uniformity.

Purchase and Processing of Test Pins. The minimum quantity of test pins purchased was 10 000 pieces from a single heat of 8620H. The OD of these pins were ±0.13 mm (±0.005 in.) for a given lot of pins with the absolute size being 12.7 to 17.8 mm (0.500 to 0.700 in.). The length was 64 ± 1.6 mm (2 $\frac{1}{2}$ ± $\frac{1}{16}$ in.). A groove was added to the pin for attaching the pin by wire to the load.

At least one test pin is processed with each batch load or one pin is run every 4 h on each row of all continuous furnaces.

Test pins were hung in all furnace loads in a location where the processing was typical of the parts processed.

The test pins are evaluated as-quenched only. *No tempering is permitted.* Test pins evaluated for purposes of SQC control were from pure cycles with no abnormal changes in times, temperatures, or quench procedure.

Testing Procedures for Test Pins. File the surface of the pin to check for file hardness and to make a smooth surface. Check three hardness readings on Rockwell C scale and record the average. Do not use V anvils but use flat or spot anvil only.

Cut parallel section 6.4 mm ($\frac{1}{4}$ in.) thick from the center of the test pin. Set the diamond and anvil by checking at mid-radius. Check the center hardness by Rockwell well C scale and record.

Effective Case Depth. On the section cut from above, grind the surface to be checked on a 120-grit or finer paper. Test from the surface in to the point where the hardness is 85.5 HR15N (50 HRC). Measure from the surface to the center of that mark using a Brinell glass. Record the reading as effective case depth in thousandths of an inch.

The referee method for checking effective case depth is by 500-g microhardness to 50 HRC equivalent. Therefore, at least one of every ten checks and/or any check of effective case depth not within the specified limits is to be verified by the microhardness method.

The results from above are to be plotted by *cycle* and *furnace* on the form shown in Fig. 5.

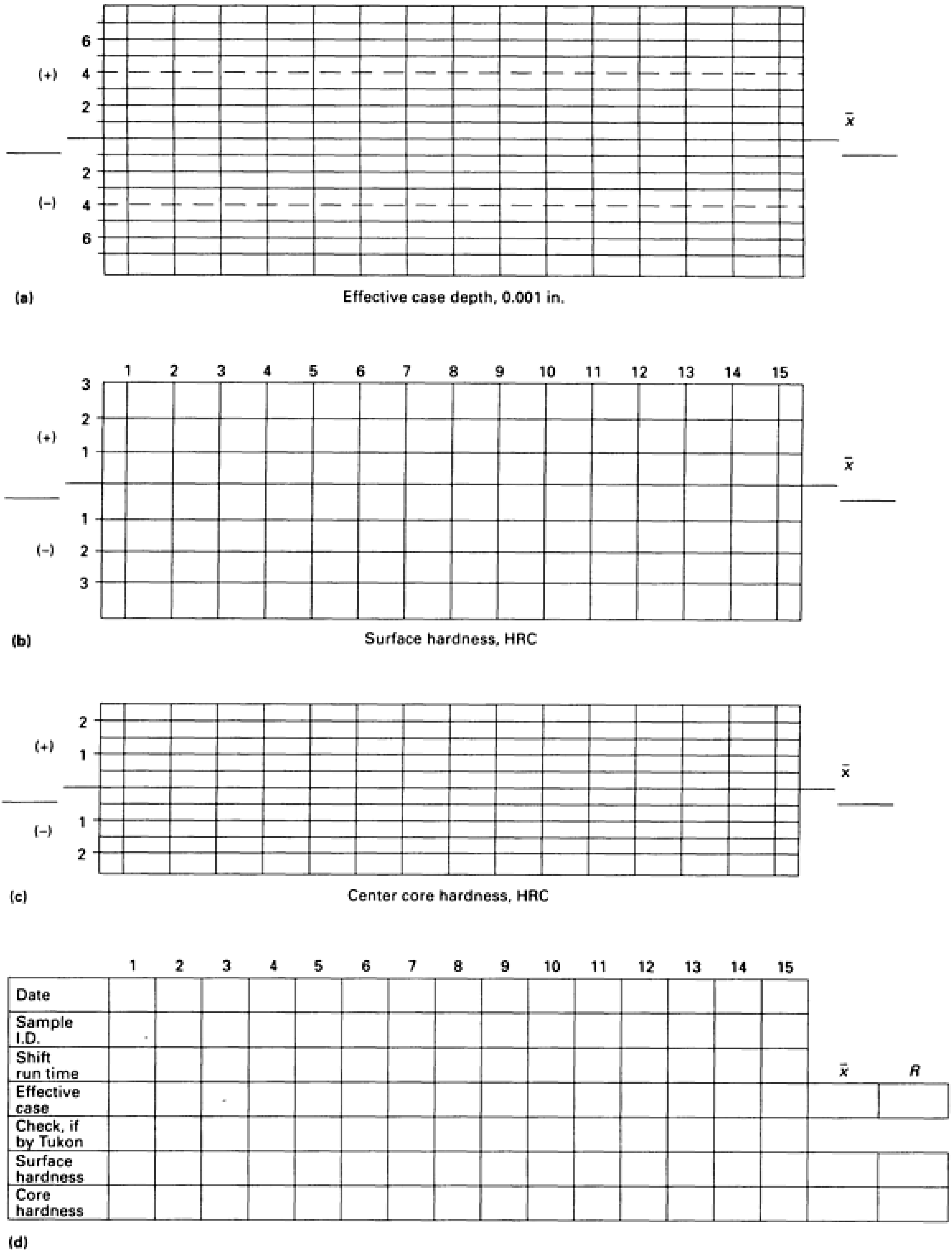

Fig. 5 Chart for plotting 8620 steel test pin variation by characteristic. (a) Effective case depth characteristic. (b) Surface hardness characteristic. (c) Center core hardness characteristic. (d) Chart to plot data from (a), (b), and (c) by cycle and furnace

This method can be started and used on a monitoring basis only for a short time until mean values with upper and lower control limits can be established.

Process-Related Contributions. This is the most important characteristic to identify and control to reduce variability of the heat treated products. Exactly how to accurately control process parameters is covered in the section "Design of

Experiments" in this article. By using standardized test pins and modeling to separate processing parameters, the individual parameter contribution to a measured characteristic such as effective case depth can be shown as detailed in Table 1.

Table 1 Contribution of selected parameters to variations in effective case depth for required 0.85 to 1.00% surface carbon level at 870 °C (1600 °F) processing temperature

Case depth		Variation in case depth for selected parameters, %[(a)]											
		Temperature variation (Δ*T*)			Time variation (Δ*t*)			Carbon variation (Δ *C*)					
								Atmosphere			Quench uniformity[(b)]		
mm	in.	11 °C (20 °F)	28 °C (50 °F)	56 °C (100 °F)	5 min	10 min	30 min	0.10%	0.15%	0.25%	0.05%	0.10%	0.20%
0.51	0.020	6	14	33	3	7	20	8	13	27	11	23	45
1.02	0.040	6	16	34	1	2	5	8	13	27	11	23	45
1.52	0.060	7	17	35	>1	1	2	8	13	27	11	23	45

(a) Total process variation = $\sqrt{A^2+B^2+C^2+D^2...+Z^2}$, where *A, B, C, D,* and *Z* are % variations attributed to Δ*T,* Δ*t,* atmosphere Δ*C,* quench uniformity Δ*C,* and additional variables, respectively

(b) Variation in case carbon level when quenched to 50 HRC.

The most significant observation from Table 1 is that quench uniformity is an equally significant factor in the carburizing process with time, temperature, and atmosphere control as variables.

Measurement Accuracy

The most important reason for calibrating with traceable test blocks and indenters and using a stable hardness standard is the U.S. industry movement toward higher levels of statistical quality control.

Testing variables must be eliminated wherever possible to permit the production part process as much range as possible. This means keeping the tester, anvil, operator, indenter, and test block error to the smallest possible percentage of the production tolerance. Test block consistency is one very important controllable variable. Some test blocks state maximum variation of 0.2 hardness units down to 40 HRC. With ten standardizing tests on a larger, thicker block that show no greater variation than 0.2 hardness units, there is the likelihood there would be few readings found above that variation. Conversely, on a thin standardizing test block with five tests where one reading out of five may show a variation of 0.4 hardness units, there is the likelihood that there would be other 0.4 or greater measurement variations. When plotting $\bar{x}$-*R* control charts (see the article "Statistical Quality Design and Control" in Volume 17 of *ASM Handbook*, formerly 9th Edition *Metals Handbook*) where $\bar{x}$ is the sample mean and *R* is the range, this greater test block variation over time could erroneously show the hardness tester is not consistently accurate within tight limits. The variation could lead to incorrect process adjustments or put into question the process capability. The higher consistency, more stable test block would show a tighter band of tester accuracy and repeatability performance.

In order to assist in reducing the variability in hardness testing, the following items should be utilized:

- Digital hardness tester with reduced operator influence features (that is, motor drive or automatic full load application and removal)
- Very stable and consistent hardness test blocks
- Certified diamond indenters as reference standards
- Good operator training program on hardness testers
- Proper clamping devices to support odd-shaped parts and/or fixtures for additional support
- Daily checks of hardness testing equipment using standardized test blocks in the range or ranges most commonly encountered on production parts tested with the machines

SPC Process Analysis

The concept of process analysis is a relatively new way to deal with a group of old ideas. For example, what is the best temperature from which to harden a particular steel? How was this temperature determined? Is this temperature the one that takes the best advantage of the material's hardenability or is it the one that gives the lowest distortion or was it chosen for other reasons? What effect will raising or lowering this temperature have on the final variation in results?

Process analysis should follow a step-by-step characterization plan as follows:

1. Determine the process capability
2. Describe the process in operational terms
3. List, in order of importance, the output characteristics for each process element
4. Decide upon the measurement method and determine instrument variability (GR & R study)
5. Estimate the process variability
6. List all input variables (both controllable and uncontrollable) for the above output characteristics
7. Select the variables to be included in the process characterization
8. Decide the objective of the process characterization
9. Determine characterization methods and how data will be displayed
10. Construct a characterization implementation plan
11. Choose analysis method for process optimization (that is, evolutionary operations, EVOP, response surface methodology, RSM, and so on)
12. Determine effective process control plan
13. New process capability determination
14. Process documentation
15. Repeat if necessary

Design of Experiments

Before anything else can be done, the important process parameters must be identified and their effects documented. While this is often a matter of metallurgical common sense, the complex interaction of many variables can often lead to results that do not appear to make sense at all.

For example, in the hardening of steel, the variables of quenchant selection and quenchant temperature are vitally imporant. Common sense (as well as heat transfer] logic) says that the higher the quenchant temperature, the slower the quench. Unfortunately, this rule may or may not be true depending on the quenchant and the temperature range.

Many quench oils show peaks in their cooling characteristics that dictate a certain quenchant temperature is required for the fastest quench. Going either above or below this temperature will slow it back down. To complicate the matter, this performance peak may change depending upon aging of the oil and the agitation level of the oil. For all quenchants, agitation is a very significant factor in cooling performance. Thus, picking the optimum quench is not an easy task.

The category of methods developed for dealing with such complexity is known as the design of experiments. These methods must not be confused with simple linear regression interpolation from empirical data.

For example, consider the fictitious empirical data on the hardening of a high-carbon steel part in Table 2.

Table 2 Determining optimum austenitizing-tempering cycle to obtain a 55 HRC hardness in a high-carbon steel part

Austenitizing temperature		**Hardness at selected tempering temperature, HRC**		
°C	**°F**	**150 °C (300 °F)**	**260 °C (500 °F)**	**370 °C (700 °F)**
790	1450	60-62	55-57	46-50
845	1550	62-63	55-62	49-53
900	1650	61-64	57-61	50-55

It is desired that the final part be 55 HRC and no other parameter (distortion, ductility, and so on) is important. Looking at the data, it is obvious that there are going to be many combinations of austenitizing and tempering temperatures that will center the results at the desired point.

A design viewpoint on these data would help the selection of the best combination from a result variability viewpoint. It can be seen that the selection of 900 °C (1650 °F) for austenitizing along with perhaps a 315 °C (600 °F) temper will center the results at around 55 HRC, just as an austenitizing-temper combination of 790 °C (1450 °F) and 260 °C (500 °F) would. The choice of which sequence is best to reduce variability in the desired hardness might be governed by two observations:

- It would appear from the data that the higher the austenitizing temperature, the wider the range of the measured hardness results
- The effect on hardness of increases in tempering temperatures seems more dramatic from 260 to 370 °C (500 to 700 °F) than from 150 to 260 °C (300 to 500 °F)

Based on these observations, one might conclude that the 790 °C/260 °C (1450 °F/500 °F) combination is more desirable than the 900 °C/315 °C (1650 °F/600 °F) combination, as the results will likely fall into a tighter range, that is, resulting in a greater process capability around 55 HRC.

The key goals in a design of experiments exercise in heat treating are generally two-fold:

- Determine which variables (and combinations of variables) have significant, observable influence over the results based on a balance between economic and quality considerations
- Determine the optimum values for these variables in order to center the process at the desired point, reduce the variation in results due to possible or expected variation in these process parameters, and reduce the variation in results due to variation in the material

The following case history is presented to illustrate a design of experiments exercise.

Example 2: Induction Hardening of an AISI 1040 Cold-Drawn Combination Yoke and Spline Shaft Bar.

The bar had a 34.11 mm (1.343 in.) diameter and was 900.68 mm (35.460 in.) in length.

These parts were being hardened on a 6-station scanner with a 10 kHz motor generator (800 V, 375 A, 300 kW). The induction coil size was 44.45 mm (1.75 in.).

The stated objective of the design exercise was to determine the relationship between various induction hardening parameters and the resultant metallurgical properties (including distortion). The ultimate goal of the project was to optimize the process to produce a part with acceptable metallurgical properties while exhibiting minimum distortion.

Table 3 summarizes the various characteristics desired in the final part.

Table 3 Desired properties of a 34.11 mm (1.343 in.) OD cold drawn combination yoke-spline 1040 steel shaft

Characteristic	Preferred dimension	Optimum condition	
		Value	**Goal**
Effective case depth	Nominal	$\bar{x}$= 4.83 mm (0.190 in.)	40 HRC
Surface hardness	Maximum	58 HRC	1040 steel
Spline size change	Minimum	0.0000 mm (0.0000 in.)	Absolute value
Out-of-straightness (TIR)	Minimum	0.000 mm (0.000 in.)	. . .

The factors affecting the process were split into two groups:

- *Process factors:* Those factors that could be changed (for example, speed and power)
- *Noise factors:* Those factors, such as the induction station number, *that cannot be changed.* One very important variable that could not be changed during the experiment was the analysis of the individual heats of steel involved

The practical limits on the process factors and noise factors (that is, factors that could not be controlled) were determined and cataloged in Table 4 and Table 5.

Table 4 Process factors for three heats to induction harden a 34.11 mm (1.343 in.) yoke-spline 1040 steel shaft per Table 3 specifications

Process factor	Process conditions		
	Heat 1	**Heat 2**	**Heat 3**
Scan speed, s/m (spf)[a]	110 (36)	120 (40)	. . .
Power supply, %[b]	98	94	90

Quench temperature, °C (°F)	25 (80)	40 (100)	50 (120)
Quench pressure, kPa (psi)	55 (8)	70 (10)	83 (12)
Speed of rotation, rev/min	10	36	60

(a) spf, seconds per foot.

(b) At 100% set point, power output is 800 V.

Table 5 Noise factors for three heats to induction harden a 34.11 mm (1.343 in.) yoke-spline 1040 steel shaft per Table 3 specifications

Degree of hardenability	Steel making process	Heat No.	Composition, %						Chemical ideal diameter, *DI*[(a)]
			C	Mn	Ni	Cr	Mo	Si	
low	Ingot cast, aluminum fine grain	M1 N26177	0.37	0.71	0.02	0.04	0.01	0.23	0.88
mid	Billet cast, vanadium fine grain	M2 B944212	0.39	0.85	0.05	0.07	0.01	0.27	1.16

(a) Calculated hardenability expressed in inches

The following series of experiments was designed to test the possible various variably combinations. The individual experiments were referred to as A1, C6, and so on (see Table 6).

Table 6 Series of experiments run to test process factor variable combinations shown in Table 4

Experimental level	A scan speed		B Power		C Quench temperature		D Quench pressure		E Speed of rotation, rev/min
	spf[(a)]	s/m	Setting, %	Voltage, V	°C	°F	kPa	psi	
1	110	36	98	785	25	80	55	8	10
2	110	36	98	785	40	100	70	10	36
3	110	36	98	785	50	120	83	12	60

4	110	36	94	750	25	80	55	8	36
5	110	36	94	750	40	100	70	10	60
6	110	36	94	750	50	120	83	12	10
7	110	36	90	720	25	80	70	10	10
8	110	36	90	720	40	100	83	12	36
9	110	36	90	720	50	120	55	8	60
10	120	40	98	785	25	80	83	12	60
11	120	40	98	785	40	100	55	8	10
12	120	40	98	785	50	120	70	10	36
13	120	40	94	750	25	80	70	10	60
14	120	40	94	750	40	100	83	12	10
15	120	40	94	750	50	120	55	8	36
16	120	40	90	720	25	80	83	12	36
17	120	40	90	720	40	100	55	8	60
18	120	40	90	720	50	120	70	10	10

(a) spf, seconds per foot

The experiments were run and the results (characteristics) measured and documented. The results were then analyzed mathematically using the concept of signal-to-noise ratio, or S/N.

(This concept is somewhat difficult to grasp as it relates to process control but it is helpful to consider the S/N phenomenon in the case of an overseas telephone call. There is almost always some hiss in the background of such a connection. The voices on the line are the *signal*, while the hissing sound is the *noise.* If the signal is much louder than the noise, it is possible to understand what is being said. This is a *high* S/N ratio. On the other hand, if the noise is almost as loud as the signal, it is not possible to understand; this is designated as a *low* S/N ratio.)

S/N ratios are measured in decibels, or dB. This is a logarithmic unit that allows very large ratios to be compressed into small units. In the case of process control:

- *Signal:* Controllable input of the process
- *Noise:* Uncontrollable variables which cause variation of the process

There are many specific formulas for calculating S/N in process control situations. Each is of the general form:

$$S/N = 10 \log_{10}\left(\frac{\bar{x}}{\sigma}\right) \qquad \textbf{(Eq 1)}$$

where σ is the standard deviation. Note that:

- A higher S/N ratio indicates a variable (or factor) with a corresponding large effect on the output characteristic of the part
- S/N measures change in both mean and/or variability
- Every time the S/N gains 3 dB, the loss by the loss function halves; thus a 3-dB change is significant

Tables 7(a) and 7(b) show the results of the mathematics as related to the characteristic of case depth. A depth of 4.83 mm (0.190 in.) was considered nominal.

Table 7(a) Signal-to-noise ratio analysis used to determine optimum process and noise factors required to obtain 4.83 mm (0.190 in.) average case depth in yoke-spline shaft

Experiment No.	Characteristic											Average case depth		Signal-to-noise ratio (S/N), dB
	Process factor									Noise factor				
	Scan speed		Power supply		Quench temperature		Quench pressure		Speed of rotation, rev/min					
	s/m	spf	Setting, %	Voltage, V	°C	°F	kPa	psi		Material hardenability	Station	mm	in.	
A1	110	36	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	4.83	0.190	131
A2	120	40	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	5.31	0.209	119
B1	. . .	. . .	98	785	. . .	. . .	. . .	. . .	. . .	. . .	. . .	5.49	0.216	79
B2	. . .	. . .	94	750	. . .	. . .	. . .	. . .	. . .	. . .	. . .	5.13	0.202	90
B3	. . .	. . .	90	720	. . .	. . .	. . .	. . .	. . .	. . .	. . .	4.57	0.180	81

C1	. . .	. . .	. . .	. . .	25	80	. . .	. . .	. . .	. . .	. . .	5.18	0.204	85
C2	. . .	. . .	. . .	. . .	40	100	. . .	. . .	. . .	. . .	. . .	5.11	0.201	92
C3	. . .	. . .	. . .	. . .	50	120	. . .	. . .	. . .	. . .	. . .	4.90	0.193	84
D1	. . .	. . .	. . .	. . .	. . .	. . .	55	8	. . .	. . .	. . .	5.05	0.199	83
D2	. . .	. . .	. . .	. . .	. . .	. . .	70	10	. . .	. . .	. . .	5.13	0.200	84
D3	. . .	. . .	. . .	. . .	. . .	. . .	83	12	. . .	. . .	. . .	5.13	0.200	84
E1	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	10	. . .	. . .	5.13	0.200	82
E2	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	30	. . .	. . .	5.13	0.200	84
E3	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	60	. . .	. . .	5.03	0.198	84
M1	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	Low	. . .	3.73	0.147	. . .
M2	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	Mid	. . .	5.66	0.223	. . .
M3	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	High	. . .	5.79	0.228	. . .
S1	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	No. 1	4.95	0.195	. . .
S2	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	No. 2	4.98	0.196	. . .
S3	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	No. 3	5.11	0.201	. . .
S4	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	No. 4	5.11	0.201	. . .
S5	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	No. 5	5.11	0.201	. . .

								.						
S6	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	No. 6	5.18	0.204	. . .

Table 7(b) Cumulative contributions to variability attributed to the individual characteristic and signal-to-noise ratio values listed in Table 7(a)

Characteristic	Variability attributed to individual characteristic, %	Contribution due to signal-to-noise ratio, %
Process factors:		
Scan speed	4.7	29.0
Power supply	11.2	40.0
Quench temperature	Insignificant	Insignificant
Quench pressure	Insignificant	Insignificant
Speed of rotation	Insignificant	Insignificant
Noise factors:		
Material hardenability	72.0	. . .
Station	Insignificant	. . .

The S/N ratios were used to pinpoint the optimum process factors to produce the desired 4.83 mm (0.190 in.) case depth. As listed in Table 6, these were (by experiment number):

Experiment No.	Process factor
A1	Scan speed: 110 s/m (36 spf)
B2	Power supply: 94% (750V)
C1	Quench temperature: 25 °C (80 °F)

D2	Quench pressure: 70 kPa (10 psi)
D3	83 kPa (12 psi)
E2	Speed of rotation: 36 rev/min
E3	60 rev/min

However, a very high noise factor was calculated. This means that 72% of the variation in case depth was directly attributable to material variation. Thus, for a 72% material factor:

Material	**Average case depth**	
	mm	**in.**
1	3.96	0.156
2	5.31	0.209

Therefore, the scan speed, power supply, and material hardenability combined accounted for 4.7% + 11.2% + 72.0% or 87.9% of the cumulative variability while quench temperature, quench pressure, speed of rotation, and station number together accounted for 12.1%o of the total variability.

The following general guidelines (applicable for a 1040 steel having midrange hardenability only) for case depth were derived from the experiment.

Process factors include:

- Scan speed: A 13 s/m (4 spf) speed change will change the average case depth by 0.48 mm (0.019 in.)
- Power: An 8% change in voltage will change the average case depth by 0.91 mm (0.036 in.)
- Quench temperature: A 25 °C (40 °F) temperature change will change the average case depth by 0.28 mm (0.011 in.)
- Quench pressure: Pressure in the range of 55 to 83 kPa (8 to 12 psi) has no effect on the case depth
- Rotation speed: No effect on case depth in the 10 to 60 rev/min range

Noise factors include:

- Material hardenability, the major factor (72%) affecting the case depth
- Case depth, which varied little from station to station

Additional Factors. Similar analyses were carried out for the other characteristics of surface hardness, distortion, and scale. Some of the observations are:

- The severity of the thermal cycle to which the shaft was subjected greatly influenced the spline size change. For example, shafts heated with the lowest heat 120 s/m × 90% V input (or 36 spf × 90% V) in combination with the slowest quench rate (50 °C × 55 kPa, or 120 °F × 8 psi), had significantly less spline distortion than the shafts heated with the maximum heat input, and quenched at the fastest rate
- The theory that a deeper case depth produces greater size change was *not* proven in this experiment (see Table 8)
- The material contribution to the spline size change was 53%, possibly due to hardenability differences, or to differing amounts of cold work in the various bars
- Analysis of total indicator runout (TIR) of the parts gave the same conclusions as those reached with spline size change
- The minimum scaling was achieved with the fastest scan times (less time exposed to oxygen at high temperature)
- Surface hardness was not significantly affected by the range of process factors allowed in the experiment

Table 8 Effect of average case depth on spline size distortion

Material	Average case depth		Spline size change	
	mm	in.	mm	in.
M1	3.73	0.147	0.038	0.0015
M2	5.66	0.223	0.013	0.0005

Overall Optimum Condition. Table 9 shows the preferred conditions when the process factors are taken into consideration as a whole.

Table 9 Signal-to-noise ratio analysis of process factors that produce optimum characteristic conditions in a yoke-spline shaft

Characteristic	Experiment No.[(b)]	Process factor								
		Scan speed		Power supply		Quench temperature		Quench pressure		Speed of rotation, rev/min
		s/m	spf	Setting, %	Voltage, V	°C	°F	kPa	psi	
Effective case depth	A1	110	36	. . .	. . .	. . .	. . .	. . .	. . .	. . .

	B2	. . .	. . .	94	750	. . .	. . .	. . .	. . .	. . .
	C1	. . .	. . .	. . .	. . .	25	80	. . .	. . .	. . .
Surface hardness	B1	. . .	. . .	98	785	. . .	. . .	. . .	. . .	. . .
	C1	. . .	. . .	. . .	. . .	25	80	. . .	. . .	. . .
	E2	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	30
	E3	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	60
Spline size change	A1	110	36	. . .	. . .	. . .	. . .	. . .	. . .	. . .
	B3	. . .	. . .	90	720	. . .	. . .	. . .	. . .	. . .
	C3	. . .	. . .	. . .	. . .	50	120	. . .	. . .	. . .
	D1	. . .	. . .	. . .	. . .	. . .	. . .	55	8	. . .
	E2	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	30
	E3	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	60
Out-of-straightness (TIR)[(a)]	A1	110	36	. . .	. . .	. . .	. . .	. . .	. . .	. . .
	B3	. . .	. . .	90	720	. . .	. . .	. . .	. . .	. . .
	C3	. . .	. . .	. . .	. . .	50	120	. . .	. . .	. . .
	D2	. . .	. . .	. . .	. . .	. . .	. . .	70	10	. . .
	E2	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	30
Heat treat scale	A2	120	40	. . .	. . .	. . .	. . .	. . .	. . .	. . .
	B1	. . .	. . .	98	785	. . .	. . .	. . .	. . .	. . .
	C1	. . .	. . .	. . .	. . .	25	80	. . .	. . .	. . .

	D2	. . .	. . .	. . .	. . .	. . .	. . .	70	10	. . .
Best overall rating	A1	110	36	. . .	. . .	. . .	. . .	. . .	. . .	. . .
	B2	. . .	. . .	94	750	. . .	. . .	. . .	. . .	. . .
	C3	. . .	. . .	. . .	. . .	50	120	. . .	. . .	. . .
	D2	. . .	. . .	. . .	. . .	. . .	. . .	70	10	. . .
	E2	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	30

(a) TIR, total indicator runout.

(b) Underline denotes best signal-to-noise ratio for that variable.

Table 9, along with human interpretation, provides the information required to make a decision as to the best overall choice of a parameter combination, as follows:

Experiment No.	**Process factor**	
A1	Scan speed:	110 s/m (36 spf)
B2	Power supply:	94% (750 V)
C3	Quench temperature:	50 °C (120 °F)
D2	Quench pressure:	70 kPa (10 psi)
E2	Speed of rotation:	36 rev/min

It should be noted that a verification test is necessary to determine whether the predicted outcome will be attained. If the outcome of the verification does not meet the expected improvement, then, it must be concluded that the experiment was unsuccessful in locating the optimum parameter settings or that the dominant parameters were not located.

The final results after optimum parameter selection are shown in Table 10.

Table 10 Optimum characteristic parameters as determined by signal-to-noise analysis of a yoke-spline shaft

	Parameter								
	Effective case depth		Surface hardness, HRC	Spline size change		Out-of-straightness, TIR[(a)]		Heat treat scale	
	mm	in.		mm	in.	mm	in.	mg	oz
Average	4.78	0.188	56.3	0.02	0.0008	2.97	0.117	648	0.0229
Goal	4.83	0.190	58	0.00	0.0000	0.000	0.000	0	0

(a) TIR, total indicator runout

Conclusions. The conclusions that were drawn at the end of the exercise were:

- The relationships between the induction hardening process parameters and the resultant characteristics can be successfully established by the design of experiments method
- Both metallurgical properties and dimensional changes can be controlled to some degree in the induction hardening process
- The amount of prior cold working and/or hardenability of the 1040 steel bar is the most significant factor affecting variations in case depth (72%), surface hardness (18%), spline size change (53%), and TIR (12%)

The following recommendations resulted from this SPC analysis:

- The hardenability of 1040 steel should be controlled to an ideal diameter range of 24.4 to 32.0 mm (0.96 to 1.26 in.)
- The cold working operators should review methods of controlling and reducing residual stresses

Example 2 shows the general application of design of experiments techniques to locate and tune the vital process parameters. Other areas where this technique has been successfully utilized to improve process reliability include press quenching of gears, gas carburizing, and quenching of aluminum.

Monitor/Control Decisions

There are many process parameters of interest in almost any heat-treating operation. These fall into three categories:

- Those variables which *must* be closely controlled in order to have the process occur (for example, temperature, time, and so on)
- Variables that are known to affect the process but are either ignored or simply monitored manually because of the complexity or cost involved
- Variables which cannot be controlled at all (for example, natural gas composition, available heat input, and so on)

On a batch atmosphere carburizing furnace, for example, the common variables that can affect the carburizing process and should be compiled are:

- Temperature
- Atmosphere carbon potential (see the article "Control of Surface Carbon Content in Heat Treating of Steel" in this Volume)
- Time
- Endothermic gas flow (see the article "Furnace Atmospheres" in this Volume)
- Enriching gas flow
- Atmosphere circulation
- Quenchant properties (temperature and agitation)

While the first two on the list, temperature and carbon potential, will commonly be automatically controlled and the third, time, will usually be held fairly closely by either automatic or manual means, the last four on the list often go without notice *until a problem develops*, at which time they are examined.

In keeping with the idea that statistical process control represents *preventative* action (in that out-of-control indications should arise before out-of-tolerance conditions arise), these other critical variables should obviously be given more attention, possibly on an automatic, ongoing basis.

The decision to control, monitor, or ignore a given variable is a decision that must be made by taking into account the importance of the variable and the ease with which it can be measured. This decision is ultimately a balance of economic and quality considerations. The diagram in Fig. 6 shows a more complete picture of the number of possible variables involved.

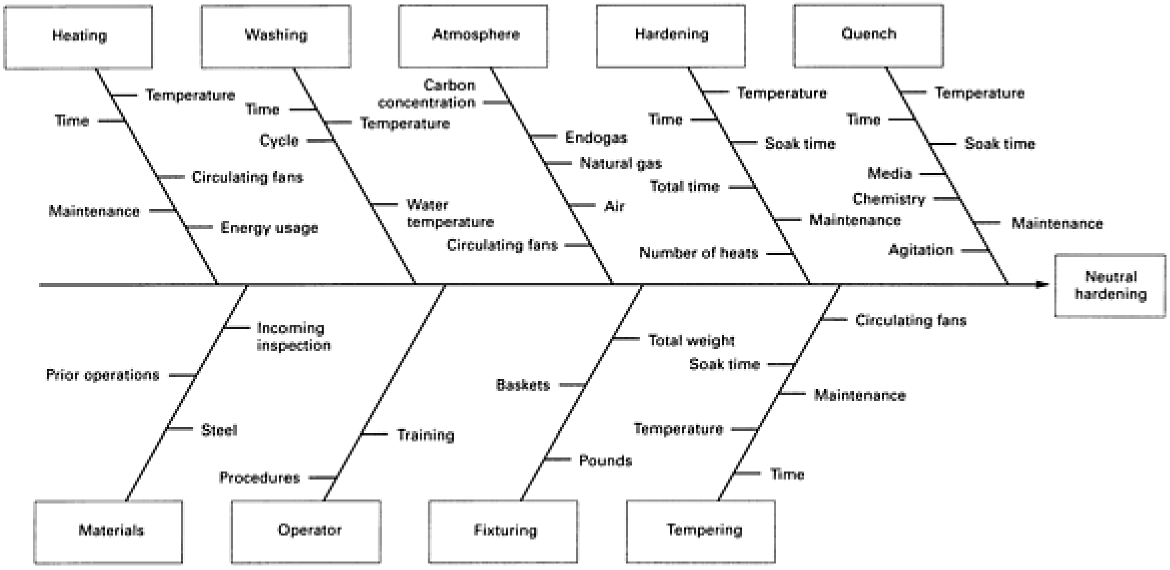

Fig. 6 Identification of heat-treating variables for the neutral hardening process

The subject of sensors and sensor technology becomes important at this point.

The focus of the data acquisition problem becomes one of finding sensors and sensor technology suitable for use in the heat-treating environment. It turns out that this is indeed a significant problem area for a variety of reasons that will be outlined later. In general, there are five critical areas of concern:

- Sensor selection
- Signal conditioning
- Control using the sensor
- Sensor maintenance

- Documentation and training

Sensor Selection. A sensor can be anything from a limit switch to a thermocouple to a pressure transducer to an electronic flowmeter.

Proper sensor selection begins with the identification of a process variable worthy of measurement. The cost of reliable measurement versus the importance of the process variable must be evaluated closely. Temperature happens to be a process variable that is usually extremely important, and a significant investment is usually made to ensure the accuracy of its measurement.

Time is also usually a critical variable, but ironically, it is still common practice to see it measured by a wall clock subject to an operator's convenience.

The signal conditioning process encompasses all those things that go into making the raw sensor data into a valuable bit of stored data. For example, the tripping of a limit switch may mean nothing by itself, but the time between two consecutive trips might be an extremely valuable piece of data.

Sensor maintenance has to be a major consideration. It does no good to put sensors on a furnace only to find that false readings are constantly coming up because of dirt build-up or other problems. Many times it is necessary to spend much more money on sensor insurance systems than on the sensors themselves. For example, an oxygen probe that constantly accumulates excessive soot in a high-carbon atmosphere may need an elaborate carbon burn-off system added to it just to get consistent and reliable readings.

Documentation and training are key elements because they determine the long-term success rate of sensor usage. The operators and maintenance people must be aware of the theory of operation and the limitations of the equipment.

Temperature Parameters. Temperature measurement and control is the most fundamental measurement in heat treatment and deserves separate consideration in this discussion.

Temperature Measurement. Temperature in the ranges of interest in heat treatment are generally measured by one of two methods: thermocouple or infrared pyrometer.

Because of its low cost, simplicity of construction, and inherent reliability, the thermocouple has always been and continues to be by far the most useful sensor in most situations. It is perfect for sensing gas temperatures, and even works well in vacuum furnaces by virtue of radiation. They are not very useful, however, for measurement of the actual temperature of parts going through a furnace.

Because thermocouples often fail slowly by losing accuracy and because two thermocouples inserted at the same time will often agree even as they are both failing, it is important to change thermocouples on a regular schedule and to alternate replacements.

Aside from the obvious process-related temperatures that are measured, it is possible that the temperature of nonprocess related items like cooling water temperature to bearings and door seals might be of interest. Thermocouples are most often used for these purposes.

The science of infrared temperature measurement has come a long way in the last 10 years. Most of this type of equipment is used in induction hardening but many have been applied with mixed results in enclosed furnaces. In these situations, results are usually better if the furnace does not use a hydrocarbon atmosphere, as the presence of soot in the optical path presents a problem.

Furnace temperature uniformity is always of tremendous concern, especially in vacuum applications where there is no convection to help even things out. While the process of making a furnace uniform with respect to temperature may be difficult, the actual uniformity results are easily documented with multiple thermocouples.

It is not at all out of the question to monitor uniformity by permanently placing thermocouples in several furnace locations and automatically calculating and alarming against their average and spread. This approach has been used for years with vacuum furnaces (where uniformity becomes more of a function of loading).

The observation of temperature measurements in a furnace under control gives some insight into how this might be handled from an SPC standpoint (see Fig. 7), where a control thermocouple is being held very closely to a setpoint (for a C_{pk} > 10), while a companion thermocouple in a different location is showing a C_{pk} = 1.2. The controlled thermocouple is of very little interest, as it will probably not deviate from the setpoint unless there is some drastic change. The subtle information from the monitoring thermocouple is of much more value in evaluating uniformity and the repeatability of uniformity which can be another problem.

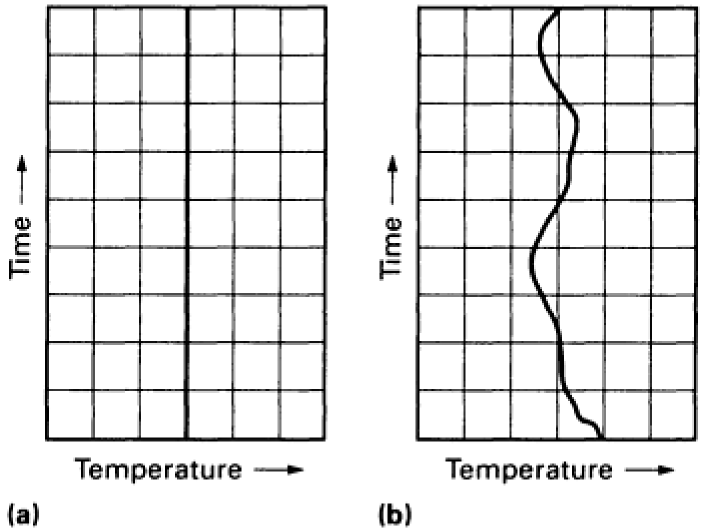

Fig. 7 Comparison of instrument temperature variations. (a) Controlling thermocouple, C_{pk} > 10. (b) Monitoring thermocouple, C_{pk} = 1.2

Combustion Efficiency. Because gas-fired burners have historically been the least expensive device to heat most nonvacuum furnaces, there has always been interest in attempting to keep them firing at optimum ratio. This was previously done using portable oxygen analyzers or with manual carbon dioxide checks. Most recently, interest in using low-cost automotive-style oxygen sensors has become possible.

Although there is nothing to prevent the *relative* measurement of burner efficiency from day to day with such techniques in an inexpensive format, it is very difficult to measure on an absolute scale that the burner is actually always firing at optimum ratio. This situation is the result of problems with sensor positioning and interpretation of results. For example, in a high-low fire system on a radiant tube in which the sensor is positioned opposite from the burner, the sensing system would have to ignore the first few seconds of high fire as the old exhaust gas is blown out. If the high fire cycle was very short, the sensor readings would mean very little. If the cycle is longer, the temperature of the sensor would change rapidly, making it necessary to provide a compensating thermocouple to make the sensor output meaningful. This complication requires a relatively high-cost measurement system to utilize the low-cost sensor.

Furnace Chamber Atmosphere. Measurement of various parameters associated with gases in a furnace chamber are of particular importance for controlling many heat-treating processes.

Gas Pressure Level. The manual measurement of pressure in a furnace atmosphere is usually done with a water manometer, with levels generally in the range of 0 to 25 mm (0 to 1 in.) water column. The reading is actually a differential reading between the inside and outside of the furnace. Inexpensive pressure transducers that produce high-level signals (for example, 4 to 20 mA) for this range are readily available, but care must be used to ensure lone-term reliability of this signal due to plugging or partial closing of tubing to the transducer.

Transducers which feature an analog display of the pressure reading as well as the retransmission signal are most useful when the signal must be trimmed for calibration. The transducer should have its own zero and span adjustments for maximum flexibility.

Furnaces in which the pressure is constantly varying over a wide range because of opening and closing doors or other upsets will require intelligent signal conditioning that ignores the peaks and valleys in the pressure.

Atmosphere pressure is sometimes controlled in a closed loop with an actuator-driven atmosphere effluent damper. This device also helps to keep the atmosphere pressure constant.

Vacuum Level. Measurement of vacuum level has been done with a variety of methods, but two of the most common have been the thermocouple gage for lower vacuum levels and the cold cathode gage for higher vacuum ranges.

Recently a fourth method has been added for measurement all the way down to 13 nPa (10^{-10} torr), based on a hot filament ionizing the residual gas. All methods except capacitance manometer are subject to error of the composition if the residual gas is different than expected.

A typical vacuum furnace will generally require at least two sensors to accurately cover the full range that the furnace is capable of operating within. Also, it is often desirable to check vacuum levels in various spots, including the foreline and vacuum chamber itself.

A microprocessor-based instrument that will automatically select the required sensor in the range of interest is required. These newer instruments also provide computer communications capability that makes data acquisition easy.

It is anticipated that a version of the zirconia oxygen sensor, discussed in the section "Analysis of Gas Composition" in this article may be applied successfully in vacuum furnaces in the future. This would represent a major step forward in vacuum technology, as low oxygen levels are desirable when high vacuums are used. The oxygen probe would then provide a direct measurement of this gas.

Additional information is available in the article "Heat Treating in Vacuum Furnaces and Auxiliary Equipment" in this Volume.

Process Gas Flows. Measurement of process gas flows in controlled atmosphere furnaces generated interest recently. There are several methods available, each varying widely in cost. The selection of a particular method must be made with extreme care because the cost of gas flow measurement must be kept in balance with the other data acquisition elements in the overall instrumentation plan.

The least expensive method to measure gas flows is with simple flow switch devices. These devices almost always operate on the principle of a pressure drop (and pressure switch) across a fixed orifice in the gas stream. Their limitation is that they can only sense whether flow above a certain fixed amount is present or absent. However, by combining two flow switches in the gas stream set at different points, it is possible to ascertain whether a gas flow is above the high limit, in the desired range, or below the low limit.

Flow switch arrangements are especially suited for gas flows that do not vary (for example, endothermic or exothermic generated gases and nitrogen) or even liquids like methanol.

Typical plumbing component costs for a dual flow switch arrangement might be in the $100 to $200 range for a single gas line. Control strategy using this technique is to have the data acquisition system sound an alarm whenever the gas flow has dropped out of the desired range, with human intervention required to correct the flow.

If an exact value of gas flow is required, there are two techniques:

- Electronic true mass flowmeters
- More familiar rotameter types with electronic adaptors

Both of these may require external power supplies and care in system wiring.

The true mass technique uses the principle of measuring the amount of heat that the gas stream can remove from a heated bulb of controlled temperature. This technique has the advantage of being inherently accurate (if the flowmeter has been calibrated against a known flow) regardless of pressure fluctuations. It has the disadvantage of being a blind technique, with the electronic signal (typically 4 to 20 mA) being the only indication of flow.

The rotameter technique, while slightly more expensive than the true mass technique (approximately $1500.00 per meter), has the advantage of having two outputs: a visual one by virtue of the float scale (see Fig. 8) and an electronic one by virtue of electronic position sensing of the same float assembly. The disadvantages of the rotameter technique lie in resolution and accuracy; the measurement is sensitive to temperature and pressure variations (good upstream regulation is required), and the electronic signal may only resolve to ±2.5% of scale. However, this technique is still preferred because of long-term calibration considerations.

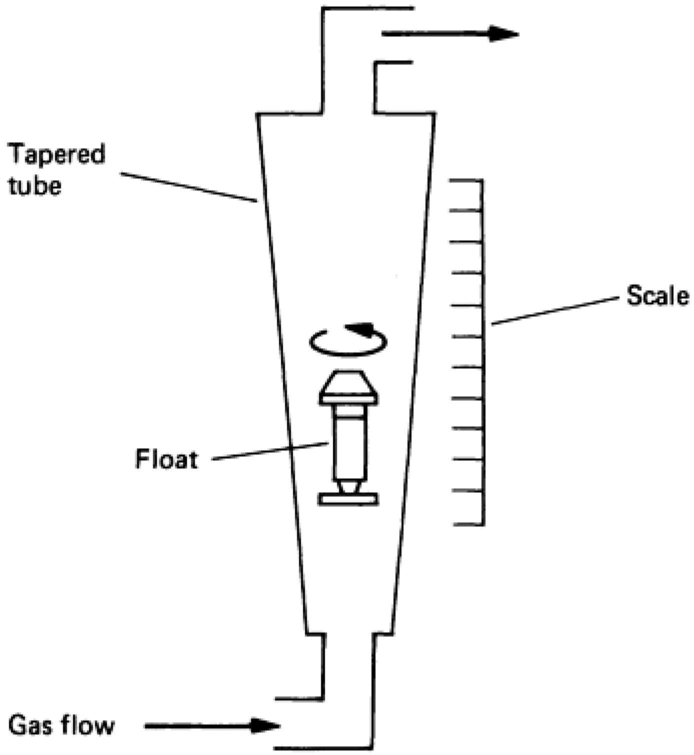

Fig. 8 Schematic showing key visual output components of a rotameter

Measurement of low liquid flows, such as in nitrogen-methanol systems, is best done with the rotameter system. However, the viscosity of methanol changes quickly with temperature, and for maximum accuracy it is necessary to electronically compensate the temperature readings from a rotameter-type device accordingly.

Control of gas flows is usually done with an adjustable port valve and motor actuator. The most easily installed and maintained motor actuator is one that accepts an electronic signal (for example, 4 to 20 mA) and positions itself accordingly. Motors that employ a slidewire feedback technique are not always desirable because of long-term maintenance problems.

One problem with motor-actuated control valves is that the flow is not proportional to the value position. For example, it is possible to have signals of 0% open and 100% open do just what is expected, while finding that the 50% open signal gives a measured gas flow of 20% of scale. This is due to a variety of factors, including linkage adjustment, pressure drops in the piping, and the inherent nonlinearity of valve ports.

Corrosive gases such as ammonia require stainless steel construction that makes these valves more expensive.

Another completely different technique of measuring and controlling gas flow that can be used in many cases is the pulse time-proportioning system. For example, if a simple on-off valve is set up in such a way that when the valve is open there is a fixed, known flow through it, then the average gas flow is always easily calculated by the formula:

$$\text{Average flow} = \frac{\text{Valve ON time}}{\text{Valve ON time} + \text{Valve OFF time}} \times \text{Flow when ON} \qquad \textbf{(Eq 2)}$$

If the ON and OFF time are automatically varied and kept short with respect to the furnace size, this type of arrangement will provide a most cost-effective, easily calibrated system for measuring and controlling gas flows. The power to perform ON and OFF time cycle control is easily found in many of the most powerful process controllers on the market today. In the case of two process gases that must stay in ratio with each other (for example, nitrogen-methanol), it is possible to design an electronic control system to measure both process gases and control one or both of them to maintain constant ratio, using the techniques outlined above. The cost of such a system can be very high, but varying methanol flow is a common problem that can significantly impact process results.

Analysis of Gas Composition. The following measurement techniques for the composition of furnace atmospheres have successfully been used:

- *Oxygen probe:* Good for measurement of oxygen levels below 0.01%, and with inference can be used to calculate percent carbon potential in a known CO gas, or percent water in a known H_2gas. Advantage of in-situ measurement and good reliability. Frequent calibration not required
- *Infrared absorption:* Good for measurement of CO, CO_2, or CH_4 concentration in ranges of interest in hydrocarbon atmospheres. Same unit can be configured to measure all of the above gases simultaneously if desired, which allows accurate calculation of percent carbon potential. Cost is high, with multiple furnaces usually routed to a single analyzer. Frequent calibration is required. Major disadvantage is that sample of gas must be transported to analyzer
- *Dew point:* If measured by variable pressure change/condensation method, results by inference can be used to calculate percent carbon potential against known carbon and hydrogen gas levels. Disadvantage is that measurements are physically difficult and operator technique and interpretation may play a major role. Sample must be transported to the analyzer. Although there are automatic dew point-measuring systems, none has worked for extended periods in hydrocarbon atmospheres without a significant amount of preventative maintenance having to be done on the system
- *Mass spectrometer:* Can determine the composition of gas completely, except for inaccuracies at low levels with some gases. Calibration is difficult. Other disadvantages are cost, required operator skill level, and sample transport. Rarely used on-line in heat treatment
- *Gas chromatography:* See mass spectrometer

While complex gas analysis systems have not yet found their way into day-to-day process control operations in heat treating, they may be of value in an off-line mode for a situation as shown in Fig. 9. Here the results of gas analysis, specifically heavy hydrocarbons, are plotted over the course of a year. The trend shows the shifting gas supplies (presumably as a result of demand). An on-site gas analysis could provide valuable information when evaluating furnace atmosphere quality problems.

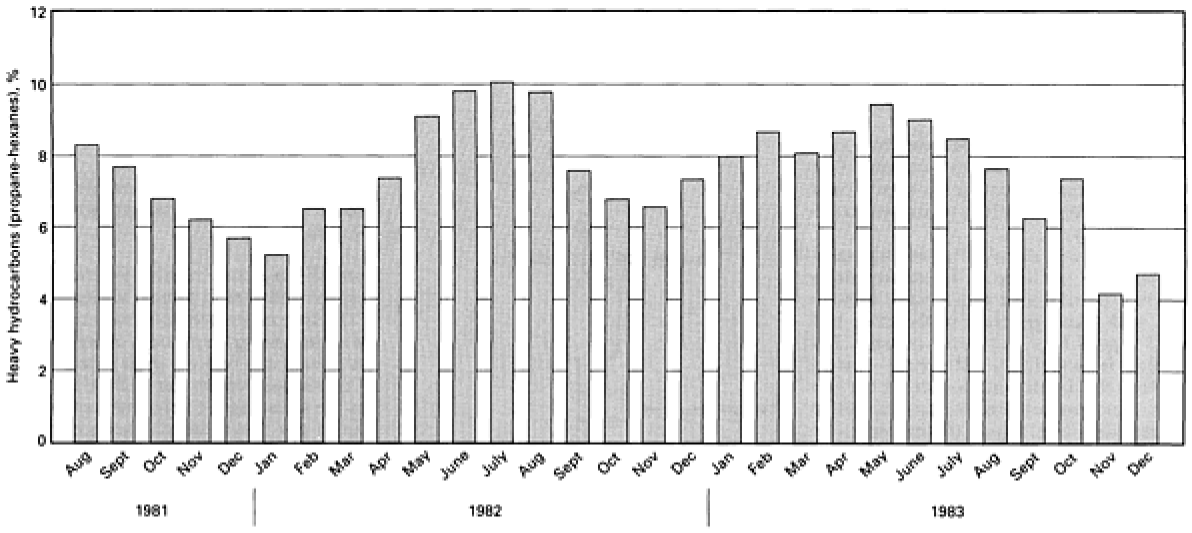

Fig. 9 Variation in natural gas composition monitored in the Canton, OH, area over nearly a 2 $\frac{1}{2}$-year period

Atmosphere Agitation. The measurement of atmosphere agitation has not been successfully done at this writing, but this certainly would be of interest, as failed atmosphere circulation systems are a common problem. A system based upon a windmill concept is the most obvious, but other possibilities exist, including measurement of heat flow into a cooled bulb in the atmosphere circulation path. In the not-so-distant future, a system will almost certainly have to be developed.

Quenching Parameters. The area of rapid cooling during a heat-treating process, generally referred to as quenching, has been perhaps the biggest source of the "black art label" put on heat-treating operations. Many heat-treating facilities have the latest microprocessors for furnace control. However, these facilities have virtually no monitoring capability for the quenching operations that can have as significant an effect on results as any other parameter (see Table 1).

Quenchant Bulk Temperature. The measurement of quenchant bulk temperature is generally the *only* measurement undertaken in most shops. Often this is a monitor-only function, with no feedback control of system heating or cooling involved.

From a data acquisition standpoint, it is interesting to look at the bulk temperature during the actual quenching operation, noting any changes. Typically the starting temperature and the highest temperature reached are recorded.

In low agitation quench tanks, care must be taken to ensure that the temperature measured is truly indicative of the bulk temperature.

Quenchant Viscosity. The viscosity of liquid quenchants, especially polymers, is an important indication of composition. In oils, it can be an indication of oil aging or contamination.

Viscosity may be measured in-situ, but the results will vary with temperature, making it necessary to compensate for variations in temperature.

Quenchant Media Composition. Measurement of composition (and contamination) of quenching media has become an important area of concern in recent years.

In the case of quench oils, the parameters of additive levels, alkalinity, oxidation or sludge content, and water content have come to be recognized as being of significant importance. Because the costs of these products have increased significantly in the last 15 years, much effort has been expended learning how to make a tank of oil last longer through the use of additives and cleaning. Unfortunately, none of the tests required for oil composition determination are suited to real-time data acquisition, except for water content analysis. Unfortunately, many commercially-available water-in-oil

analyzers are subject to frequent malfunctions and while required for safety reasons, are not really suited to the purposes being discussed here.

Solutions of various polymers in water have the common characteristic that the concentration of polymer (which combined with the degree of agitation determines quenching performance) is usually easily measured with temperature-compensated viscosity sensors, as mentioned above.

Solutions of salts and other additives in water are commonly monitored with specific gravity determination. While this test is easily done with a hydrometer in the lab, it is not so easy to do in-situ in an automated data acquisition environment.

Quenchant Agitation. While the primary heat removal rate in a quenching system is generally considered to be a function of the quench media, there is the significant modifying effect of agitation. Agitation of a quenchant is a parameter that is easily controlled with variable-speed propellers or pumps. However, measurement of this agitation, which may be different from time to time depending on load size and configuration, is another matter.

First, there must be agreement on what units agitation is to be measured in. Most people would agree that units of velocity (for example, feet per second) or volume (for example, gallons per hour) are logical, but this does not always account for the *pattern* of flow in a given load and how this pattern might change load to load, with identical velocities.

It is intuitive that measurement of pump or propeller and angular velocity and subsequent linear velocity calculation is not going to be indicative of what's really happening in the quench tank. (What if the propeller motor is still running but the propeller has fallen off, or the flow of quenchant is blocked somewhere else in the system?) It may then be necessary to place a sensor, commonly configured as a tiny free-spinning turbine, in the flow stream directly ahead of or behind the load to directly monitor the quenchant flow rate.

The problems with these systems are two-fold. First, the turbine may become clogged with solid contaminants and give a falsely low reading. Secondly, it is often difficult to position the spinner so that it can provide an accurate measurement.

Quenchant Cooling Efficiency. Perhaps the largest area of interest in terms of quenching parameter control is in the measurement of actual cooling performance of a quenchant with a standardized test. In the past few years, a number of quenching evaluation tests have been developed for laboratory use that operate by heating and quenching a probe with an embedded thermocouple into a sample of the quench media under test. The results are often presented as raw cooling curves, or perhaps as plots of instantaneous cooling rate against probe temperature (see Fig. 10).

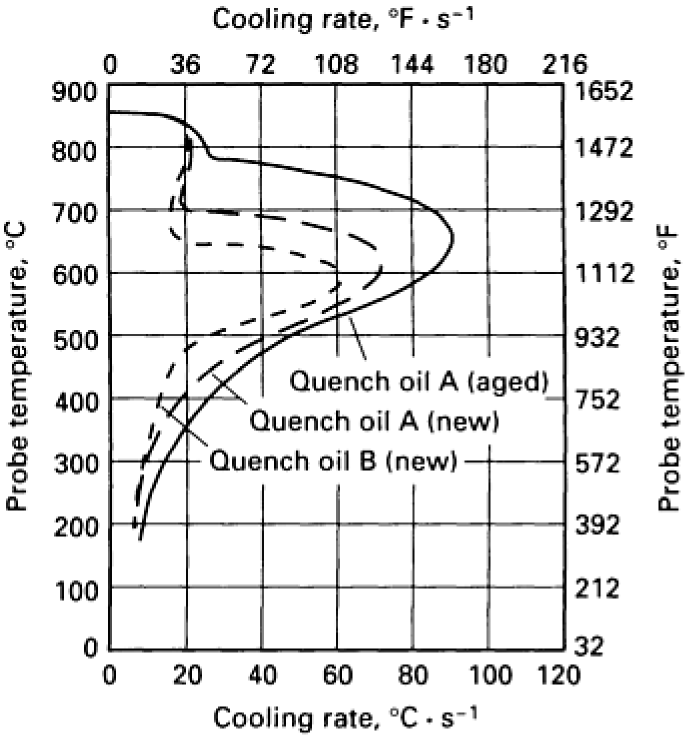

Fig. 10 Probe cooling rate curves for quench oils having approximately the same GM quenchometer and viscosity values

The availability and use of this equipment has led to a push for a standard quenchant evaluation procedure. Unfortunately, the SE tests are all manual and cannot to date be made in-situ by an automated data acquisition system.

Mechanical Motion Components. The idea of including mechanical items like doors, quench elevators, pusher mechanisms, and fans in the category of process data acquisition and statistical process control may seem a little strange. However, when one considers the impact of any of these items malfunctioning or failing during a process, it is easy to see that the consideration of these mechanical items has merit.

Fans and Pumps. Atmosphere and quench circulation/agitation systems are vital to the success and repeatability of any process. If the idea of measuring the *effect* of the circulation system (that is, atmosphere or quench velocity) is not practical, then the next best thing is to infer that all is normal by measuring some other characteristic of the circulation system.

There are several devices available capable of measuring fan and pump speeds:

- *Zero-speed switches:* Relatively inexpensive (that is, $300 to $400) devices are easily positioned near a driven rotating shaft or wheel so that rotation above a certain minimum speed can be verified.
- In the case of belt-driven devices, this is invaluable because it is the only way to detect belt breakage or slippage
- *Current switches:* Also inexpensive (that is, $200 to $300 per phase), these simply verify the presence of a current above a certain value. In the case of a belt-driven oil pump, normal operating conditions will see the motor drawing a current of perhaps 5 A. If the belt suddenly breaks, or the prop falls off, the motor current draw will quickly drop to perhaps 3 A. If a three-phase motor is involved, a decision as to whether all three phases be monitored must be made. Other applications for current switches include belt drive motors in belt furnaces, where increased current draw might mean a belt getting bound up
- *Current transducers:* Similar to the current switch, except a low-level signal (for example, 4 to 20 mA) is developed that is proportional to the current being drawn. The application of a current transducer over a current switch would be determined by the complexity of the data acquisition hardware available.

Current transducers are useful with quench oils, as they will show the current draw of the agitator rising and falling with oil temperature and load density

Belt and Rotary Retort Mechanisms. The measurement of belt speeds and feed rates on furnaces provides useful process information in that the product residence time as well as load sizes, densities, and their respective uniformity may be directly or indirectly measured or controlled. In the case of constant-rate mechanisms like furnace belts, there are several methods:

- *Tachometers:* Most obvious choice for measuring almost any motor-driven device. The advantage of tachometers is that they are very fast at providing information on otherwise slow-moving mechanisms. The problem with tachometers is two-fold: first, they are measuring the motion of a *driving* member instead of a *driven* member; and second, they usually rely on transmission of the reading by analog means, setting up more calibration problems
- *Limit switches:* Measuring any slow mechanical motion such as belt travel, drum rotation, or mechanism indexing is quite simple with a limit switch in combination with a known time base. For example, on a belt, a driven sprocket often provides a reliable spot to pick up a periodic pulse on the limit switch. The frequency or duration of this pulse can be directly related back to belt speed. The disadvantage of this type of technique is that the information sometimes takes quite a while to collect

Furnace Loading Rates. The limit switch philosophy applies to furnace loaders as well. We are able to obtain a pulse-type loader frequency based on the time between actuation of limit switches, in combination with an analog or even digital weigh scale. Useful statistics such as pounds per hour may be compiled and data logged, and process adjustment based on weight may be initiated.

Load Tracking. The tracking of loads through multitray furnaces or through multifurnace plant layouts is an idea that is rapidly gaining interest for documentation and SPC purposes.

The data acquisition system monitors relevant mechanical signals that determine when a tray has been moved from one position to another. The data being collected are sorted and assigned only to those trays for which they are applicable. For example, the computer record for a given tray in a large pusher furnace will end up containing the average temperature for zone 2 for the period during which the tray was actually in zone 2. Also present in the record will be the times that the tray entered and left zone 2.

The sorting and storing data using this concept will not be possible with many data acquisition systems currently available. Care must be exercised in equipment selection if this type of instrumentation is to be a requirement.

Mechanical Performance. There is a wealth of data available having significant impact on the process that can be gathered by simply watching and analyzing existing limit switches, resolvers, and signals already available on many furnaces.

For example, it may be desirable to measure and log the amount of time required to move a load from the hot zone to the quench operation. This result will vary over time and can warn of serious mechanical problems before they affect the process.

Looking at actual push times on a large continuous pusher furnace against *specified* times is often enlightening. Conversely, looking at the number of pushes made during a fixed time period may also be of interest.

Vibration Monitors. Any furnace that uses motors can develop an excess vibration due to an imbalance, bearing failure, and so on. Vibration sensors can be strategically mounted on the equipment to detect this problem before a catastrophic failure occurs.

Although rather expensive ($500 or more), units are available that can transmit a low-level signal that is proportional to the amplitude of the vibration cycle. The data acquisition system would have to be smart enough to ignore the sensor during heavy mechanical operations (for example, doors opening).

Signal conditioning can be described as the science of making sensor data useful. It has nothing to do with alarming the system. The basic requirement in dealing with furnace data is flexibility in conditioning options.

Discrete data is, very simply, ON-OFF data. For example, a fan is either running properly or it isn't; a gas flow is either in range or it isn't.

Conditioning of discrete data is usually a matter of telling the data acquisition system when the data are valid and when they are invalid.

Sometimes complex counting and timing schemes are required to coax the meaningful data out. This means that the primary vehicle for conditioning is software.

For example, a nitrogen flow switch is only valid if there is supposed to be nitrogen flowing. A quench cycle time measurement can only be done when a quench cycle is in progress.

Continuous (Analog) Data. A 1000 to 1200 mV signal from an oxygen probe is a good example of analog data. We may find that this signal is overly noisy and that some hardware low-pass filtering is required to smooth it out. The signal might be combined with another analog signal from a thermocouple (which has to be cold-junction compensated and linearized). This is typical of classic analog signal conditioning. The result of the combination is the calculation of a third piece of analog data, which is percent carbon. This final process is an example of advanced analog signal conditioning done in the digital domain.

Many analog signals need to be validated. For example, the reading from an endothermic flowmeter is only valid when endothermic gas is really flowing.

Closed Loop Control Monitoring. It should go without saying that any instrument used to control temperature in heat-treating operations should have computer communications capability for data acquisition purposes.

Most temperature control applications in heat treating are of the on-off type, such as electrical contactors for heating elements or high-low fire systems for combustion burners. Others are proportional, utilizing stoichiometric gas-air ratios for burners or variable current systems for heating elements.

All of these systems have a common effect of delivering a certain amount of energy to achieve and maintain the furnace at a given temperature. The amount of energy may be known by *direct* measurement with gas or electrical meters but *relative* measurements may also be made by more advanced instrumentation doing the control.

The amount of energy consumed is of course important from a cost standpoint. It is equally interesting, however, from the process/data acquisition standpoint. If the relative amount of energy required to heat and maintain a given furnace at a given temperature is known, then any additional energy consumed by any process run in this furnace must be absorbed by the load. This effect has been successfully utilized in helping to determine when loads are at heat, as shown in the following figures.

Notice in Fig. 11 how the heat input to the process drops down to some equilibrium value after the process has reached setpoint. This is the point at which heat input to the furnace equals heat loss through the walls and atmosphere effluent.

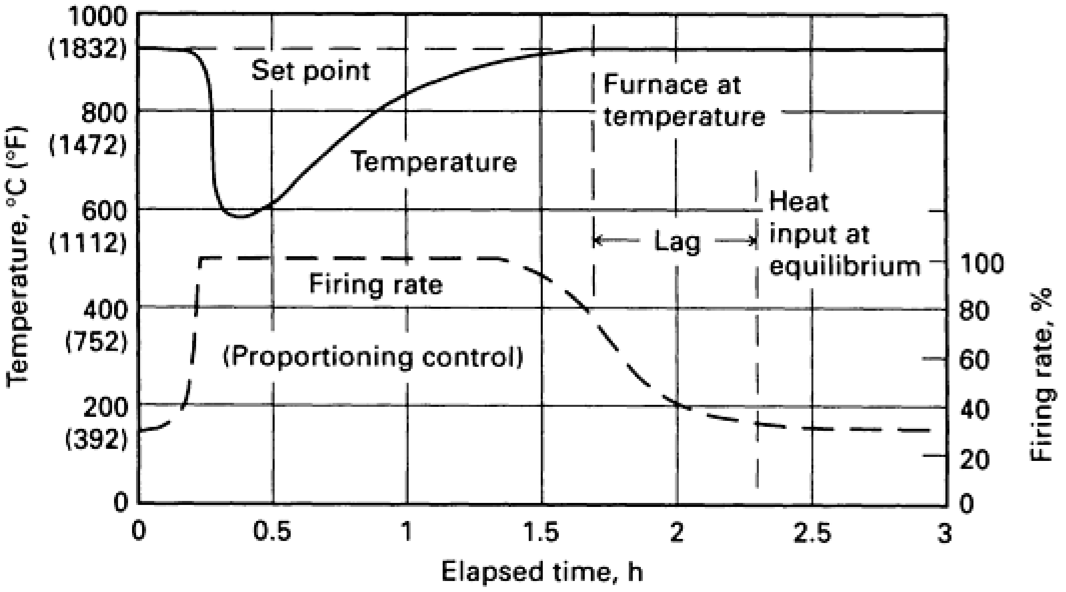

Fig. 11 Plot of furnace temperature versus elapsed time to show that heat input equilibrium lags behind attaining of setpoint temperature after furnace loading

When load size is varied, as happens in most shops, the process suffers because of a lack of input as to how this might affect the results. By taking into account a very inexpensively-acquired piece of information such as the percent output of a properly-tuned proportioning temperature controller, it is possible to begin compensating for load size by taking advantage of the fact that a heavier load requires more heat to reach setpoint.

The effect of load size on heat input is shown in Fig. 12. Notice that although the light and heavy loads have a relatively minor effect on how long it takes for furnace temperature recovery, load size has a potentially dramatic effect on heat balance equilibrium.

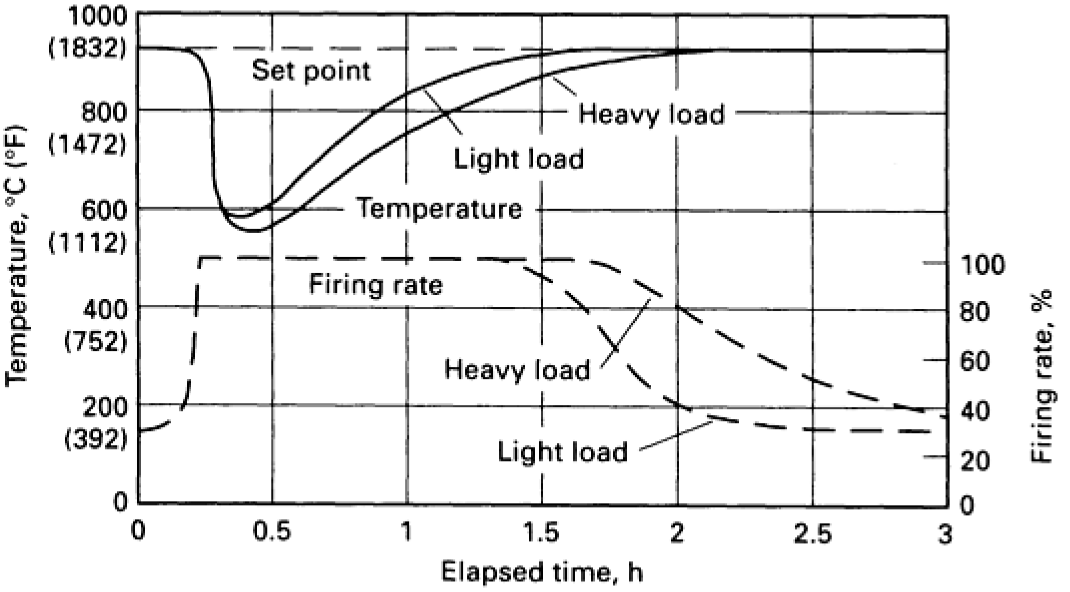

Fig. 12 Plot of furnace temperature versus elapsed time to show effect of load size on heat balance equilibrium

In terms of data acquisition, the heat input to a furnace is a piece of information that is usually easy to capture and might be of significant value in learning to more tightly control the process.

Computerization of SPC/SQC Systems

The ideal data acquisition system has the following capabilities:

- It has plenty of discrete and analog inputs, electrically isolated, with automatic, configurable linearization, filtering, and other conditioning options
- It is easily software-configured to perform both data acquisition and control tasks
- It is easily networked with other plant equipment if required

Figure 13 demonstrates how a deviation in the measured surface carbon in a carburizing process may or may not be traceable to a deviation in some process parameters that are being logged by an automated SPC system. In Fig. 13(a), a period of high surface carbon readings is observed, with a subsequent return to nominal.

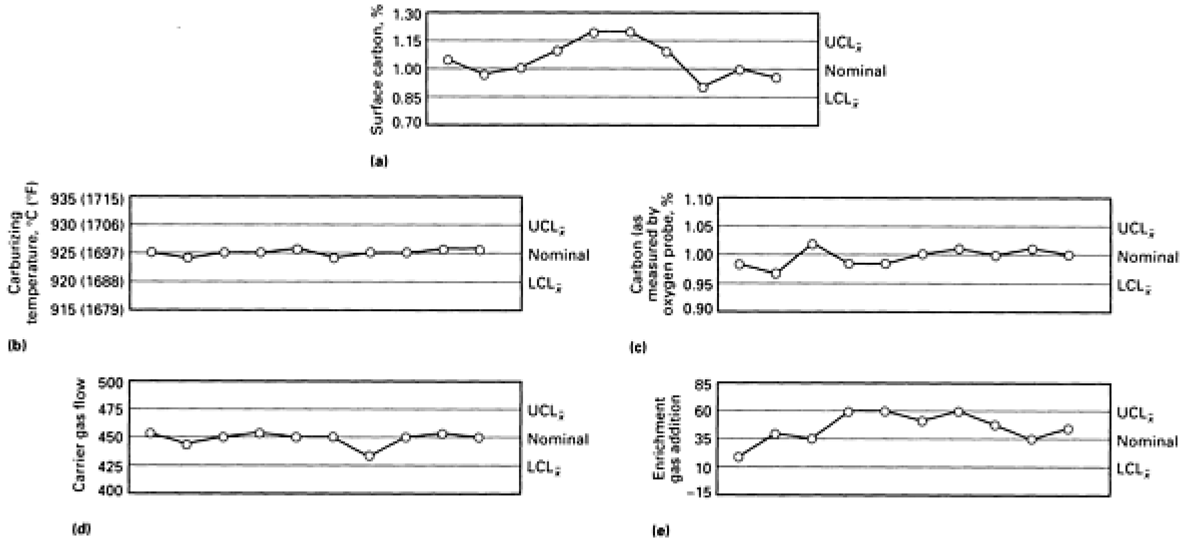

Fig. 13 Plot of several process-related characteristics for a carburizing process. (a) $\bar{x}$-chart of surface carbon concentration in carburized parts. (b) Average temperature during carburizing cycle. (c) Average carbon concentration measured by oxygen probe during carburizing cycle. (d) Average carrier gas flow during carburizing cycle. (e) Average enrichment gas addition. Note correlation of graphs (a) and (e). UCL$\bar{x}$, upper control limit on an $\bar{x}$chart; LCL$\bar{x}$, lower control limit on an $\bar{x}$chart

Figure 13(b) examines a controlled variable, temperature, and finds no deviation. (It could be argued that it is a waste of time and effort to chart this variable in this fashion because it could be handled much more efficiently with a simple deviation alarm in real time.)

Figure 13(c) looks at what *should* be the answer, the readings from the oxygen probe that was in control of the atmosphere carbon potential. Unfortunately, no deviation is noted because again, carbon potential is a controlled variable. The control system would have done anything in its power to keep that reading at setpoint at all times. It might be concluded from this chart that the oxygen probe control system was in error, perhaps because one of its base assumptions (for example, a fixed carbon monoxide concentration) was not as expected during the period in question.

Figure 13(d) shows a chart of carrier gas flow that will naturally show no significant deviation because the operator who is responsible for keeping it at the desired value is the same person who must chart it. (This points out that the automation of data collection is required if the integrity of the data is to remain unquestioned.)

Figure 13(e) gives a clue. It is noted that during the period in question, the enriching gas flow was at or near the upper control limit by action of the automatic oxygen probe control system. (Ironically, in years past, where control of atmosphere carbon potential was manual against a dewpoint-measuring instrument, this would have been picked up as a potential problem right away by an experienced operator. With the advent in the mid-1970s of automatic oxygen probe control systems, especially those with simple on/off control valving, the ability to monitor trends in enrichment gas usage was typically either lost or ignored. Newer microprocessor-based units restore this capability, along with alarms for high/low enrichment flow.)

It is possible to imagine a special case scenario where for some reason the gas equilibrium in the furnace was upset to the point where the control system was calling for more enriching gas than usual, which could have resulted in an excessive residual methane content in the furnace atmosphere, which in turn could have produced a higher surface carbon on the parts than the oxygen probe system indicated. A number of things could have been the root of this problem, such as a furnace leak, a sudden rise in relative humidity (sending the endothermic generator out of control), or a change in enrichment gas composition. The important point is that if there had been sufficient monitoring of the enrichment flow from the start, the problem could have been noted and possibly corrected before any loads were affected. This would have been a successful implementation of statistical process control in a batch situation.

Integration of SPC and SQC

Combining the disciplines of statistical process control, which focus on the process variables, and statistical quality control, which focus on resultant product quality, offers the potential for real-time process improvement. Computer capability is required to statistically analyze data in a fashion that will allow timely adjustments to the process.

As a product characteristic (as-quenched hardness, for example) is shown to be trending away from average, a special cause, such as oil quench temperature, may be identified quickly. The ability to compare process variable trend charts to the product characteristics trend chart, for the same time period, offers a valuable tool for continuing improvement of the heat treatment.

This can be valuable information even if no special cause can be identified among the monitored process variables to correlate with a change in the product quality. This may lead the heat treater to an uncontrollable variable more quickly, such as material.

Modeling and Feedback for Process Refinement

The use of complete theoretical process models in real-time process control is not as far-fetched as might be imagined in some cases.

Forging Applications. The technique has, in fact, been applied very successfully, for example, in forging. Here it is used to provide accurate control of billet temperature during reduction, where the billet heat content is a function of thermal losses to the environment and thermal gains from mechanical working. The complex real-time model used to continuously calculate the thermal gradients within the billet (and control auxiliary cooling) is in use in many mills today.

Carburizing Applications. It has also been applied in carburizing, where complex models of the chemical, transport, and diffusion reactions are used in combination with more complete process measurement to construct a theoretical carbon profile in real-time and to provide feedback control to the process (Fig. 14). If this type of model had been in use in the previously cited SQC surface carbon deviation example, the process would have remained under control during the period in question. The problem, of course, is economics. In order to make such a real-time model completely accurate, it is necessary to provide much more information to it than is available from a simple oxygen probe. A complete carbon monoxide/carbon dioxide/methane infrared system, or even a mass spectrometer, would be required. This type of expenditure is widely (and understandably) viewed as impractical.

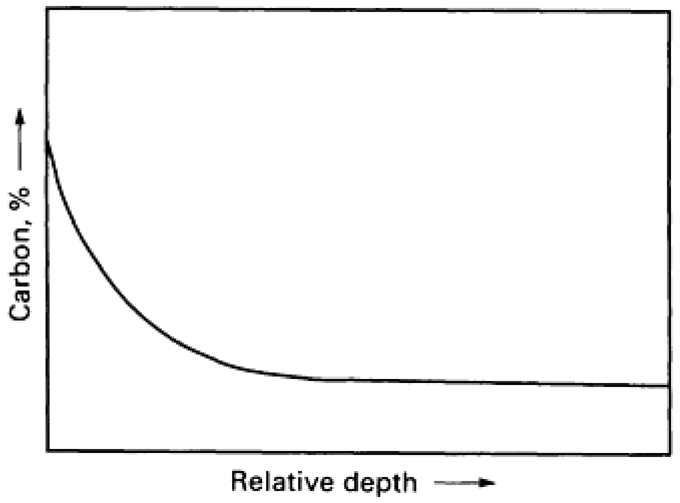

Fig. 14 Typical gas/solid reactions for the carburizing process showing carbon diffusion profile. Following diffusion and reaction of carbon monoxide, hydrogen, and methane gases, transport reactions at surface yield carbon dioxide, water, and hydrogen as byproducts.

Steel Hardening Applications. Other areas in heat treatment could benefit from real-time modeling. For example, the control of steel hardening is a function of many parameters that can be tied together by centralizing control of the process within a model built around a calculated continuous-cooling-transformation (CCT) diagram in a finite-element format for the material in question. The model could take into account the material analysis, initial microstructure, austenitizing temperature and time (and the resulting thermal gradient across the work piece just before quench), transfer time, quenching media type, agitation and temperature, and many other items. It would use real or calculated cooling curves superimposed upon the CCT diagram (Fig. 15) to determine final microstructure and hardness gradients. Another part of the model would specify (and of course monitor) the correct tempering temperatures and time required to achieve the desired finished results.

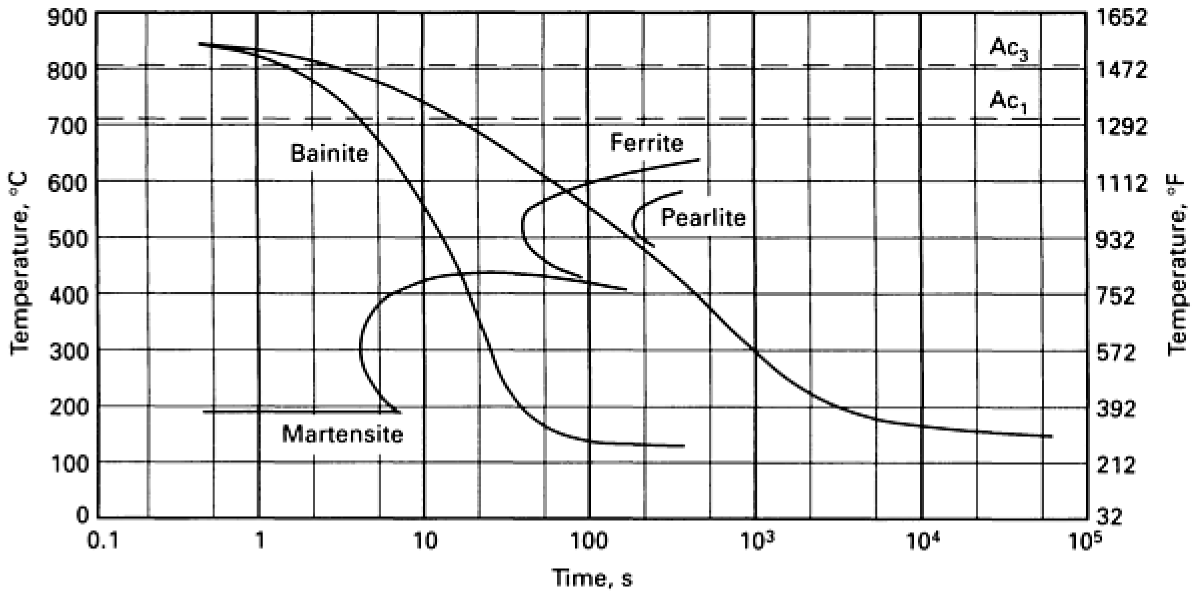

Fig. 15 Calculated CCT diagram from actual part composition with modeled part cooling rates. Ac_1: temperature at which austenite begins to form during heating. Ac_3: temperature at which transformation of ferrite to austenite is completed during heating

Quenchant Control. A model such as this would be extremely useful today in quenchant control. With the latest sophistication and standardization of quenchant evaluation methods, data such as those shown in Fig. 10 are now available. It has long been understood that trying to classify a quenchant by assigning it one number, such as in the electronic quenchometer test (the magnetic test method for the evaluation of quenchants), is convenient but often significantly misleading. A finite-element model for steel hardenability would be able to predict the difference in final microstructural and hardness results that would be obtained from the new versus aged oil in Fig. 10, for example. It would also allow "what if" testing of alternative oils, varying quenchant temperatures, and varying quenchant agitation.

Economic Considerations

The initiation of an SPC system always initially involves increased costs. In heat treating, as in most business environments, the economic benefit must be determined in order to justify this investment. In general, this benefit is derived from removing some of the traditional inspection plans that have been incorporated in the process to ensure that acceptable quality parts were produced.

From the acquisition and statistical analysis of sufficient data from the process, the improvements can be made in areas that make the most positive impact on product quality. Productivity improvements are also realized from knowing exactly how the parts need to be processed.

A classical example is soak time required to austenitize parts before quenching. By monitoring and analyzing the furnace heat input, the actual time the furnace reaches steady state can be determined. This method has replaced rules of thumb, such as one hour per inch of cross section for heat treatment. Improved productivity and energy conservation have resulted from the utilization of SPC systems.

In another situation, it was determined that the balance-beam scale-type loading mechanism for a continuous rotary retort furnace line operated within an accuracy of ±25% during the initiation of an SPC system. This led operators to underload the furnace in order to avoid overloading. The risk of overloading was that parts would distort excessively and not quench to maximum hardness. The loading system was replaced and upgraded to a digital load cell system with an accuracy of ±5%. The result was a 19% improvement in productivity.

Carburizing offers significant opportunities for productivity improvements through improved process control. If a typical carburizing specification requires a depth of 0.51 to 1.02 mm (0.020 to 0.040 in.), the traditional approach by the heat treater is to target 0.76 mm (0.030 in.) to give plenty of leeway for the uncontrollables. However, it is feasible to reduce the variation in the process so that the target can be reduced to 0.58 mm (0.023 in.) through SPC techniques. The resultant reduction in processing time results in a 25% increase in productivity.

True statistical quality control can be successfully and economically implemented today in a heat treatment shop to augment an existing SPC program. The major contributing parameters in each process must be identified and monitored or controlled depending on both economic and quality considerations. At some point in the future, today's investment in statistical process control or statistical quality control will pay off as the move to more complex process modeling for process understanding is developed.

Computerized Properties Prediction and Technology Planning in Heat Treatment of Steels

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Introduction

COMPUTER SIMULATION is a method of computer application that is expected by heat treaters to yield great results in the future. In recent years, the establishment of prediction methods based on the phenomenological description and computer simulation of the transformation processes during heat treatment and the development of software for technological planning have been of major interest. The steady development of this topic is aimed at meeting the requirements of metallurgists producing basic materials, design engineers dealing with material selection and dimensioning, and technologists planning heat-treatment processes. In this article, the topic of computer simulation is restricted to quenched and tempered or case-hardened steels.

Basic Objectives of Computer Simulation

The development of computer simulation of heat treatments, which is obviously due to the widespread growth of computer miniaturization, has been motivated by several factors. Research in this field of computer simulation has been concentrated so far on two main areas of interest:

- Modelling of transformation processes and the prediction of microstructures and/or properties
- Developing program packages (designed in the majority of cases to be purchased on the market for direct industrial use) to help solve concrete tasks such as material selection, property prediction, and the design of heat-treating operations

These basic areas of interest are discussed briefly in the following paragraphs.

Material Selection. Design engineers, metallurgists, and heat-treatment technologists need to assess the effects of material selection on heat treatment, dimensional control, and distortion. Consequently, one basic objective of computerized modelling is the use of algorithms for material selection. This process may involve not only selection of the cheapest material or type of steel suitable for a particular application, but also the assessment of processing alternatives and their effect on manufacturing characteristics and properties.

Process Analysis and Optimization. By introducing computer methods, steel heat treatments can be analyzed and/or optimized in terms of product quality, property scatter, processing time, and energy consumption. For example, the energy consumption of a heat-treatment procedure depends on such factors as the temperature, duration, mass of charge, and equipment. A proper computer algorithm makes it possible to select the heat-treatment parameters that result in minimum energy consumption and optimum mechanical properties. Because of the many factors involved, reducing energy consumption is an optimization task that can be done only by applying a suitable simulation computer program.

Another important application of process analysis by computer simulation is in the area of product development and order bidding. During the development phase, time may be lacking for lengthy experiments, not to mention the ever-growing expenses of material testing in connection with heat treatment. Considerable time and expense can be saved by replacing heat treatment and time-consuming analysis by the computer simulation of heat-treatment processes. Furthermore, qualified labor force can also be spared to a certain degree.

On-Line Programs for Process Control and Monitoring. During recent years, the steady development of the control and monitoring of heat-treatment processes has called for, or rather, forced the development of new models and simulation processes. For example, the development of models and softwares for the prediction of carbon profile has been particularly encouraged by an up-to-date control of the processes during gas carburizing and by the monitoring of case properties. On-line heat-treatment programs can also assist in the monitoring and control of energy consumption.

Property Prediction. Both solving the problems during heat treatment and choosing the basic material and the set of characteristics can be hindered by the large number of property combinations. This is particularly true in the case of steel, which can be altered within broad limits merely by heat treatment (Table 1). These broad property ranges in Table 1, which are beneficial in some sense, can also be a problem for the user because it is difficult to decide which possible combinations of mechanical characteristics can be considered realistic, or realized at all, for heat treatment. Similarly, the type of heat-treatment technology that should be used and its degree of accuracy (that is, manufacturing probability) should be set to achieve a certain combination of characteristics.

Table 1 Range of property values attainable in quenched and tempered and case-hardenable steels

Property	Measured values
Hardness, HV (30 kgf)	130-700
Tensile strength, MPa (ksi)	400-2000

	(58-290)
Yield strength, MPa (ksi)	300-1800
	(43-261)
Elongation in 50 mm (2 in.), %	8-28
Reduction in area, %	5-68
Charpy impact, J (ft · lbf)	10-180
	(7-133)

Naturally, an experienced engineer or metallurgist is aware of the qualitative interrelations among the different properties and can decide off-hand which combinations obviously cannot be realized. For example, a tensile strength approaching the upper limit cannot be accompanied by the same degree of elongation. Yet, it can be quite complicated and time-consuming even for an experienced expert to choose an optimum combination of characteristics from the range of possible property variations. The situation is even more complicated if the variable of section thickness is added to the decision-making process.

General Description of Simulation Softwares

Simulation softwares can be classified either as on-line programs for process control or as programs to assist decision making and process analysis. The latter classification of software programs can be subdivided further into:

- Property prediction programs
- Process planning programs
- Material selection programs and their data bases
- Programs for special technical and economic problems in connection with heat treatment (programs estimating the energy consumption of a heat-treatment process or calculating the expenses of heat treatment, and so forth
- Finite-element analysis for modelling the effects of quench severity on distortion and dimensional control of parts

Examples of various types of available software for either on-line applications or the above-mentioned decision-making applications are listed in Table 2.

Table 2 Examples of available computer programs and data bases on the field of steel selection, microstructure, properties, and heat-treatment technologies

Name of the software	**Availability**	**Features**
Computerized materials properties storage, retrieval, and use		

Mat. DB	ASM International, U.S.A.	Materials data base management program containing the designations, chemical compositions, forms (sheet, bar and so forth), and properties (up to 40 properties). It is designed to select alloys on the basis of many characteristics
EQUIST 2.0	SACIT Steel Advisory Centre for Industrial Technologies, Hungary	Contains the chemical compositions, mechanical properties, application fields, and the international comparison (equivalent steels) of 6500 standard steels from 18 countries
Database SteelMaster	Dr. P. Sommer Werkstofftechnik GmbH., Germany	Contains compositions, mechanical properties, heat-treatment parameters, CCT diagrams, tempering charts for commonly used German structural and tool steels. The heat-treatment technologies designed by the user of the software can be stored and retrieved
PERITUS	Matsel Systems Ltd., Great Britain	This data base provides engineers with up-to-date information about the range of materials from traditional metals to new polymers. The range of information: mechanical and physical properties, environmental resistance, material forms, processing methods, trade names, and standards
AMETA	SACIT Steel Advisory Centre for Industrial Technologies, Hungary	This data base of individual measured steel properties contains data collected from laboratories of industry quality control departments. The range of data: steel designation, heat number, dimensions of the machine part, composition, heat treatment of the part, results of tensile tests, impact test results, measured Jominy curve of the heat, and other tests. The system makes statistical analysis of the data
KOR	SACIT Steel Advisory Centre for Industrial Technologies, Hungary	KOR is a corrosion information system, which contains a data base of 300 corrosive media, more than 15 000 individual corrosion dataset, 150 metallic structural materials, and 200 isocorrosion diagrams. Structural material selection is possible according to prescribed mechanical, physical, technological properties, or it is possible to find a suitable resisting material for a corrosive medium with given temperature and concentration. The system will also accept the user's own data
Computer programs for calculations of processes occurring in steels during heat treatment		
PREDIC & TECH	SACIT Steel Advisory Centre for Industrial Technologies, Hungary	Simulates the cooling, transformation of austenite in cylindrical, plate-shaped workpieces, Jominy specimens made of case-hardenable and quenched and tempered low-alloy steels and calculates the microstructure and mechanical properties in any location of the cross section of the workpiece taking into account the actual chemical composition, dimensions, austenitizing temperature, durations, cooling intensity of quenchant, tempering temperature, and time. The same program works as technology planning program if the prescribed mechanical properties and composition are given
AC3	Marathon Monitors Ltd., Great Britain	Hardenability model designed to predict the response to quenching of through-hardening and carburized low-alloy steels in terms of microstructure and hardness distribution
CETIM-SICLOP	Centre Technique des Industries Mechaniques PROGETIM, France	Contains a steel data base for the selection of structural and tool steels and calculates the mechanical properties along the cross section of workpieces
SteCal	Comline Engineering Software, Great Britain and ASM International	Calculates the heat-treatment response and properties of low-alloy steels from composition
PREVERT	Creusot-Loire Industries,	Calculates the microstructure and mechanical properties of quenched and tempered low-

	France	alloy steels from composition and heat-treating parameters
CHAT	International Harvester Company, U.S.A.	CHAT is a two-part system for selecting the optimum steel composition to be used where heat treating is performed to develop required engineering properties
MINITECH	Minitech Limited, Canada	The Minitech Alloy Steel Information System consists of twelve computer programs which generate a series of hardenability-related properties of steels, such as Jominy curves, hardenability bands, mechanical properties of hot rolled products, hardness distributions for quenched and tempered and carburized products
PREDCARB	SACIT Steel Advisory Centre for Industrial Technologies, Hungary	This computer program determines the gas carburizing technology and calculates the carbon profile and hardness distribution in the case and core on the basis of chemical composition, dimensions of the workpiece, cooling intensity of the quenchant, prescribed characteristics of the case
SIMULAN	Lammar, Ensam Bordeaux, France	Simulates the gas carburization and induction hardening process, and calculates the carbon and the hardness profile
CARBCALC	Marathon Monitors Ltd., Great Britain	Simulates the carburizing reactions between a steel and surrounding atmosphere. It calculates the carbon profile
CARBODIFF	Process Electronic, Germany	Monitoring of carbon profile during carburizing and prediction of hardness distribution after quenching of case-hardened steels
Carbo-O-Proof	lpsen Industries Ltd., U.S.A.	This software is able to optimize the carburizing process, calculates continuously the carbon profile, and regulates the process in accordance with program target values
SYSWELD	Framasoft, Great Britain	This system is based on finite-element technique and simulates the transformation processes in steel during heat treatment or welding. The program calculates the temperature distribution, microstructure, hardness, and stresses

General aspects of these simulation software packages are described below. In general, the "inner core," or essence, of different simulation programs for process planning or material selection contains in most cases a property prediction model, although this is not realized by the user. Property prediction softwares consist of module elements that form, in a chain-to-chain connection, a functionally comprehensive structure (see, for example, the modules described below in the section "Calculation of Microstructure and Properties"). Each module can be regarded as a submodel of a certain part of the total heat-treatment process. Knowing the necessary input data, this model provides a theoretical possibility for the simulation of processes taking place during heat treatment. The result of the simulation is output data. The reliability and accuracy of prediction softwares depend, of course, on the applied metallurgical model.

Development Trends in Computer Simulation Modelling

In the last 20 years there were many computerized data banks created in different countries that tried to help the metallurgists and material engineers with bibliographic (for example, METADEX) and factual (for example, Metals Datafile) data bases. To a certain extent, independent of this activity, but in the same time period, the property predictors were starting to be developed. Naturally, there were earlier calculation methods such as the well-known calculation of critical diameter with the Grossmann formulas, but the widespread growth of computer methods opened new options. The computer techniques made it possible to reevaluate the conventional formulas, to expand their application fields, and to develop more complex and accurate prediction methods.

During the last two decades in the field of heat treatment, various mathematical models with different accuracy and complexity have been developed. There are three general types of models used in property prediction and computer simulation of heat-treatment effects:

- Static models based on empirical formulas
- Dynamic models based on differential equations or differential equation systems
- Programs with both static and dynamic models

The static models are useful because of their simplicity, but their accuracy does not always satisfy demands and expectations. In most simulation algorithms and softwares, the static and dynamic models are mixed.

Static models are based on simple empirical formulas that can be derived from physical principles and observation or from statistical methods. Generally, statistical models use regression analysis.

A good example of a static model is the formulation or prediction of Jominy hardenability from austenitic grain size and chemical composition. This type of quantitative methodology (Ref 1, 2, 3), which has been a subject in the study of hardenability for several decades, is discussed in the article "Quantitative Prediction of Transformation Hardening in Steels" in this Volume.

Dynamic models are based on the solution of differential equations or differential equation systems. Examples of dynamic models include programs for predicting carbon and nitrogen profiles (Ref 4, 5, 6) as well as the phenomenological models developed to describe the transformation of austenitc under nonisothermal conditions (Ref 7, 8, 9, 10, 11).

Another important category of dynamic models is the use of finite-element analysis in predicting residual stress and distortion (Ref 12, 13, 14) or in determining suitable quenchants (gas, oil, or water) for a given alloy (Ref 12). Examples of programs based on finite-element analysis include:

- The CONTA program for calculating surface heat fluxes (Ref 15)
- The TOPAZ 2D program for calculating temperatures (Ref 16)
- The NIKE 2D program for calculating stresses (Ref 17)

Sophisticated dynamic simulation models, such as those based on finite-element analysis, are rather complicated to run and require expert knowledge. As far as the purchase is concerned, both the software and the hardware can also be rather expensive. Consequently, the development of prediction software is often first aimed at the accessibility of personal computer systems.

References to State-of-the-Art Applications

In the following paragraphs an attempt is made to outline some important results in computer simulation of heat-treatment processes without aiming at completeness. General overviews of these activities in the latter half of the 1970s are also given in Ref 18 and 19. Publications on the structure of the simulation models and softwares are often laconic and do not contain directly usable information. The reason for this is mostly that the publication of details would hurt business interests; the systems are also developed as commercial ventures, and parts of the programs are proprietary.

Data Base Systems. Data bases containing the main characteristics of several metal alloys are being marketed. Different kinds of information can be retrieved from these data bases (chemical composition, mechanical characteristics, continuous cooling transformation [CCT] curves, and so on). The data base can be loaded with the results of the process planning so that the user's own specially designed technology can be stored in the data base. Research workers at Minitech Ltd (Canada), for example, designed a software package to estimate various properties (for example, weldability, phase diagrams, hardenability) of low-, medium-, and high-carbon steels (Ref 18). Chrysler Corporation developed an interactive system that makes it possible for the designers and technologists to get material information on their own local computer terminal (Ref 18). Utilization of data bases of measured steel properties is discussed in Ref 20.

Recently, a program system was developed in CETIM Institute (France) for the planning of heat-treatment technology and for steel selection. The essential part of the software is a data base containing the chemical composition, mechanical properties, and Jominy curves of the most often used quenched and tempered and case-hardened steels as a function of section size (Ref 21).

Hardenability Prediction. As previously mentioned, quantitative prediction of hardenability has been a longstanding subject of theoretical and practical interest. A basic overview, along with prediction of isothermal transformation (IT) and CCT curves, is provided in the article "Quantitative Prediction of Transformation Hardening in Steels" in this Volume. Hardenability prediction is also covered in Ref 22, 23, 24, 25, and 26.

In applying a static model, Murry *et al.* (Ref 27) developed a computing method for predicting the hardness of cylindrical workpieces along the cross section after quenching. The input data are: chemical composition, austenite grain size, geometrical characteristics, and the cooling time from 700 to 400 °C (1290 to 750 °F). In the central laboratory of Creusot-Loire (Ref 18, 28), nonlinear multiple regression analysis was used to derive a series of formulas for the estimation of critical cooling rates from 700 °C (1290 °F). They also published equations to calculate the as-quenched and tempered hardness from the chemical composition and cooling rate from 700 °C (1290 °F).

The coworkers of the McMaster University (Hamilton, Ontario, Canada) starting from a metallurgical thermodynamic basis, developed methods for the computer-aided determination of equilibrium diagrams of multicomponent steel alloys and for the calculation of the starting curves (incubation time) of the isothermal transformation diagrams as well (Ref 19, 25, 29). They also investigated the tempering process and developed usable computer programs for the prediction of hardenability and its application in steelmaking.

Programs for material selection and/or analysis of heat-treatment processes usually contain a system for property or hardenability prediction. Liscic and Filetin (Ref 23, 24), for example, published a computerized process-designing system for the heat treatment of quenched and tempered steels. This system is suitable for the determination of technological parameters (austenitization and tempering temperature) knowing the steel type and the required properties. More sophisticated models based on finite-element analysis are also being investigated as a way of modelling distortion and analyzing quench methods (see, for example, Ref 12). A general review on the application of computerized information for steel selection and their heat treatments is given in Ref 30.

Analysis of residual stresses and distortion generally involves finite-element analysis of the internal stresses developed during transformation sequences. Typical examples are given in Ref 12, 13, 14 and 31. A method for calculating transformation sequences in quenched steels is given in Ref 32. For case-hardened steels, a software package has been developed for the prediction of residual stresses by tracing the transformation of the case and the core of the work-piece (Ref 33, 34).

Simulation of Case Hardening. New type models have been developed for the prediction of carbon and nitrogen profile during and after the gas carburizing and nitriding (Ref 5, 6, 35, 36, 37, 38, 39, 40, 41). In this field, calculation methods can be used to model case depth and hardness profiles (Ref 37, 42, 43). Ingham and Clarke (Ref 41) developed a well-applied computerized method for the prediction of microstructure and hardness profile of case-hardened parts. Methods of microstructure prediction are described in Ref 8 and 44.

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General Concept of a Property-Prediction System

A detailed property-prediction system (PPS) used for simulating the metallurgical process occurring during heat treatment and predicting the microstructure and mechanical properties of quenched and tempered or case-hardened steels is described in this section. The system consists of several modules, which form a logical chain for property prediction.

Model Description

Before starting to design a PPS, one has to ascertain first those internal parameters (for example, Ac_3 temperature, transformation kinetic data, hardness values of the microstructural elements, and so on) that have the most determinative effects on the properties. Then the algorithm, the logical chain of these internal parameters, has to be stated and finally, the connections between the input data, the internal parameters, have to be investigated. If all of these connections are clear, mathematically formulated, and joined into a chain, one can handle this set of connections as a system.

The programs of the PPS are based on a phenomenological model of kinetics of transformation taking place in nonisothermal conditions. The program permits the prediction of the progress of transformations, of the microstructure, and of the mechanical properties as a function of time and of position in the cross section of the heat-treated workpiece. The equations forming the base of the model belong to three main groups as follows:

- *The differential equation of heat conduction:* By a numerical method, the temperature field in the given

workpiece is solved

- *The system of kinetic differential equations* for describing the transformation processes occurring in the microstructure
- *Equations describing the relation between the microstructure and properties*

Modelling of transformation kinetics can be done with differential equations such as:

$$\frac{\partial Y_j(\mathbf{r},t)}{\partial t} = g_j(Y_1, Y_2, \ldots Y_J, T, t) \qquad \textbf{(Eq 1)}$$

where t denotes time; **r** is the vector representing a given point of the workpiece (the position vector); T is the temperature, which is a function of time t and position **r;** Y_j (j = 1,2, . . . J) is a so-called microstructural parameter; and g_j = 1,2 . . . J is an appropriately selected real value function.

The microstructural parameters Y_j in Eq 1 are numerical quantities that may be interpreted within relatively wide limits. For example, Y_j may denote the volume fraction of the transformed phase, its average dimension, or the mean free distance between particles.

Relating Microstructure to Properties. The starting point for predicting mechanical properties such as hardness and yield point is that the properties are related to microstructural parameters. It was assumed that after transformation at a given location **r** in the workpiece, a numerical property P(**r**) of the steel may be calculated with a precision satisfying practical demands as a function of a small number of elementary microstructural properties p_j (j = 1,2 . . . M) according to the formula:

$$P(\mathbf{r}) = f_l(p_1, p_2, \ldots p_M) \qquad \textbf{(Eq 2)}$$

where f_1 is an appropriately selected function.

In most cases, the so-called generalized linear law of mixture represented by the following Stieltjes integral was used to calculate the elementary microstructural property p_j (j = 1,2, . . . M):

$$p_j = \int \chi(T, Y_j) dY_j \qquad \textbf{(Eq 3)}$$

where $\chi[T(\mathbf{r}, t), Y_j]$ is a suitably defined weighting function containing and summarizing the numerical information on the given property of the microstructural parameter Y_j. For more details, see Ref 45.

Calculation of Microstructure and Properties

The block diagram of a PPS program is shown in Fig. 1. The upper part of the diagram refers to the processes occurring during austenitization and quenching; the lower part refers to tempering processes. The "black boxes" of the quenching and tempering calculation unit are within the frames shown with dashed lines. The programs that form the system are numbered 1 to 12. The models and the parameters used as input to the modules are being developed continuously according to the latest experience and can be changed. Each module is described in this section.

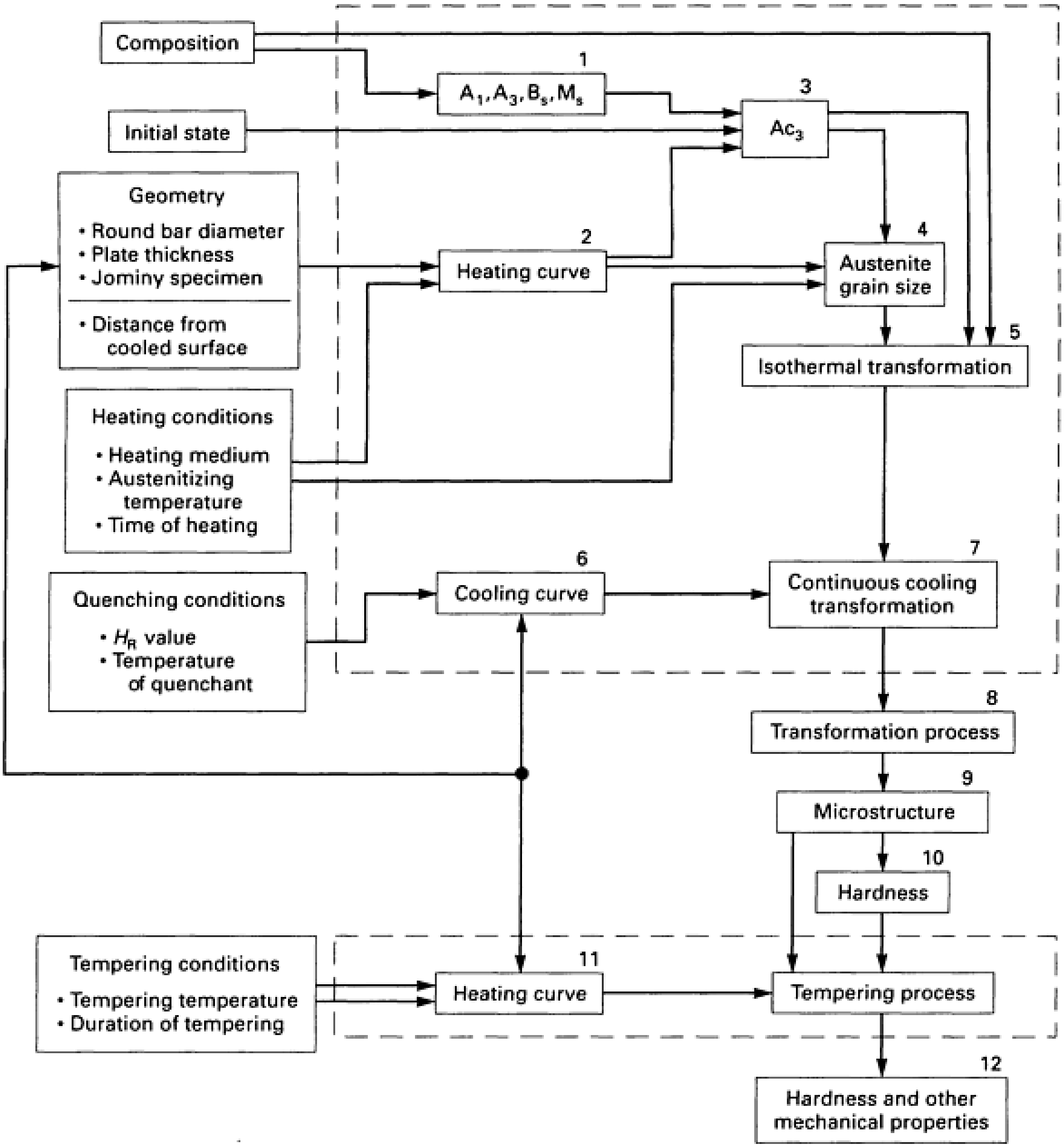


Fig. 1 Block diagram of the PPS simulation model

The input data are seen on the left side of the block diagram. They are as follows:

- Chemical composition of the workpiece to be hardened
- Initial state of the workpiece (annealed, normalized, quenched, and tempered)
- Geometry: shape and size of the workpiece (round bar or plate) characterized by its diameter or thickness, or Jominy specimen and the distance from the cooled surface to the point where the microstructure and properties are to be predicted
- Heating conditions: heating medium, austenitizing temperature, and the total time spent by the workpiece in the austenitizing furnace
- Quenching conditions characterized by the H_R value (relative heat transfer coefficient specifying the cooling severity, for example, in the case of oil, 0.3 to 0.6) and the temperature of the quenchant
- Tempering conditions given by the tempering temperature and the duration of tempering

Determination of Martensite Start (M_s), Bainite Start (B_s), and the Equilibrium (A_1, A_3) Transformation Temperatures from Compositions (Module 1). The chemical composition of the workpiece is first verified against the specified composition range of the steel type for which the predictor program was developed. From the composition, Module 1 then calculates A_1, A_3, B_s, M_s transformation temperatures by formulas based on dilatometrical measurements and regression analysis (Ref 46, 47). There are also numerous formulas in the literature for the estimation of these transformation temperatures (Ref 19).

Computation of the heating curve (Module 2) takes into account the furnace features. Calculations are based on the application of an approximate method developed to solve heat conduction problems for simple geometries.

In most practical cases, it is not necessary to expend much effort for the accurate calculation of the heating curve. The accuracy of the following Newtonian approximation can also satisfy the requirements:

$$T = (T_0 - T_a)\exp\{-\alpha_h t\} + T_a \qquad \textbf{(Eq 4)}$$

where T is the temperature in the given point of the workpiece; t is the time; T_a is the austenitization temperature; T_0 is the temperature at t = 0; and α_h is a constant, depending on the furnace, mass of workpiece, heating medium, quality of the surface, and agitation of the medium.

Calculation of Time and Temperature to Austenitization (Module 3). This module calculates the austenitizing temperature (Ac_3) to the nearest 20 °C (35 °F) and the time to reach the Ac_3 temperature. The Ac_3 temperature is determined--apart from the chemical composition--by the initial microstructure and the heating rate. The interactive computer program based on this model permits the user to select one of four of initial microstructures. The experimental results may be described with the following equation:

$$Ac_3 = A_3 + a\,v^{\frac{1}{3}} \qquad \textbf{(Eq 5)}$$

where v is heating rate at temperature A_3, and a is a parameter depending on the initial state of microstructure, that is, the finer the microstructure is, the lower the value of a. The value of the empirical parameter a is estimated by least squares analysis on the basis of grain growth diagrams of different steel grades (see Fig. 2 and the corresponding discussion of grain growth given below).

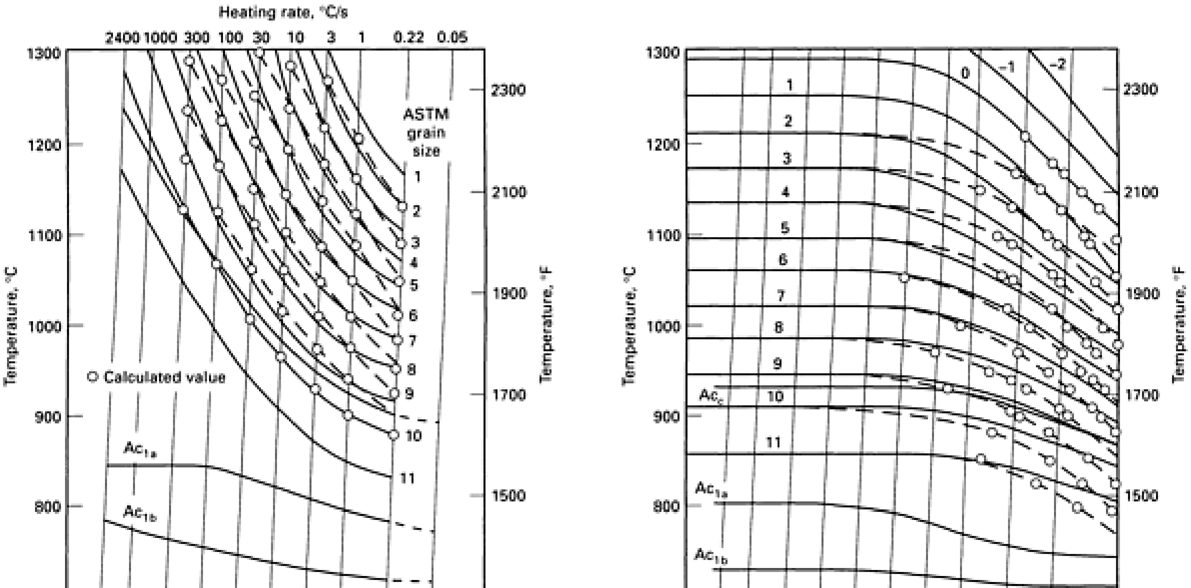


Fig. 2 Measured and calculated austenite grain growth diagrams of 90MnV8 steel (0.85-0.95% C, 0.15-0.35%

Si, 1.8-2.0% Mn, 0.07-0.12% V) during (a) continuous heating and (b) isothermal heating at 1.3 °C/s (2.3 °F/s)

For the chromium-molybdenum low-alloy steels with 0.5% C content, the numeric value of the *a* parameter can vary from 3 to 15, if the temperatures are measured in degrees centigrade. For example, in the case of a quenched microstructure, $a = 3$; for quenched and tempered state, $a = 5$; for the normalized state, $a = 10$; and for the annealed state, $a = 15$.

Computation of the austenite grain size (Module 4) also requires consideration of nonisothermal conditions. The extent of grain growth taking place during austenitization is known to have a decisive effect on the characteristics of steel; therefore, its prediction is a task of considerable practical interest (Ref 48).

Grain growth diagrams were worked out for the various types of steel on the basis of tests, but their usefulness was restricted by the condition that they must be valid for the case of isothermal or linear heating. It was shown (Ref 7) that using the data of the known austenite grain growth diagram valid for linear heating, a generalized kinetic function can be produced by calculation, which allows computed tracking of grain growth taking place at changing temperature, and thus prediction of grain size.

It was assumed that grain size D_a of steels at constant temperature T_c is described by an isothermal kinetic function of the following type:

$$D_a^N - k_0 \exp(-Q_a/RT_c)t = 0 \qquad \textbf{(Eq 6)}$$

After derivation, the generalized kinetic differential equation type (Eq 1) is obtained:

$$\frac{dD_a}{dt} = \frac{k_0}{N} \exp\left(-\frac{Q_a}{RT}\right) D_a^{1-N} \qquad \textbf{(Eq 7)}$$

The unknown parameters k_0, N, and Q_a of differential equation (Eq 7) can be estimated by regression analysis using measured data*. According to the published method (Ref 7), the average grain size D_a may be calculated with the generalized kinetic function:

$$D_a = \left[\int_0^t k_0 \exp\left(-\frac{Q_a}{RT}\right) dt + D_0^N \right]^{1/N} \qquad \textbf{(Eq 8)}$$

produced by integration of the generalized kinetic differential equation (Eq 7). Knowing the heating curve, the solution can be obtained by numerical integration of Eq 8, where D_0 is the initial grain size at Ac_3; N and Q_a are parameters depending on the composition; and R is the universal gas constant. The values of the parameters k_0, Q_a, and N may be determined by the method of least squares from grain growth experiments (Ref 7, 48).

Figure 2 shows two grain growth diagrams for steel 90MnV8 as examples. In Fig. 2, the solid lines represent the original test results taken from Ref 49, while the dashed lines show the results calculated with Eq 8. For this calculation, the time-temperature function had to be substituted before integration. The applied parameters were as follows:

$$k_0 = 6.087 \times 10^7$$
$$N = 2.44$$
$$Q_a = 317 \text{ kJ mol}^{-1}$$

Figure 2(b) shows the grain growth for the same steel but, for isothermal conditions, taking into account the heating rate as well. The coincidence of the grain sizes determined by measurements and those calculated by Eq 8 are satisfactory according to practical demands.

Calculation of TTT Diagram (Module 5). The characteristics of the isothermal time-temperature transformation (TTT) chart are calculated as a function of the chemical composition and austenite grain size, also taking into account the temperatures A_1, A_3, B_s, and M_s.

A complete mathematical description of the isothermal transformation, starting with nucleation and growth, is presently not possible for large volume fractions transformed (Ref 50). The reason is that an analytical description of the growth is not possible if the single nuclei touch each other. Therefore, in general, empirical descriptions are used that are appropriately fitted to the measured curves. Some of the applicable methods are listed below.

Avrami Estimate of Isothermal Transformation. One of the most frequently used equations for the isothermal transformation is Avrami's equation:

$$y = 1 - \exp\{-bt^n\} \qquad \textbf{(Eq 9)}$$

where y is the volume fraction of the transformed austenite; t is the time spent on the isotherm; and b and n are temperature, grain size, and composition-dependent constants, evaluated from the isothermal TTT diagram or from measurements with continuous cooling (Ref 50).

For calculations detailed below, the parameters b and n can be given in tabulated form, but also in mathematical form as functions of temperature, composition, and grain size.

Estimates of 1% and 99% Transformation. The second possibility is to define functions for the beginning (1% transformed austenite) and for the end (99%) of isothermal transformations. These curves can be described with equations of the following form:

$$t = f_2(C, D_a)\exp\{h_0 + h_1T + h_2T^2 + h_3T^3\} \qquad \textbf{(Eq 10)}$$

where C is the composition vector; D_a is the austenire grain size; T is the temperature; h_0, h_1, h_2, and h_3 are composition-dependent constants; and f_2 is a suitable selected real function.

Transformation Estimates from Isothermal Kinetic Differential Equations. In the PPS program discussed here, the information content of the traditional TTT charts is built into the program in the form of isothermal kinetic differential equations as follows:

$$\frac{dy}{dt} = Ky^{b_1}(1-y)^{b_2}\ln\left[\left(\frac{1}{1-y}\right)^{b_3}\right] \qquad \textbf{(Eq 11)}$$

where y is the relative amount of transformed products; K, b_1, b_2, and b_3 are appropriately selected parameters depending on temperature, austenite grain size, and composition (Ref 30, 32). The most important kinetic functions (Table 3) can be considered as special cases of Eq 11.

Table 3 Summary of most important kinetic functions for isothermal conditions

Source: Ref 32

Condition	Differential equation	Solution at $y(0) = 0$	Parameter
1	$y' = nK(T)(1-y)\left(\ln\frac{1}{1-y}\right)^{(n-1)/n}$	$\left(\ln\frac{1}{1-y}\right)^{1/n} = K(T)t$	$b_1 = 0$ $b_2 = 1$ $b_3 = (n-1)/n$
2	$y' = nK(T)y^{(n-1)/n}(1-y)^{(n+1)/n}$	$\left(\frac{y}{1-y}\right)^{1/n} = K(T)t$	$b_1 = (n-1)/n$ $b_2 = (n+1)/n$ $b_3 = 0$
3	$y' = nK(T)y^{(n-1)/n}$	$y^{1/n} = K(T)t$	$b_1 = (n-1)/n$ $b_2 = 0$ $b_3 = 0$
4	$y' = K(T)y^{2/3}(1-y)$	$\frac{1}{2}\ln\frac{1+y^{1/3}+y^{2/3}}{(1-y^{1/3})^2} + \sqrt{3}\tan^{-1}\frac{2y^{1/3}+1}{\sqrt{3}} - \sqrt{3}\frac{\pi}{6} = K(T)t$	$b_1 = 2/3$ $b_2 = 1$ $b_3 = 0$
5	$y' = K(T)y^{1/3}(1-y)$	$\frac{1}{2}\ln\frac{1+y^{1/3}+y^{2/3}}{(1-y^{1/3})^2} - \sqrt{3}\tan^{-1}\frac{2y^{1/3}+1}{\sqrt{3}} + \sqrt{3}\frac{\pi}{6} = K(T)t$	$b_1 = 1/3$ $b_2 = 1$ $b_3 = 0$
6	$y' = K(T)y^{-1}(1-y)^2$	$\frac{y}{1-y} + \ln(1-y) = K(T)t$	$b_1 = -1$ $b_2 = 2$ $b_3 = 0$

Source: Ref 32

Computation of the cooling curve (Module 6) at the given point of the workpiece can involve a simple method similar to the one described in Module 2, that is, to use a Newtonian cooling:

$$T = (T_a - T_q)\exp\{-\alpha_c t\} + T_q \qquad \textbf{(Eq 12)}$$

where T_a is the austenitization temperature; T_q is the temperature of the quenchant; and α_c is the geometry and quenchant-dependent parameter.

In the case of cylindrical workpiece and water cooling, the equation for calculating α_c can be suggested in the following form:

$$\alpha_c = \frac{A}{D^{1.726}\exp\{(B - 0.013D)[(D - 2X)/D]^3\}} \qquad \textbf{(Eq 13)}$$

where D is the diameter; X is the distance from the cooled surface; and A and B are agitation-dependent constants (Ref 46).

The computer program discussed here takes into account the individual geometry (plate, cylindrical workpiece) and calculates the cooling on the basis of the principles similar to one-dimensional un-steady-state heat conduction, which is formulated by the Fourier differential equation as follows:

$$\frac{\partial}{\partial r}\left(\lambda\frac{\partial T}{\partial r}\right) + \beta\frac{\lambda}{r}\frac{\partial T}{\partial r} + q_v = \rho C_p\frac{\partial T}{\partial t} \qquad \textbf{(Eq 14)}$$

where t is time; r is locale coordinate; $T(r,t)$ is temperature; q_v is rate of heat generation due to the austenite transformation; ρ is density; C_p is specific heat; λ is thermal conductivity; $\beta = 0$ for the plate; and $\beta = 1$ for the cylinder.

With the cylinder diameter and the plate thickness equal to $2R$, the corresponding boundary and initial conditions are:

At the surface ($r = R$) with $t > 0$:

$$-\lambda \left.\frac{\partial T}{\partial r}\right|_{r=R} = \alpha \left[T_q - T\left(R,t\right)\right] \quad \textbf{(Eq 15)}$$

At the centerline (r = 0) with $t > 0$:

$$-\lambda \left.\frac{\partial T}{2r}\right|_{r=0} = 0 \quad \textbf{(Eq 16)}$$

Elsewhere ($0 \leq r \leq R$) with $t = 0$:

$$T(r,t) = T_a \quad \textbf{(Eq 17)}$$

where α is the heat transfer coefficient; T_q is the temperature of the quenching media; and T_a is the initial austenitizing temperature.

In many cases, the heat generated in the workpiece during cooling is disregarded (q_v = 0). On the other hand, some simplifying assumptions are used relating to the surface heat transfer represented by Eq 15.

By introducing the relative heat transfer coefficient H_R defined as:

$$H_R = \frac{\alpha}{2\lambda} \quad \textbf{(Eq 18)}$$

then Eq 15 can be rewritten in the form:

$$-\left.\frac{\partial T}{\partial r}\right|_{r=R} = 2H_R \left[T_q - T\left(R,t\right)\right] \quad \textbf{(Eq 19)}$$

The parameter H_R (assumed to be constant) is formally equal to the widely accepted quenching factor proposed by Grossmann for characterizing the quenching power of different cooling media (Ref 22, 51).

The dimension of H_R is the reciprocal of length (1/m, or 1/in.). In heat-treating practice, the range of H_R is in the interval of 8 to 195 m^{-1} (0.2 to 5.0 $in.^{-1}$), where the 8 m^{-1} (0.2 $in.^{-1}$) is for an oil quenchant without agitation and the maximum value 195 m^{-1} (5 $in.^{-1}$) corresponds to a brine quench with strong agitation.

Starting with an appropriately selected cooling intensity H_R, it is very easy to generate the cooling curves for the workpiece of cylindrical or plate form. The disadvantage of this model approach is that the value H_R is not constant and varies during the cooling process. This fact may lead to computation inaccuracies, which must be taken into consideration.

A more exact and more complicated way to characterize in a quantitative manner the surface heat transfer process during quenching is based on the use of the boundary condition formulated as:

$$-\lambda \left.\frac{\partial T}{\partial r}\right|_{r=R} = \phi\left(T_s\right) \quad \textbf{(Eq 20)}$$

where ϕ is the surface heat flux as a function of the surface temperature T_s. The surface heat flux ϕ can be measured for different quenching conditions (for different quenchants, temperatures, agitations, workpiece geometry, and so forth). It can be stored in a data base and can be retrieved for practical computations (Ref 23, 52).

Modelling of Continuous Cooling Transformations (Module 7). Calculating the progress of the transformation process during continuous cooling from the TTT characteristics is a crucial part in property prediction. Estimation of the ferritic, pearlitic, and bainitic fractions during each step is based on published methods (Ref 53, 54). The principle of the method is described below.

In the first step, the isothermal kinetic differential equation is appropriately generalized in the form:

$$\frac{dy}{dt} = f_3(T,y) \quad \textbf{(Eq 21)}$$

where T = T(t) is the temperature as a function of time, and f_3 stands for a selected real function. In the second step, this equation is solved by a numerical method known as the recursive algorithm. The extension and generalization of this method was published in Ref 9.

The recursive algorithm for the well-known Avrami kinetic function was first formulated by M. Gergely (Ref 53, 54). The volume fraction of ferrite-pearlite and bainite are evaluated according to the Avrami expression defined by Eq 9. The cooling curve is approximated by a staircase, and the transformation is then calculated isothermally during each time step. The recursive algorithm is actually a special numerical procedure for solving the generalized kinetic equation (Eq 21). The verification of this is published in Ref 30.

For the calculation of the amount of martensite, a novel formula is used (Ref 8) instead of the well-known equation proposed by Koistinen and Marburger (Ref 55). According to Ref 8, the martensitic transformation can be described in the following differential form:

$$\frac{dy_m}{dT} = K_m\, y_m^{a_1}\,(1 - y_m)^{a_2}\left\{\ln \frac{1}{1 - y_m}\right\}^{a_3} \quad \textbf{(Eq 22)}$$

where y_m is the relative amount of martensite transformed from austenite; and K_m, a_1, a_2, and a_3 are composition-dependent parameters. The numerical values of these parameters for a quenched and tempered low-alloy chromium steel and six case-hardened steels are also published (Ref 8).

Determination of Microstructural Transformations (Modules 8 and 9). Information about transformation temperature definitions for the initiation of the ferrite-pearlite reaction and for the beginning temperature range, B_s, of the bainite reaction is first provided by Module 8. In practice, the beginning is defined as either 1 or 5%. Actually, the complete transformation curve is available as one of the outputs for further evaluation. On the basis of this curve, the temperatures belong to 5%, 10%, . . . 50%, . . . 95%, and the quantities of the microstructural elements can be displayed. Module 9 gives the microstructure, namely, the amounts of ferrite-pearlite, bainite, martensite, and retained austenite. The program uses definitions given above, for example, bainite is the transformation product obtained from austenite between the temperatures B_s and M_s.

Calculation of Hardness (Module 10). When the hardness after quenching is calculated on the basis of microstructure and the carbon content, many investigations are still necessary to ascertain the best rule of mixing. In the Creusot-Loire system (Ref 18) the hardness at room temperature of martensite, bainite, and ferrite-pearlite is calculated separately taking into account the chemical composition and cooling rate at 700 °C (1290 °F). Then a linear mixing rule is applied to get the final hardness.

The PPS model discussed in this section predicts the hardness by the help of the individual isothermal hardnesses of the microstructural elements (Ref 45). As mentioned in the description of Module 7, the solutions of the differential equation (the recursive formulas) trace the nonisothermal phase transformation. Consequently, in the calculation of the hardness after quenching, the transformed amounts of austenite on each isothermal step, and their individual isothermal hardness can be taken into account. The amounts of the microstructural elements are calculated by the help of the stepwise method. The individual hardnesses of the microstructural elements are taken from a hardness-temperature table or function valid for the actual steel, and the resultant as-quenched hardness H_q is composed from these components with the formula:

$$H_q = \sum_{i=1}^{v} y_i(T_i)H(T_i) + y_m H_m + y_a H_a \quad \text{(Eq 23)}$$

where T_i is the temperature of the *i*th step; $y_i(T_i)$ is the transformed amount at temperature T_i; $H(T_i)$ is the isothermal hardness; v is the number of isothermal steps, until temperature reaches M_s; Y_m is the volume fraction of martensite; Y_a is the volume fraction of retained austenitc; H_m is the hardness of martensite; and H_a is the hardness of retained austenite.

Tempering Computer Model (Modules 11, 12, and 13). Module 11 computes the heating curve to reach the tempering temperature. Modules 12 and 13 calculate the final hardness after tempering according to the published method (Ref 7), together with the prospective tensile strength, elongation, reduction in area, and impact energy (Ref 46).

The tempering of steels forms a significant part of practical heat treatment, and therefore its study and mathematical description are of greatest importance. Several generally applied methods are available for the isothermal case (see the discussion of the Creusot-Loire system in Ref 18). In the PPS model discussed here and other systems doing mathematical simulation, the calculation of hardness as a function of time with continuously changing temperature has to be solved. From computational considerations, it is assumed that the kinetic equation describing the change in hardness under nonisothermal conditions is of the form:

$$H_t = f_4 (P_g) \quad \text{(Eq 24)}$$

where H_t stands for the instantaneous hardness after tempering; f_4 is a suitably selected function; and P_g is the so-called generalized time-temperature parameter, which is applicable to the description of tempering processes with changing temperature (Ref 7, 9).

The form of the parameter P_g can be selected in many ways. For example, the generalized version of the widely used Hollomon-Jaffe parameter is:

$$P_{g,H} = \ln \int_0^t T \exp\{CT\} t^{T-1}\, dt \quad \text{(Eq 25)}$$

where C is a composition-dependent constant. It follows from Eq 25 that if the tempering temperature is constant, that is, $T = T_c$, the conventional Hollomon-Jaffe parameter:

$$P_H = T_c(C + \ln t) \quad \text{(Eq 26)}$$

is obtained as a special case.

As an example for an unalloyed steel containing 0.6% C, the kinetic equation that is valid for continuously changing temperature and describes the changing Vickers hardness (HV) of martensite during tempering is as follows:

$$H \text{ (in HV)} = 849 - 139.24 \times \left[\int_0^t T \exp(33.21\ T) t^{T-1} dt\right]^{4.48 \times 10^{-5}} \quad \text{(Eq 27)}$$

Using this method, a microprocessor-based system can be designed that continuously displays the instantaneous value of the required characteristic (for example, hardness), from measurement of the actual temperature of the piece during heat treatment. When the preset hardness value is achieved--using the programmability of the processor--a variety of interventions can be made to the heat-treatment process (Ref 56).

From Eq 24 a new type of tempering chart, of more general validity than before, may be obtained. This case used the generalized Dorn parameter defined as:

$$P_D = \int_0^t \exp(-Q_D/RT)dt \quad \textbf{(Eq 28)}$$

The tempering chart (Fig. 3) is composed of two independent parts. The lower part of Fig. 3 refers to isothermal heat treatment and shows the relationship of tempering parameter P_D to temperature and time. This chart can be applied to convert from one tempering time and temperature to any other, on the basis that combinations of tempering temperature and time having the same value of tempering parameter will produce the same hardness. The upper part of Fig. 3 represents the relationship between parameter P_D and the tempering hardness for 50CV2 steel (0.5% C, 1% Mn, 1% Cr, 0.15% V).

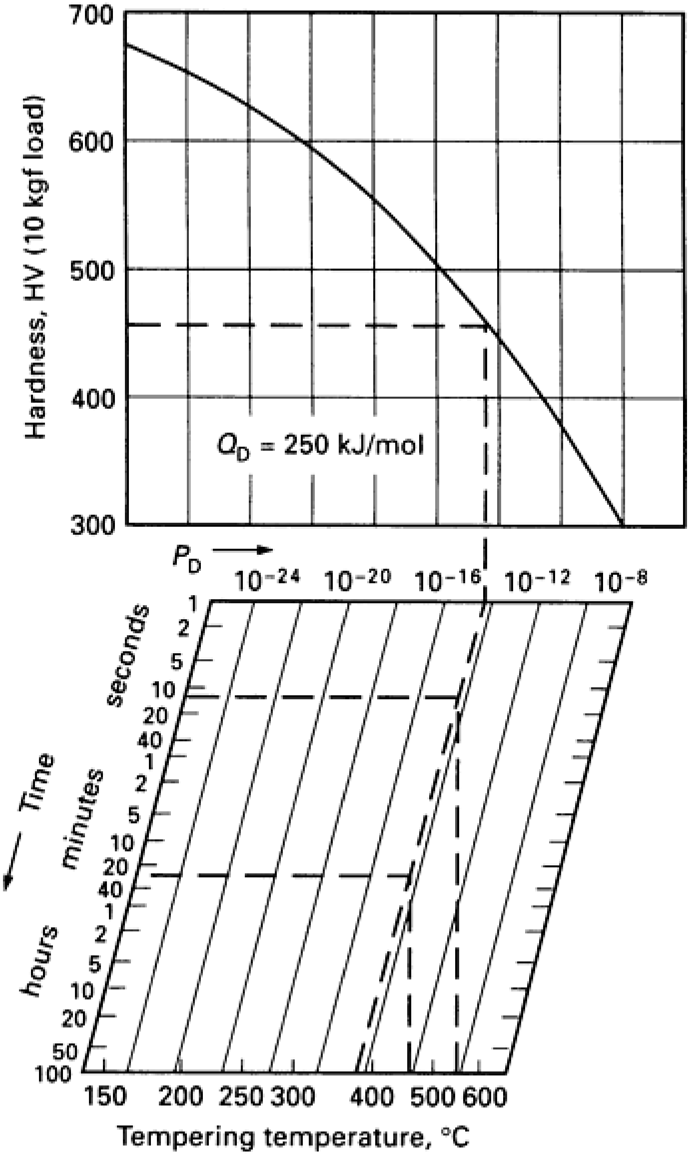


Fig. 3 Generalized tempering chart obtained using the generalized Dorn parameter (P_D) described in Eq 28

For tempering at varying temperatures, the value of the parameter P_D required to achieve the specified hardness may be determined with the aid of the upper part of Fig. 3. For isothermal tempering, the various time-temperature combinations for the given parameter value P_D, which may be used to achieve the specified hardness, may be read from the lower chart in Fig. 3.

In the kinetic function employed for the phenomenological description of hardness decrease occurring during tempering, the value of the apparent activation energy (Q_D = 250 kJ/mol) is essentially identical to the activation energy for the self-

diffusion of ferrite in steel that is not alloyed with molybdenum. It follows from this assumption that the lower chart in Fig. 3 may be used generally for all hardenable steels free of molybdenum. However, the upper chart representing the so-called master curve must be deduced and plotted individually for the various steel types from measured data.

Mechanical Property Estimates. Module 12 estimates not only the hardness, but also the other mechanical properties, namely the tensile strength, yield strength, elongation, reduction in area, and the Charpy value of the impact energy with the following formulas** (Ref 57):

$$R_m = 3.412 \text{ HV} - 64.3 \quad \textbf{(Eq 29)}$$

where R_m is the ultimate tensile strength in MPa, and HV is the Vickers hardness.

For the calculation of the yield point R (MPa), elongation A_{50} (%) in 50 mm (2 in.), reduction in area Z (%), and Charpy value KU (Joules), the equations below have been suggested:

$$R = (1.17 - 0.0007y_m)R_m + 3.72y_m - 484 \quad \textbf{(Eq 30)}$$

where y_m is the volume fraction of martensite in %.

$$A_{50} = 40 - (0.03 - 0.0001y_m)R_m \quad \textbf{(Eq 31)}$$

$$Z = 100 - (0.06 - 0.00024y_m)R_m \quad \textbf{(Eq 32)}$$

$$KU = 296 - (0.285 - 0.00098y_m)R_m \quad \textbf{(Eq 33)}$$

There are some other possibilities developed by utilization of the data base of individual steel properties published in Ref 20, 30, 57.

Examples of PPS Applications

Property prediction computer programs have been developed for solving the following tasks:

- Generation of CCT diagrams for cylindrical, plate-shaped parts, and for Jominy test pieces
- Prediction of microstructure and properties obtained after quenching and tempering with specified heat-treating parameters
- Computer-aided design of heat-treating methods
- Selection of steels with the aid of a computer in consideration of the part dimensions and of the required mechanical properties

The various types of computer programs, composed of modular elements for various purposes, may be run on different personal computers. Without aiming at completeness, some concrete examples of applications are described below.

Example 1: Types of Computer-Generated Outputs from the Simulation of Quenching and Tempering.

A simulation of quenching and tempering on a 100 mm (4 in.) diam steel cylinder was used to predict the microstructure and mechanical properties at 25 mm (1 in.) from the surface. The input data for the program were:

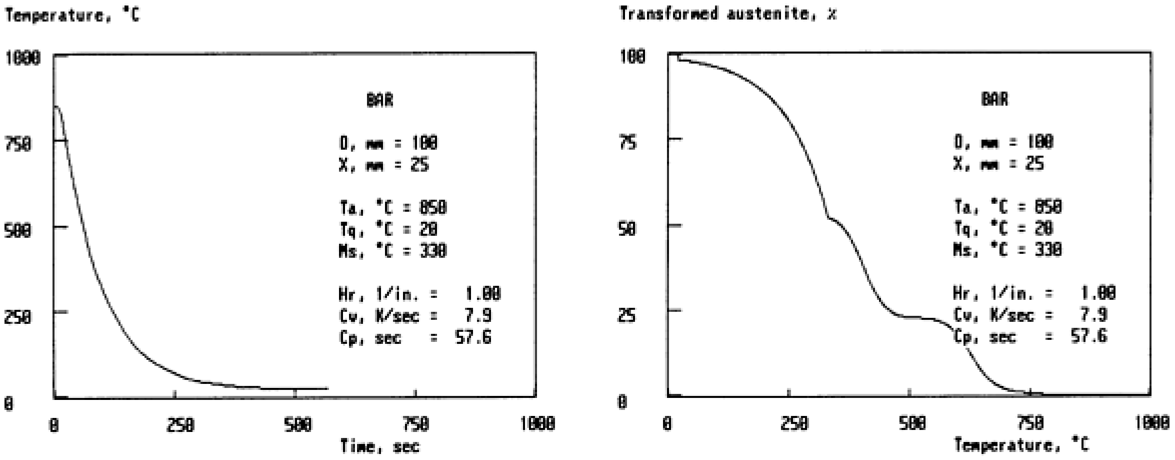
- Steel composition of 0.41% C, 0.25% Si, 0.75% Mn, 1.05% Cr, 0.13% Ni, 0.042% Mo, 0.04% V, and 0.15% Cu
- A prior normalized microstructure
- Austenitization at 850 °C (1560 °F) in a forced-air circulation furnace for 60 min

- Cooling in a quenchant at 20 °C (70 °F) having an H_R value of 39 m^{-1} (1.0 $in.^{-1}$)
- Tempering at 500 °C (930 °F) for 120 min

Figure 4 shows the output of the PPS program for the circumstances defined above. The program output provides the input data, predicted properties (Fig. 4a), the cooling curve (Fig. 4b), and the transformation of austenite (Fig. 4c).

```
      COMPOSITION:          C:41CR4     |     QUENCHING AND TEMPERING:
C % =  0.360 - 0.470        0.410       | cooling int. 1/inch          1.00
Si% =  0.070 - 0.430        0.250       | quenchant temp. °C            20
Mn% =  0.560 - 0.940        0.750       | tempering temp. °C           500
P % =  0.001 - 0.040        0.018       | tempering time, min          120
S % =  0.001 - 0.040        0.018       | Continue Y-CR?
Cr% =  0.850 - 1.250        1.050       |
Ni% =  0.080 - 0.400        0.130       |  A1 = 739             A3 = 787
Mo% =  0.020 - 0.120        0.042       |  Bs = 570             Ms = 330
V % =  0.001 - 0.080        0.040       |                       Cp(sec)=  57.6
Cu% =  0.100 - 0.300        0.150       |  AUSTENITE GRAIN SIZE    0.029520 mm,
                                        |  corresponding to       8 ASTM No.
GEOMETRY:bar-1, plate-2, Jominy-3       |  FERRITE+PEARLITE=  21.6  %
bar diameter, mm           100.0        |  BAINITE=  30.3 % MARTENSITE=  46.6 %
distance from  surface, mm              |
                             25.0       |  HARDNESS (QUENCHED)  43    HRC
                                        |  HARDNESS (TEMPERED)  33    HRC
    INITIAL STATE:                      |  TENSILE STRENGTH   1021    MPa
annealed  (1), normalized  (2)    2     |  YIELD STRENGTH      850    MPa
    AUSTENITIZATION:                    |  ELONGATION (A5)      14    %
temperature , °C             850        |  REDUCTION IN AREA    50    %
time,  min                    60        |  IMPACT ENERGY (KU)   52    J
```

(a)



(b) (c)

Fig. 4 Sample output of a PPS program. C_v refers to the cooling rate at 700 °C (1290 °F); C_p represents the cooling time from the austenitizing temperature (T_a) to 500 °C (930 °F). All other abbreviations defined in text (see Eq 12 and 13)

Generation of Transformation Diagrams. By running the program with systematic changes in the input data for the distance from the cooled surface and the H_R value, a transformation diagram system can be generated from the calculated results for cylindrical, plate-type workpieces and Jominy specimen (Ref 30). Figure 5 shows this type of transformation diagram for two different H_R values as indicated in the diagrams. Similar transformation diagrams can of course be developed for core transformations as a function of product diameter.

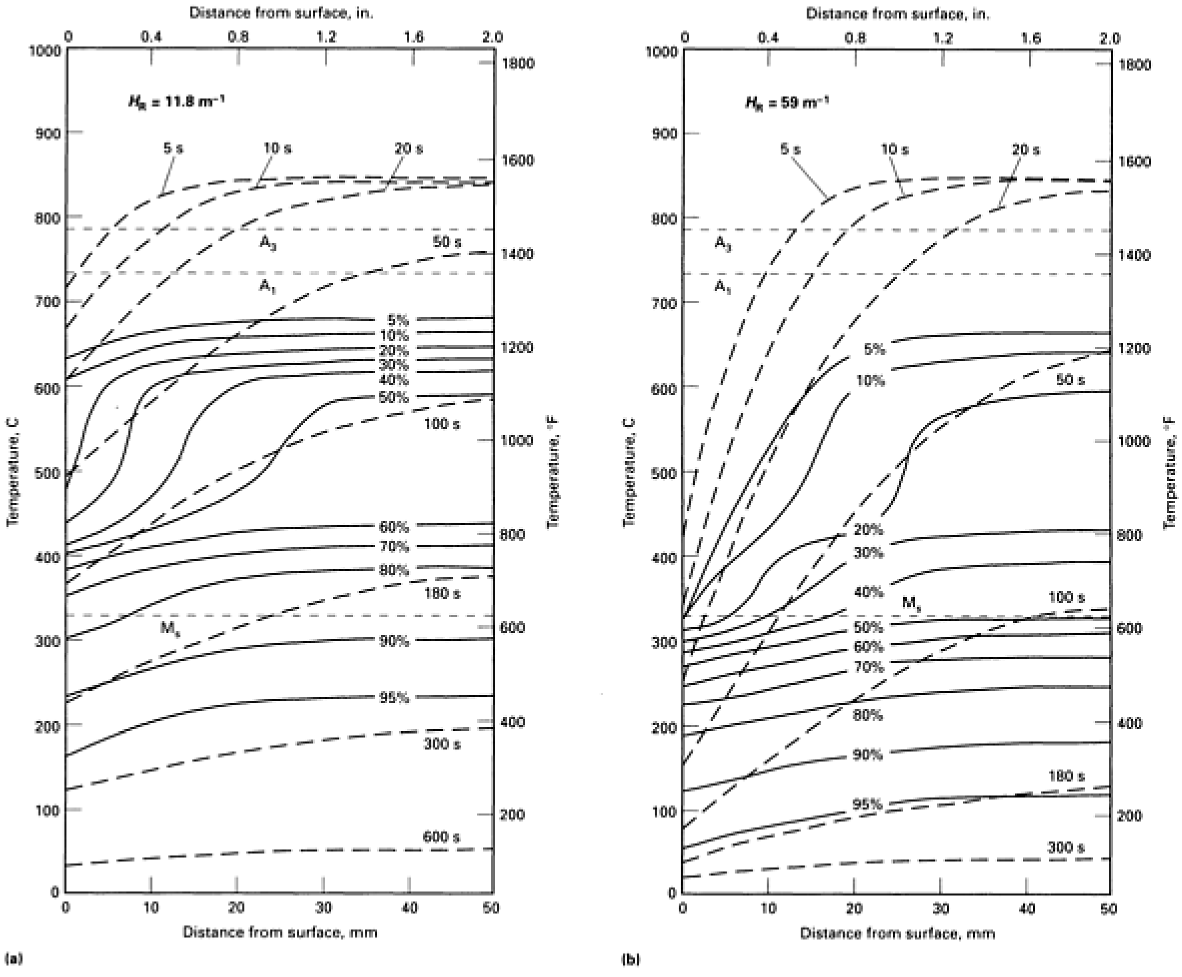


Fig. 5 Transformation diagrams generated by a PPS program for a 100 mm (4 in.) diam steel bar (0.41% C, 0.25% Si, 0.75% Mn, 1.05% Cr, 0.13% Ni, 0.042% Mo, 0.04% V, 0.15% Cu) with a prior normalized microstructure and with quenching intensities (H_R) of (a) 11.8 m^{-1} (0.3 in.$^{-1}$) and (b) 59 m^{-1} (1.5 in.$^{-1}$). The dashed curves represent temperatures at the indicated duration in seconds (s) and the solid lines represent the percentage of transformed austenite.

Microstructure and Property Generation. The percentage distribution of the reaction products at room temperature is shown in Fig. 6(a) and (b). The hardness distribution across the cross section after quenching and after tempering at 400 °C (750 °F), 500 °C (930 °F), 600 °C (1110 °F) for 2 his illustrated in Fig. 6(c) and (d).

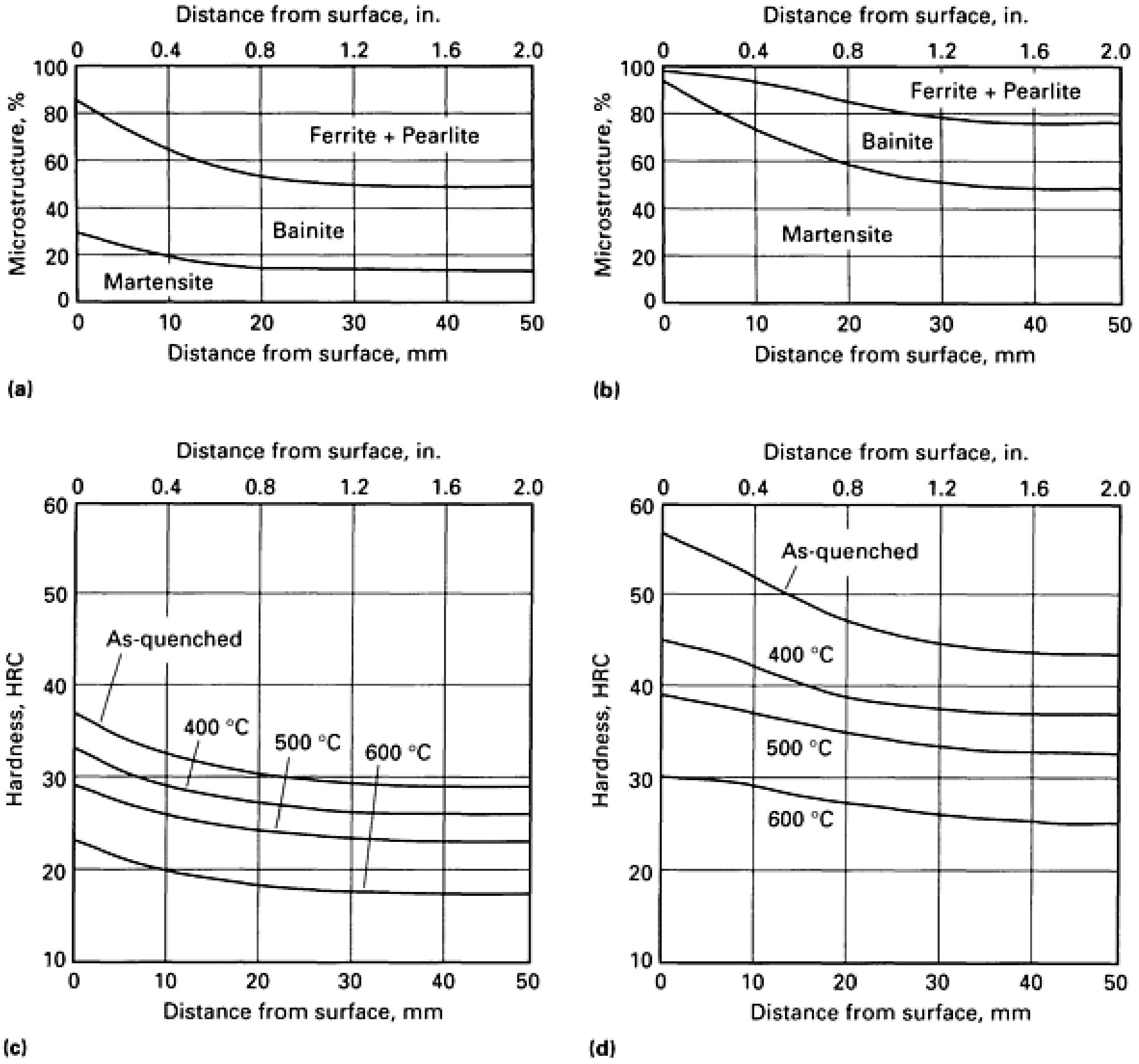


Fig. 6 Calculated values of microstructural constituents (a and b) and hardness values (c and d) from the transformation characteristics of Fig. 5

Figure 7 presents an alternative transformation diagram system used to determine core characteristics of cylindrical workpieces. Three different quench conditions are considered for 5140 steel specimens. In the first condition (see arrow 1 in Fig. 7), the user wants to know the starting temperature of the austenitc transformation in the core of 60 mm (2.4 in.) diam workpiece that has been quenched in a slow-cooling oil with H_R value of 11.8 m^{-1} (0.3 $in.^{-1}$). Starting with Fig. 7(b), arrow 1 has to be drawn horizontally until the line denoting a 60 mm (2.4 in.) diam is reached. The arrow is then continued vertically into Fig. 7(a) until the 5% ferritic transformation curve is reached. The arrow then travels to the left horizontally until the starting temperature, which is 660 °C (1220 °F), can be read.

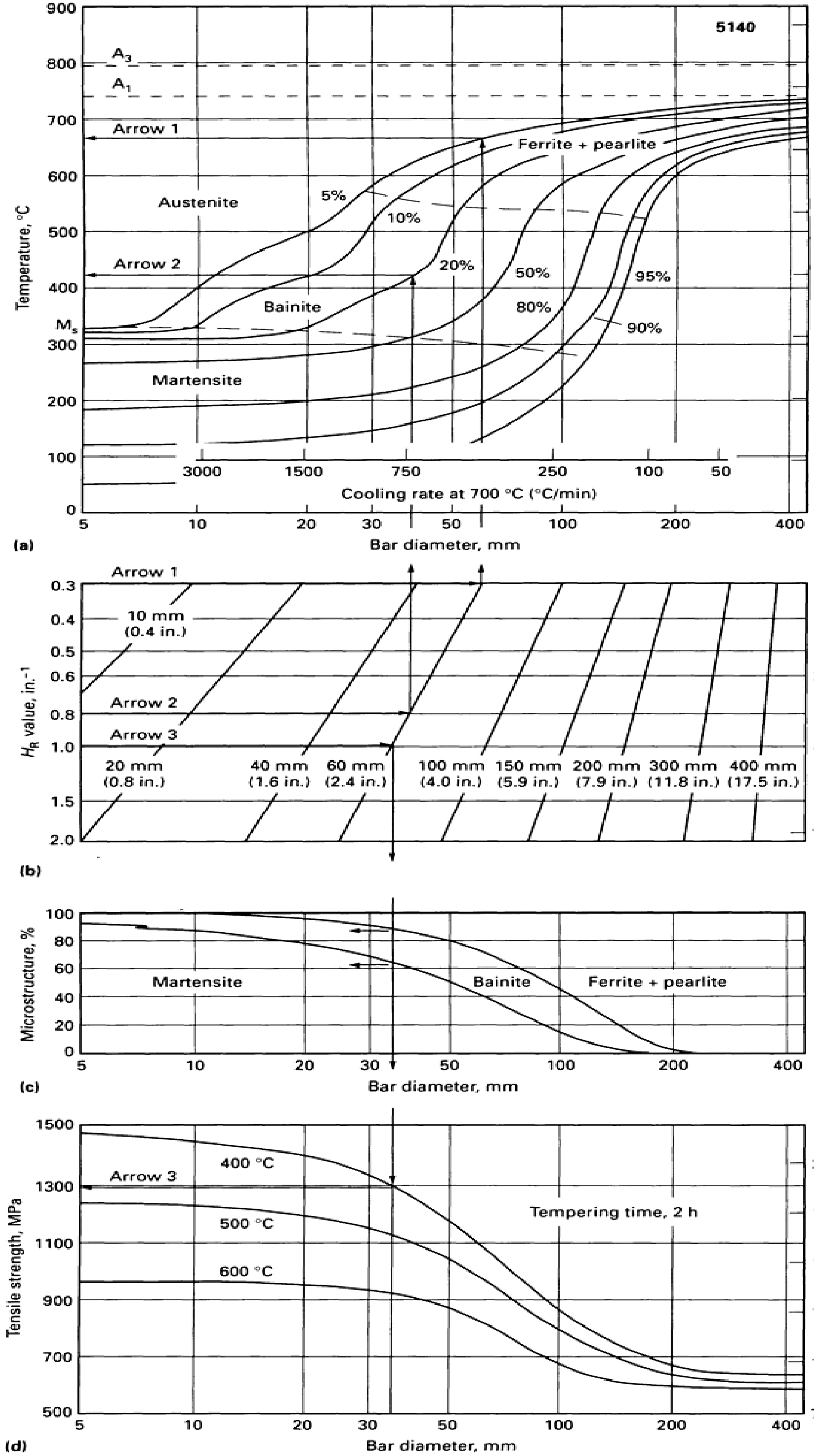

5140
A3
A1
Arrow 1
Ferrite + pearlite
Austenite
5%
10%
20%
50%
95%
Arrow 2
Bainite
80%
90%
Ms
Martensite
3000
1500
750
250
100
50
Cooling rate at 700 °C (°C/min)
Temperature, °C
Temperature, °F
Bar diameter, mm
(a)
Arrow 1
10 mm (0.4 in.)
Arrow 2
Arrow 3
20 mm (0.8 in.)
40 mm (1.6 in.)
60 mm (2.4 in.)
100 mm (4.0 in.)
150 mm (5.9 in.)
200 mm (7.9 in.)
300 mm (11.8 in.)
400 mm (17.5 in.)
H_R value, in.$^{-1}$
H_R value, m^{-1}
(b)
Microstructure, %
Martensite
Bainite
Ferrite + pearlite
Bar diameter, mm
(c)
400 °C
Arrow 3
500 °C
600 °C
Tempering time, 2 h
Tensile strength, MPa
Tensile strength, ksi
Bar diameter, mm
(d)

Fig. 7 Calculated transformation diagram system for the core of cylindrical workpieces quenched in different media. See text for details.

In the second condition (arrow 2), the diameter of the specimen is the same, but the cooling intensity of the quenchant (H_R-value) is 31.5 m^{-1} (0.8 $in.^{-1}$). The user now wants to know the temperature in the core when the ratio of the transformed austenitc is 20%. Starting again in Fig. 7(b), the arrow begins horizontally to 60 mm (2.4 in.), then travels vertically into Fig. 7(a) until the 20% value is reached, which corresponds to a temperature of 425 °C (797 °F).

For the third condition (arrow 3), the user wants to know the core microstructure after quenching and the core tensile strength after tempering at 400 °C (752 °F). Once again, a 60 mm (2.4 in.) diam specimen is used, but the quenchant is water with H_R value of 40 m^{-1} (1.0 $in.^{-1}$). Starting again in Fig. 7(b), the arrow travels horizontally to the line marked 60 mm (2.4 in.) then turns vertically downward until the lines for microstructure (60% martensite and 25% bainite as indicated in Fig. 7c) and the tempering curve are reached. As indicated in Fig. 7(d), the tempered core has a tensile strength of almost 1300 MPa (188 ksi).

Figure 8 and Table 4 compare measured and calculated (PPS) hardness values and tensile properties for low-alloy steels similar in composition to the steel described in the above example. As indicated from these data, calculated and measured values closely correlate.

Table 4 Comparison between measured and calculated mechanical properties of different machine parts made from low-alloy steels

Part	Chemical composition, %								Diameter		Heat treatment[(a)]	Tensile strength				Yield strength				Elongation, %		Reduction in area, %	
												Measured		Calculated		Measured		Calculated					
	C	Si	Mn	Cr	Ni	Mo	V	Cu	mm	in.		MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi	Measured	Calculated	Measured	Calculated
Spring saddle	0.47	0.33	0.70	1.1	0.1	0.04	0.03	0.18	24	0.94	860/120/OQ/540/120	1007	146	999	145	936	136	919	133	14	18	. . .	59
Front axle	0.32	0.26	0.60	0.92	0.11	0.03	0.13	0.19	50	2.0	840/240/WQ/530/120	856	124	875	127	762	110	785	114	19.6	20.7	67.6	64.1
Crankshaft	0.36	0.27	0.66	0.91	0.19	0.04	0.04	0.18	78	3.1	850/300/WQ/600/120	856	124	867	126	712	103	745	108	19.4	20	61.5	62.4
Front axle	0.43	0.24	0.57	0.2	0.08	0.02	0.01	0.13	30	1.2	900/200/WQ/570/120	950	138	985	143	770	112	813	118	15.5	15.2	48.5	52.2
Front axle	0.42	0.26	0.72	1.1	0.1	0.03	0.02	0.19	50	2.0	850/240/OQ/630/120	799	116	804	117	649	94	634	92	19	20.4	62.8	62.6
Front axle	0.42	0.31	0.84	1.0	0.13	0.18	0.05	0.16	25	1.0	860/216/OQ/570/120	1025	149	1018	148	949	138	937	136	17	18.3	59	60.1

(a) Heat-treatment procedures shown represent the austenitization temperature in °C/austenitization time in minutes/quenching/tempering temperature in °C/tempering time in minutes. OQ, oil quenching; WQ, water quenching; PQ, polymer quenching

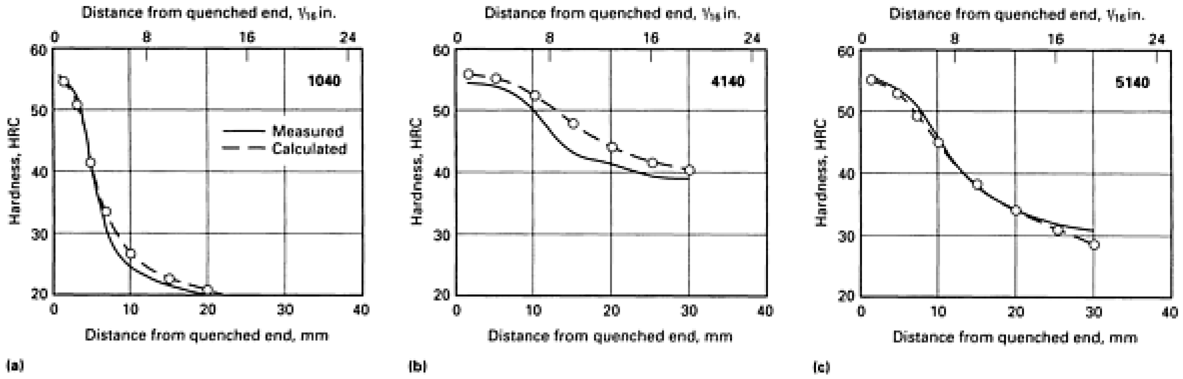


Fig. 8 Comparison between measured and calculated Jominy curves for 1040 (a), 4140 (b), and 5140 (c) steels

Example 2: Designing a Heat-Treatment Method.

This example describes a technology planning system for producing optimum properties of heat-treated steels. The goal was to achieve a specified yield point of 780 MPa (113 ksi) at 16 mm (0.6 in.) below the surface of a cylindrical steel specimen (0.42% C, 0.31% Si, 0.85% Mn, 1.02% Cr, 0.05% Mo, 0.07% Ni). Because applicable standards for this steel called for a yield point value of only 510 MPa (74 ksi) in the range of 40 to 100 mm (1.6 to 4 in.), the first question that had to be answered was whether the 780 MPa (113 ksi) value could be achieved with the available steel.

Figure 9 shows the flow chart of the technology planning system used to determine the most effective heat treatment/ property combination. The input data are shown on the left side of the flow chart. Important parameters addressed are:

- Chemical composition of the workpiece to be heat treated
- The initial state of the workpiece prior to heat treatment
- Geometrical and quenching conditions
- The required properties after heat treating

The predictor unit (PPS detailed above) starts the calculation. For this, it needs preselected initial process parameters. Then the predicted properties are compared with the required properties. If one of the calculated properties is less than the corresponding prescribed property, the process parameters are modified. The loop continues until the calculated properties are better than the required ones. Then the process parameters are printed. Table 5 outlines the heat treatment predicted to provide the desired properties.

Table 5 Calculated heat-treating parameters for the low-alloy steel workpiece described in Example 2

Parameter	Value
Input data	
Chemical composition	C = 0.42%
	Si = 0.31%
	Mn = 0.85%
	Cr = 1.02%

	Mo = 0.05%
	Ni = 0.07%
Initial state	Normalized
Type of heating	Air chamber
Diameter, mm (in.)	72 (2.8)
Distance from surface, mm (in.)	16 (0.6)
Prescribed mechanical properties:	
Hardness (minimum), HRC	22
Tensile strength, MPa (ksi)	920 (133)
Yield strength, MPa (ksi)	780 (113)
Elongation, %	14
Reduction of area, %	60
Charpy value, J (ft · lbf)	60 (44)
Proposed heat treatment	
Austenitization, °C (°F)	840 (1545)
Holding time, min	110
Quenchant	Water
Tempering, °C (°F)	580 (1075)
Holding time, min	120

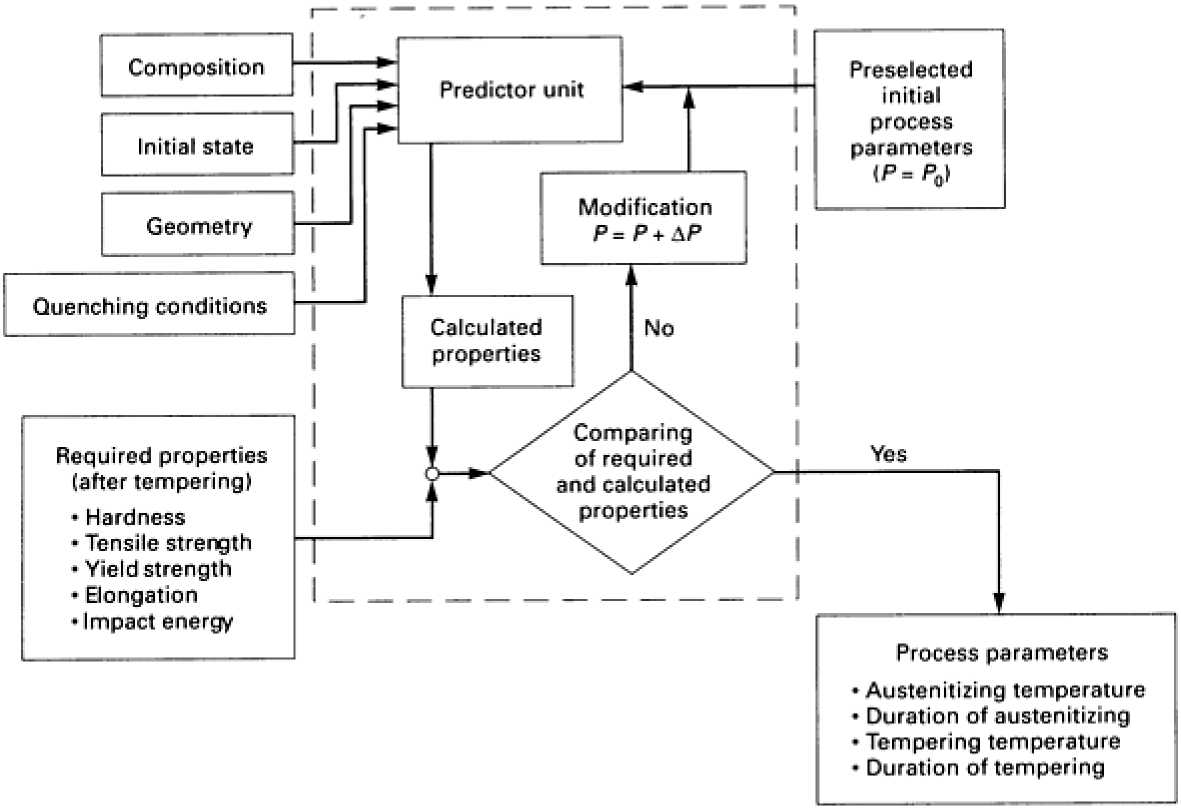


Fig. 9 Block diagram of the technology planning program of a property prediction system

Example 3: Selection Program for Hardenable Steels.

The analysis of the mechanical properties of the different steel grades as well as the systematization of the derived relationships among these properties can be utilized in practical steel selection. This example describes a steel selection procedure for hardenable steel grades, which can be characterized by their Jominy end-quench bands.

Figure 10 shows the flow chart of the steel selector software. The left side of the figure contains the input parameters, the inner side contains the algorithm, the right side of the figure shows necessary data that are stored in a data base and are used by the program, and in the bottom of the figure the output data can be seen.

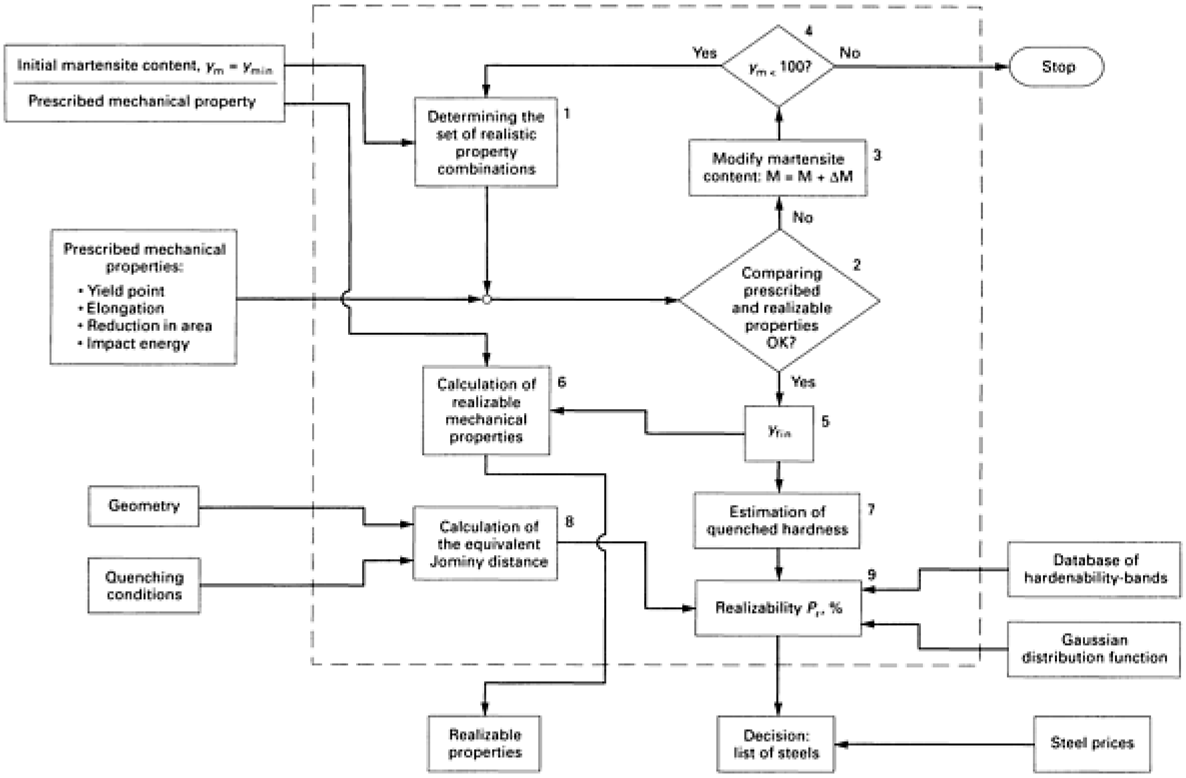


Fig. 10 Block diagram of a computer program used for the selection of hardenable steels

Suppose the following mechanical properties are prescribed: tensile strength (R_m), yield point (R), elongation (A_{50}), reduction in area (Z), and impact energy (KU). First, the knowledge concerning the steel properties and their correlations among each other are checked with formulas similar to Eq 30, 31, 32, and 33. The calculation is started with a predefined initial martensite content $y_m = Y_{min}$ and the given R_m value. According to the flow chart (Fig. 10), the output of Unit 1 is a set of realizable mechanical properties, calculated with the initial minimum martensite content on the basis of the prescribed tensile strength.

Unit 2 (Fig. 10) compares this output to the input requirements. If any of the requirements are not fulfilled, the initial martensite content has to be increased by a small amount Δy_m in Unit 3. The calculation is then executed with this martensite content, and the martensite content is increased again and again to the very y_{fin} value that satisfies the requirements. In this loop, it is controlled by Unit 4, whether the martensite content is less than 100%. If the martensite content reaches 100%, and the realizable properties still do not meet the requirements, it means that none of the case-hardened or quenched and tempered steels can be used to achieve the given properties. With this value y_{fin}, the realizable mechanical properties are then calculated in Unit 6.

The next decision in the selection procedure is based on the Jominy hardenability band (see Fig. 11). Unit 7 estimates the minimum hardness J_q, which has to be realized after quenching. This value is one of the inputs of Unit 9, which has the most important role in the decision procedure. The second input comes from Unit 8. For a given point on the workpiece, where the properties are prescribed, a distance E from the quenched end on the Jominy bar, where the quenching conditions are very similar, must be determined. This is called equivalent Jominy distance, E_e.

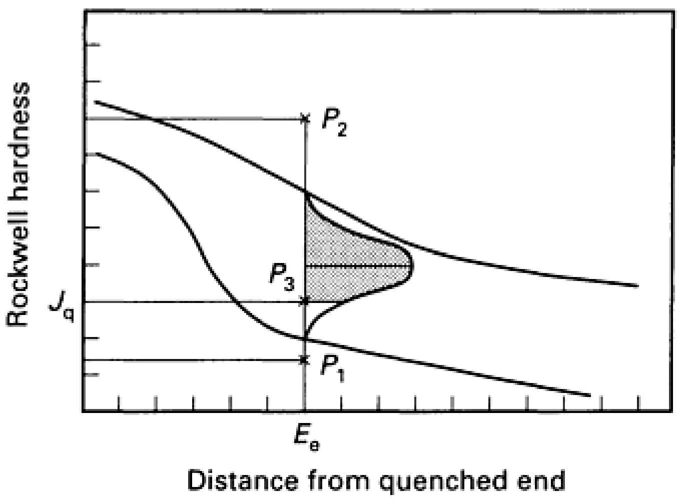


Fig. 11 Illustration of the hardenability parameters in the steel selection program

The calculated E_e and J_q values determine a point in the coordinate system in Fig. 11. Three possible positions of this point (E_e, J_q) may occur (Fig. 11):

- Point P_1 is below the hardenability band and even the lowest allowed hardenability curve will result in a higher quenched hardness than the necessary hardness J_q
- Point P_2 is above the upper curve of the hardenability band and meeting the prescribed hardness requirements with this steel is out of the question
- Point P_3 is between the two curves. Normally, it can be supposed that at this E_e Jominy distance, the hardnesses of the steel grade follow the Gaussian distribution (Fig. 11). The probability of achieving J_q hardness is proportional to the shaded area and can be calculated from the Gaussian distribution function. This probability in percentage is called realizability P_r

The Jominy bands of the standard steel grades are stored in a data base, from which Unit 9 retrieves them one after the other and calculates the realizability for every steel. It is reasonable to predefine a limit, for example 70%, and in case the realizability is less than this value, the steel grade will not be included in the list of steels, which will probably satisfy the hardness requirement. Another data base shown in the right side of Fig. 10 contains the price of the steels, which is displayed then together with the realizability to the designer's convenience.

Reference cited in this section

30. M. Gergely and T. Réti, Application of a Computerized Information System for the Selection of Steels and Their Heat Treatment Technologies, *J. Heat Treat.,* Vol 5 (No. 2), 1988, p 125-140

Computer Prediction of Process Parameters for Gas Carburizing

Gas-carburizing practice involves either a single-stage or, even more so, a two-stage boost/diffuse technique to produce the desired carbon profile and hardness distribution on the workpiece surface. In what follows, a simulation program is outlined that helps the user in steel selection and the heat treater to minimize the total time required for one- or two-stage gas-carburizing processes controlled in terms of carbon potential. The block diagram of the program is shown in Fig. 12.

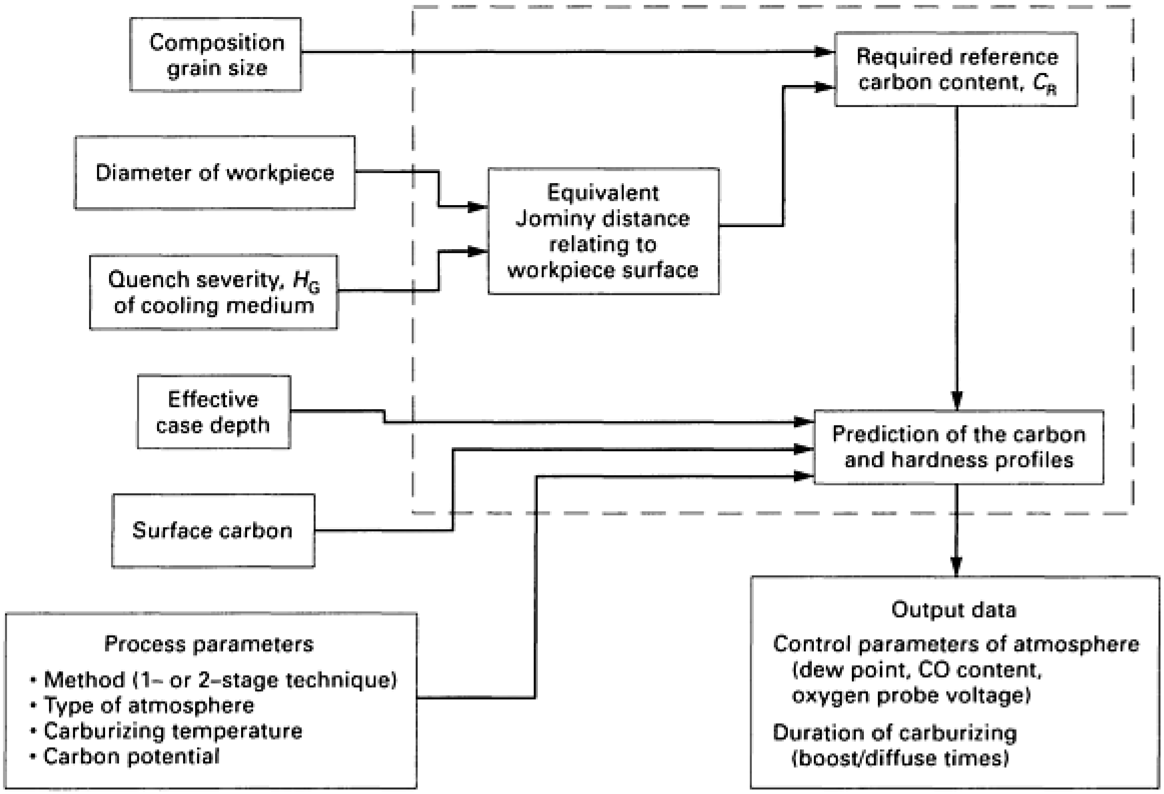


Fig. 12 Block diagram of the simulation model used for process planning of gas carburization

The computing algorithm simulates the total carburizing process, predicts the carbon and hardness profile after quenching and calculates the main process parameters of practical interest (Ref 35, 36). The input data on the left side of the block diagram are as follows:

- Data on the steel grade (chemical composition, grain size)
- Diameter of the workpiece (supposed to be a cylindrical bar)
- Quench severity of the quenchant used for quenching after carburizing (H_G = Grossmann quench factor)
- Effective case depth, *d*, defined in terms of either a prescribed reference carbon content, C_R, or as a depth to 52.5 HRC required after quenching
- Data on the process parameters such as technique of carburizing, type of atmosphere, carburizing temperature in the boost and the diffusion period, carbon potential, and so on

The output data are:

- Data on the atmosphere composition required to control the carburizing process (dew point, CO_2 content, oxygen probe voltage, and so forth)
- Calculated values of the time parameters of carburizing
- Predicted carbon profile and hardness distribution curve generated as a function of the distance below surface

The algorithm used to predict the hardness distribution on the basis of the calculated carbon profile is of particular importance in the applied model. The basic principle of this algorithm proposed by Wyss is demonstrated in two examples (Ref 37).

Example 4: Prediction of Case Hardness from the Carbon Profile of a Carburized Steel.

Assuming that the carbon profile has already been calculated (Fig. 13), the task now is to predict the hardness value HRC_1 in an arbitrarily selected distance d_1 = 1.25 mm (0.05 in.) below the surface on the basis of the corresponding case carbon content C_1 = 0.4%. As an example, let us take a cylindrical bar of diameter D = 50 mm (2 in.) made of case-hardenable steel, which must be quenched after carburizing in oil characterized by the quench factor H_G = 0.6. If the Jominy curves for the carburized steels are available, the unknown hardness value HRC_1 can be predicted using the relationship between the bar diameter D, the value H_G, and Jominy curves of the carburized steel.

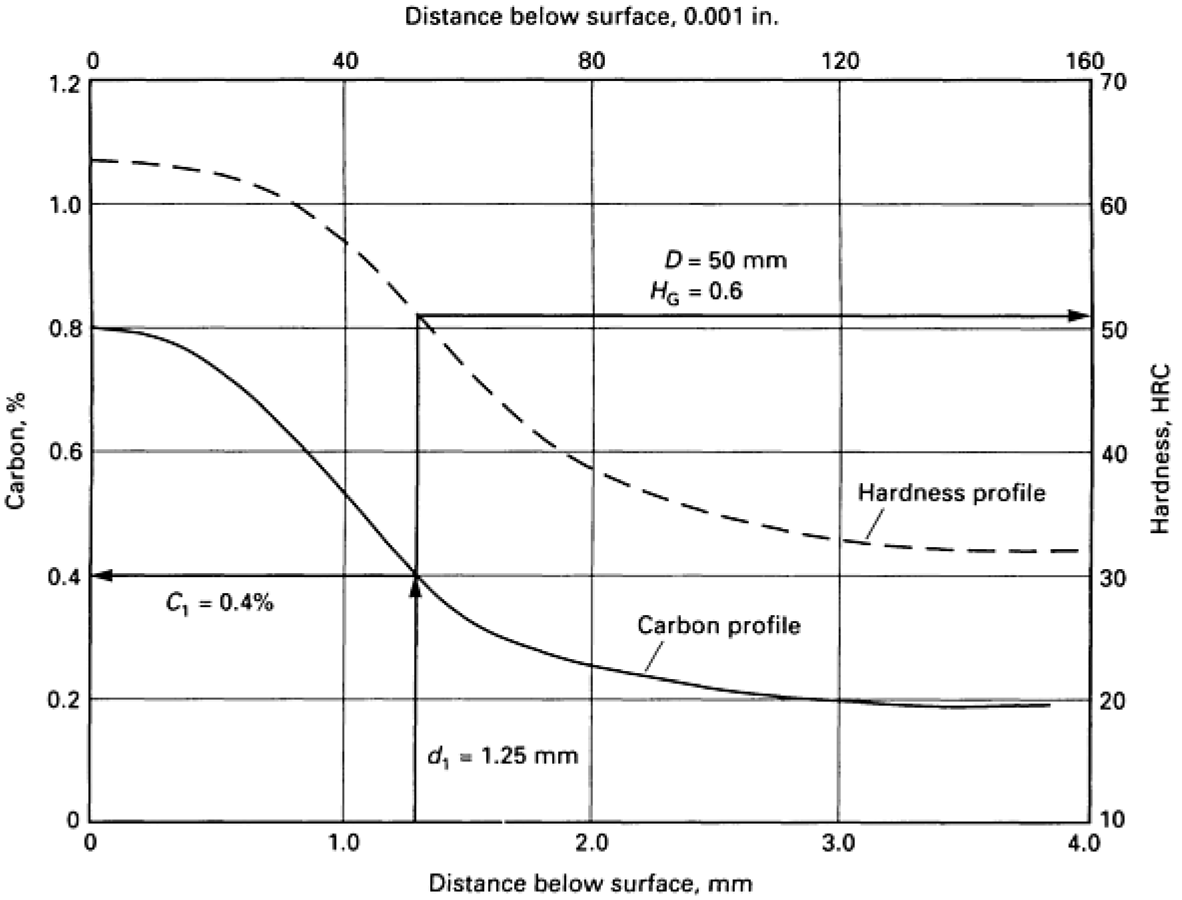


Fig. 13 Relation between the carbon profile and hardness in a carburized case

If the Jominy curve is not available, the Jominy curve of a steel in the composition range given below may be computed by the empirical formula derived by Just (Ref 2):

$$J_{6\text{-}80} = 95\sqrt{C} - 0.00276\,E^2\sqrt{C} - 12.28\sqrt{E} + 0.898\,E - 0.81G + 20\text{Cr} + 38\text{Mo} + 14\text{Mn} + 5.5\text{Ni} + 6.1\text{Si} + 39\text{V} + 96\text{P} - 13 \quad \textbf{(Eq 34)}$$

where E is the Jominy depth in mm, G is the ASTM grain size, and J is the calculated Rockwell hardness. This formula is applicable for steels with the following ranges: 0.13 to 0.55% C, 0.15 to 1.40% Si, 0.4 to 1.78% Mn, 0.11 to 2.07% Cr, 0 to 0.25% Mo, 0.01 to 2.02% Ni, 0.01 to 0.12% V, 0.008 to 0.035% P, and 6.5 to 10.5 ASTM grain size (G). The calculated Jominy curves for the steel described above with the core carbon content of 0.2% and a case carbon content of 0.4% are shown in Fig. 14.

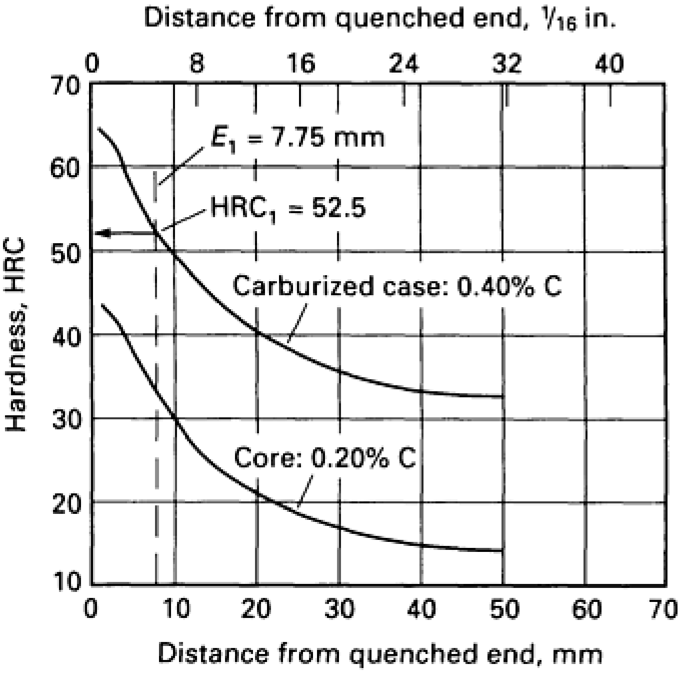


Fig. 14 Prediction of the hardness profile on the basis of computed Jominy curve of a carburized steel (0.20% C, 0.8% Mn, 0.6% Cr, 0.55% Ni, 0.20% Mo)

In order to determine the unknown hardness value HRC_1, the equivalent Jominy distance, E_1, must be determined. This Jominy depth, E_1, can be estimated on the diagram proposed by Grossmann (Fig. 15). This diagram enables the computation of the equivalent Jominy distance as a function of the bar diameter and the value H_G. The relationship between the E, D, and H_G can be represented by the following equation:

$$\log E = \left\{0.23581 - 0.28155 \ln H_G + 0.18904\sqrt{H_G} - 0.000052D\right\}\log D \qquad \textbf{(Eq 35)}$$

where the Jominy depth E and bar diameter D are in mm, and H_G value is in in.$^{-1}$. This formula is valid for 5 to 300 mm (0.2 to 12 in.) bar diameters and an H_G value of 8 to 80 m^{-1} (0.2 to 2 in.$^{-1}$).

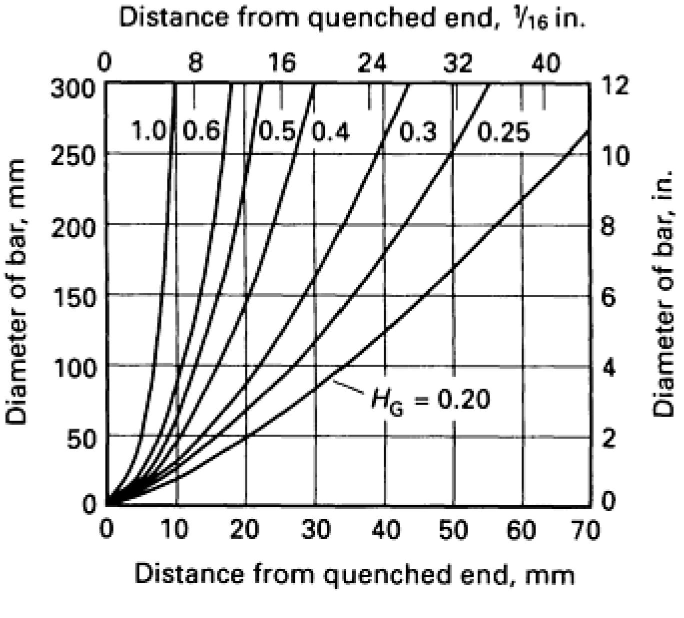


Fig. 15 Curves showing correlation between rates of cooling in the Jominy specimen and rates of bars cooled in various quenching media. The diagram applies to the surface of a cylindrical bar.

Substituting the corresponding values D and H_G into Eq 35, E_1 = 7.75 mm (0.3 in.) can be obtained. The use of the diagram in Fig. 15 leads to the same result. Knowing value E_1, the hardness belonging to distance d_1 can be obtained from the Jominy curve in Fig. 14, that is, HRC_1 = 52.5 HRC.

Example 5: Determination of Required Carbon Profile for a Specified Case Depth in a Carburized Steel.

If the effective case depth is defined as depth to a specified hardness such as 52.5 HRC (550 Hv), and is used as an input to the model, the reference carbon content C_R necessary to achieve that hardness must be calculated on the basis of the previously detailed considerations. It is clear that the required reference carbon content is determined by the chemical composition, grain size, bar diameter, and quench severity of the cooling media. In case of a given steel composition, the reference carbon content C_R depends on the bar diameter D and the H_G value of the quenchant. This conclusion is demonstrated by computation results for the 4820 steel (0.20% C, 0.65% Mn, 3.5% Ni, 0.25% Mo) in Fig. 16. The required value of C_R may vary significantly as a function of bar diameter and of the cooling power of the quenchant. In practice, the value of reference carbon content is chosen in the interval 0.33 to 0.45%. This is because if C_R is less than 0.33%, the necessary surface hardness cannot be achieved; on the other hand, if C_R is higher than 0.45%, the required carburizing time increases considerably.

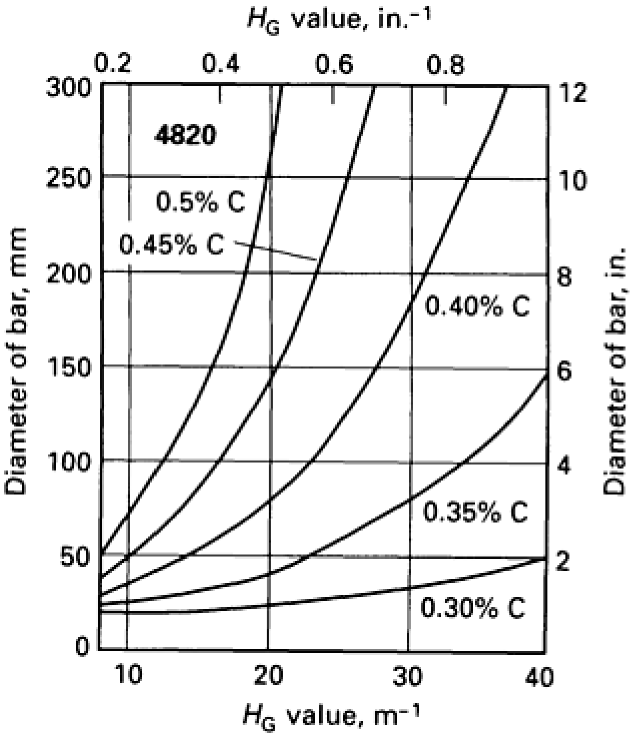


Fig. 16 Relationship between diameter of workpieces, Grossmann's quench factor, and the reference carbon content necessary to achieve the specified case hardness defined as 52.5 HRC (550 HV)

Analysis of Process Parameters. Simulation of gas carburization allows the analysis of different process parameters such as temperature, steel composition, carbon potential, part size, and treatment time. All of these variables affect the carbon profile, and the resulting case hardness for a given quench. By using the computer simulation, several kinds of carburizing cycles can be tested and compared, and there is no need for expensive and time-consuming heat-treatment experiments.

PREDCARB (Ref 35, 36) is an example of a simulation program developed for the analysis of gas-carburization cycles. A simulation run of this program was performed for 8620H steel (0.2% C, 0.28% Si, 0.8% Mn, 0.5% Cr, 0.55% Ni, 0.2% Mo) with the following input parameters:

- 50 mm (2 in.) diam bar
- Quench intensity of 24 m^{-1} (0.6 $in.^{-1}$)
- Atmosphere of 20.5% CO and 40.5% H_2 for both the boost and diffuse periods
- ASTM grain size of 7
- Effective case depth of 1.25 mm (0.05 in.) defined by a hardness of 550 HV (52.5 HRC)
- Surface carbon content of 0.8%
- Boost temperature of 900 °C (1650 °F)
- Boost carbon potential of 1.15%
- Diffuse temperature of 900 °C (1650 °F)

From these parameters, a 12.5-h boost period and a 1.3-h diffuse period were the predicted time periods necessary to achieve the specified case and hardness profiles shown in Fig. 17. These predicted process times can then be varied as a function of different process variables such as workpiece/specimen diameter, quench severity, core carbon content or the carbon potential during the boost phase.

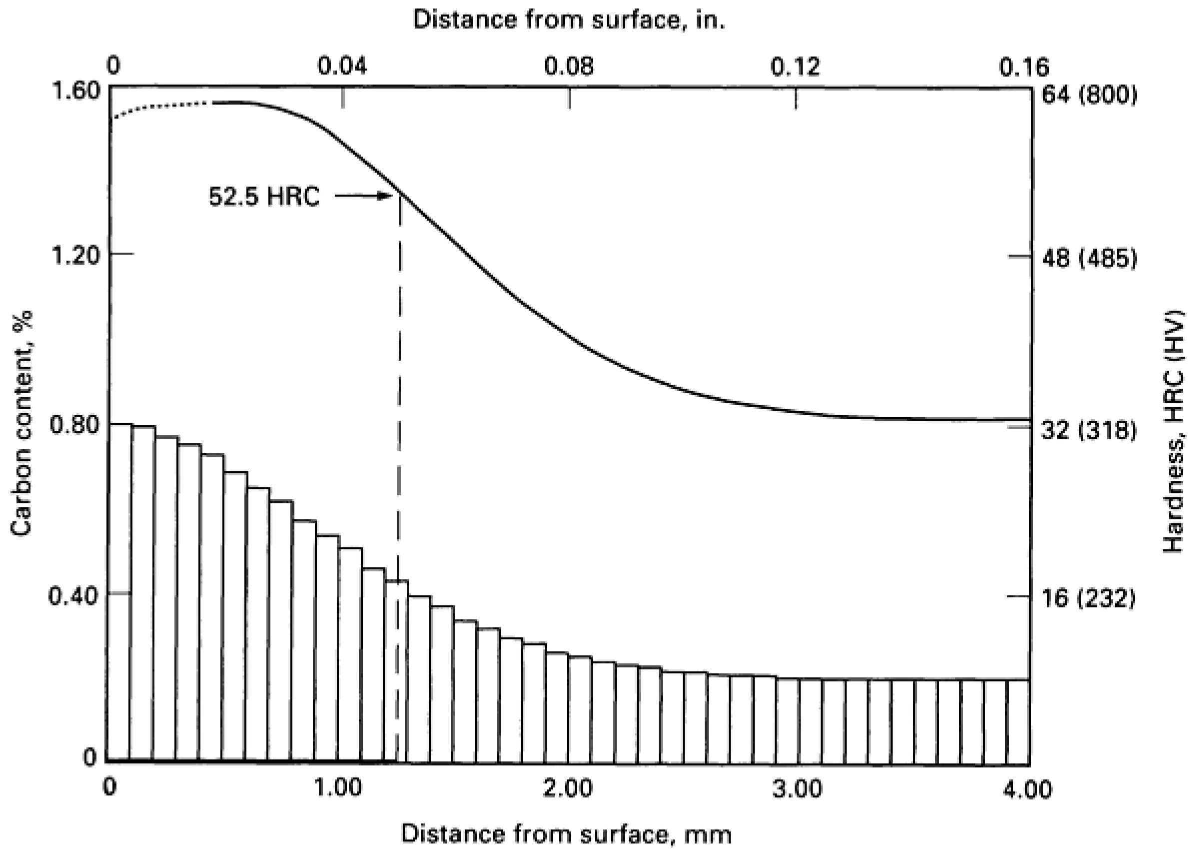


Fig. 17 Calculated carbon and hardness profiles for two-stage carburizing of an 8620H steel. The effective case depth of 1.25 mm (0.05 in.) is defined by a hardness of 52.5 HRC (550 HV).

For example, in order to demonstrate how the workpiece diameter and the H_R value influence the duration of a two-stage gas-carburizing process, Table 6 summarizes some computational results for the required boost time, t_A, the diffuse time, t_B, and reference carbon content. As indicated by these data, the time required for carburizing can be reduced considerably by decreasing the diameter of the workpiece or by increasing the quench severity of the cooling medium.

Table 6 Effect of workpiece diameter and quench severity on process times and reference carbon content during two-stage gas carburizing in endothermic atmosphere from natural gas. Effective case depth to 52.5 HRC is equal to 1.25 mm (0.05 in.)

Process parameters[(a)]	**Diameter of workpiece**			**Quench factor, H_R**	
	25 mm (1 in.)	**50 mm (2 in.)**	**100 mm (4 in.)**	**m^{-1}**	**$in.^{-1}$**
Boost time, h	13.6	19.5	. . .	11.8	0.3
Diffuse time, h	1.4	2.1	. . .	11.8	0.3
Reference carbon content, %	0.46	0.54	>0.6	11.8	0.3
Boost time, h	10.4	12.5	16.1	23.6	0.6
Diffuse time, h	1.0	1.3	1.7	23.6	0.6
Reference carbon content, %	0.41	0.44	0.5	23.6	0.6

(a) Required surface carbon content: 0.8%: Boost and diffuse temperature: 900 °C (1650 °F); Boost carbon potential = 1.15%; Diffuse carbon potential: 0.8%

Figure 18 shows the relationship between the core carbon content and the predicted process time for a carburized low-alloy steel (0.16% C, 0.32% Si, 0.49% Mn, 1.03% Cr, 3.04% Ni, 0.22% Mo). A nitrogen/methanol mixture (CO% = 19.7) was used during the boost stage; the diffuse period utilized pure nitrogen. Other carburizing conditions included:

- Boost/diffuse treatment at 930 °C (1705 °F) to produce a case depth of 0.8 mm (0.03 in.) based on a reference carbon content of 0.35%
- Boost carbon potential: 1.1%
- Diffuse carbon potential: 0.7%

As can be seen in Fig. 18, by increasing the core carbon content, the time of a two-stage carburizing process can be decreased and energy subsequently saved.

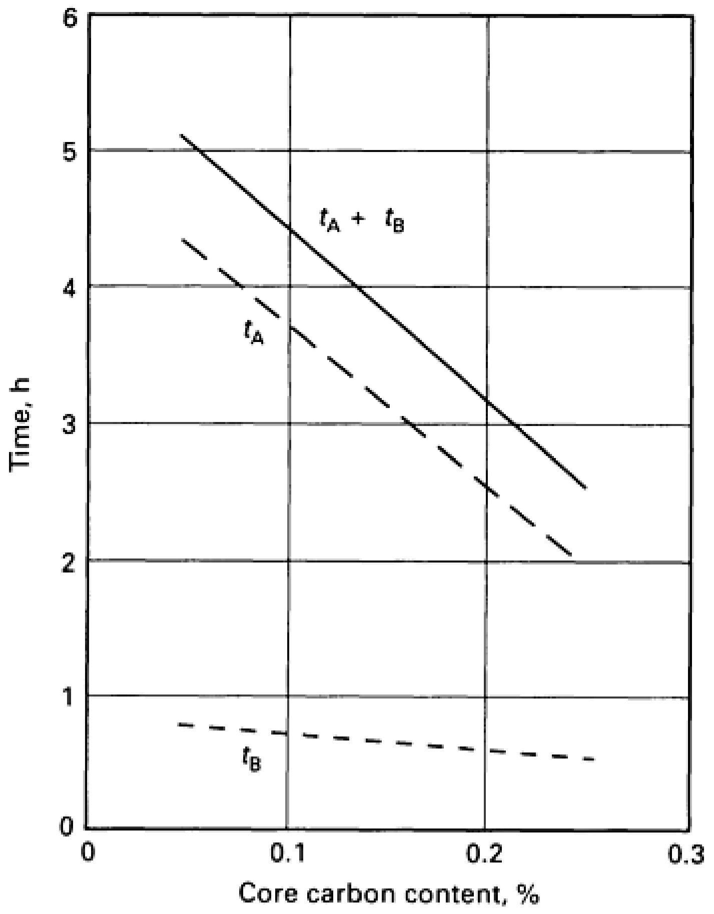


Fig. 18 Relationship between core carbon content of steel and predicted process times for two-stage carburizing in nitrogen/methanol-based atmosphere at 930 °C (1700 °F) (t_A = boost time, t_B = diffuse time, and t_A + t_B = total time)

Figures 19 and 20 compare measured and predicted (PREDCARB) values for hardness profiles, carbon profiles, and case depths for low-alloy steels similar in composition to the steel described in the above example. In Fig. 19, a steel bar (0.18% C, 0.34% Si, 0.91% Mn, 0.61% Cr, 0.4% Ni, 0.2% Mo) was given a boost/ diffuse treatment at 930 °C (1705 °F) using an endothermic atmosphere derived from natural gas to produce a case depth of 1.3 mm (0.05 in.). The case depth is defined as the depth that corresponds to the prescribed reference carbon content of 0.35% C.

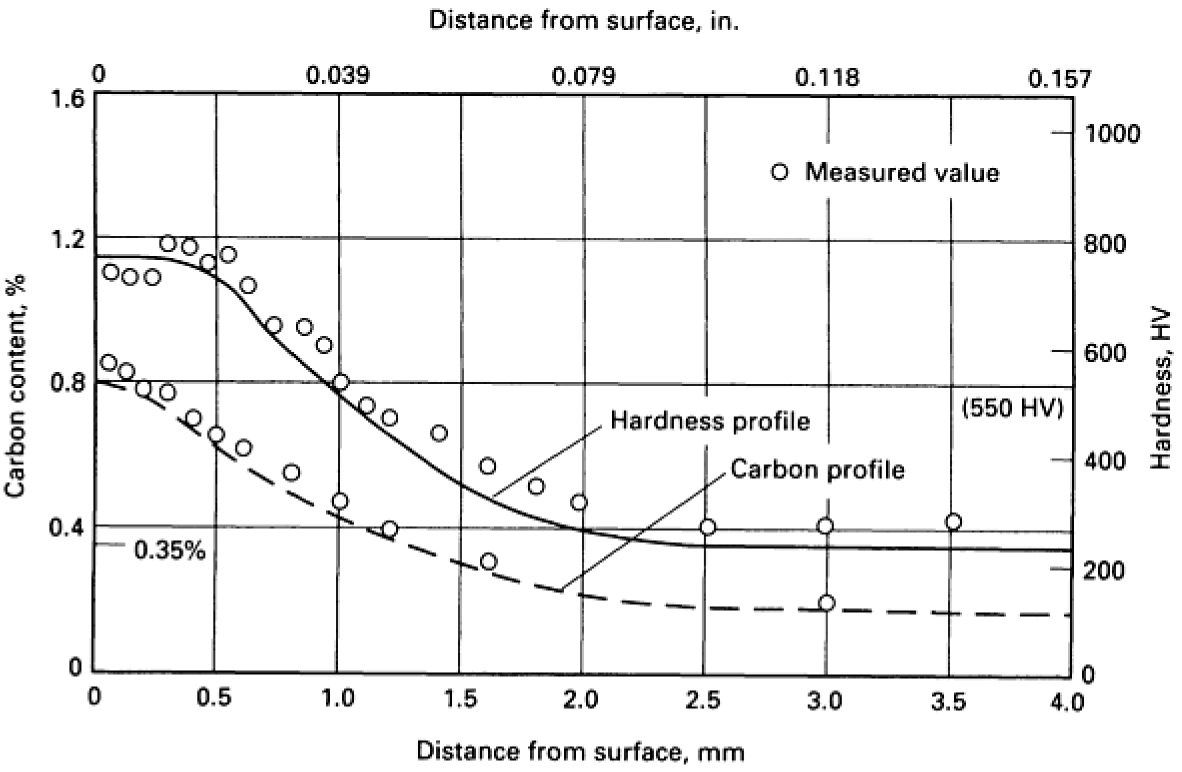


Fig. 19 Comparison of the measured and predicted carbon and hardness profiles in a carburized case of an oil quenched 50 mm (2 in.) diam bar. Steel composition: 0.18% C, 0.34% Si, 0.91% Mn, 0.61% Cr, 0.4% Ni, 0.2% Mo

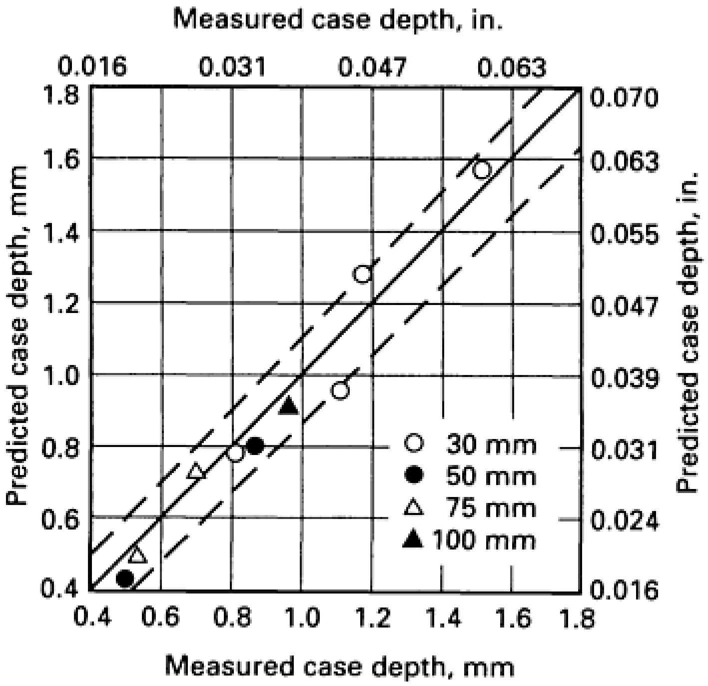


Fig. 20 Comparison of the measured and predicted case depths after boost/diffuse gas carburizing and oil quenching of low-alloy steels

Heat-treating parameters were:

- Boost conditions: 7 h at 1.06% carbon potential
- Diffusion conditions: 1.5 h at 0.78% carbon potential
- Quench from 850 °C (1560 °F) in oil
- Estimated quench severity: *H* = 0.25
- Oil temperature: 60 °C (140 °F)

Figure 20 compares the measured and predicted case depths taken from a variety of low-alloy steels after boost/diffuse gas carburizing and oil quenching treatments similar to those described in Fig. 19. The effective case depth was defined as the depth that had a hardness value of 550 HV measured with a 500 g load. The estimated quench severity was between 0.25 and 0.35. As can be seen in both Fig. 19 and 20, PREDCARB-predicted values closely matched the actual measured values.

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Furnace Safety in Heat Treating

Revised by Raymond Ostrowski, Protection Controls, Inc.

Introduction

HEAT-TREATING FURNACES require safety procedures common to all industrial installations, but they also have requirements specific to the use of high-temperature energy sources and potentially explosive gases and liquids used as aids to chemical processing.

Because these heat-treating processes require careful control for optimum technical results and for safety, proper training of operating personnel is a primary consideration. Proper equipment design is also critical.

The information presented here is not intended to be interpreted as a safety standard but is offered only as a set of guidelines. Safety standards for furnaces are maintained by the National Fire Protection Association (NFPA), by the U.S. Occupational Safety and Health Administration (OSHA), and by insurance underwriters.

All equipment should be installed and operated with awareness of the potentials for fire and explosion and the hazards to operators and equipment. Equipment designs should ensure reliable, safe operation over the expected maximum life of the equipment.

Fuel-Fired Furnaces

Fuel-fired furnaces for heat treating have several major control requirements that depend on whether the process must be directly or indirectly fired; whether heat treating is to be done under a particular pressure or vacuum, or in a controlled atmosphere; and whether the product uses a special precoat or laminant. In all situations there are fundamental control variables, and instrumentation is available to identify and control change and drift, thus achieving the desired results.

The main control elements are the three requirements for proper combustion: a source of heat, an oxidizing agent, and time.

Fuel-fired furnaces can be automated to the extent that manual intervention is not required for normal operation. However, many processes and operations require manual control, thereby furnace controls range from almost completely manual devices to highly sophisticated computer-controlled devices.

The major control variables and types of instrumentation used in each instance are described below, in sequence, from startup through final cycle control.

Electrical Power for Fuel-Fired Furnaces

The safe use of electrical energy employed in heat-treating control processes requires adherence to National Electrical Codes and to local requirements of states and communities. Good practice dictates that a circuit breaker be positioned within view of the operator. Control cabinets must be designed to ensure that operators cannot inadvertently become a path to ground. Wiring type should be based on the environment of use, and wiring for all motor and control circuits should be contained in appropriate conduits. Numbers of wires within specific conduits should be governed by the fact that elevated temperatures may be encountered. All enclosures for electrical apparatus should be designed to protect the contents from the environment. The furnace should be grounded for proper control.

The source of electrical power to the furnace installation should be equipped with fuses. Each motor should also be equipped individually with fuses and protected with thermal-overload elements based on operating temperatures. Motor selection should be based on such conditions of use as temperature, weather, dust, dirt, atmosphere, and humidity. Manufacturers should be consulted on motor design and selection. Control-panel power should be fused and provided with externally operated switches to allow safe entry by authorized personnel.

Electronic-signal wiring from the flame-safety circuits should have its own conduit, free from the "noise" and induction present in normal power and control circuits. Thermocouple wiring also should be contained in its own conduit to avoid creating induced errors from such random sources as power lines, signal wiring, motors, and ballasts.

Control Circuits for Fuel-Fired Furnaces

Combustion-Air Blower Control. Combustion-air blowers must be interlocked with the combustion-limit circuits to shut down the process in the event of failure. The flow of combustion air must always be proven before and during a processing cycle with two independent sources of information. The motor should be protected from short circuits with fuses and from overheating or amperage draw with thermal breakers (heaters). The motor starter should be wired so that it will disconnect when any phase is interrupted or when the motor malfunctions. It should not be assumed that the blower is providing combustion air just because the blower motor is operating; combustion-air flow must be proven. At one time, an end switch, or rotary switch, on the motor was a common indirect method of gaining this information. A better method is to use a pressure switch in the air line for direct sensing. A sail or flag switch, although not quite as good because of the mechanical movements required, can also be used to directly sense air flow.

Programmable Controllers. The development over the last decade or so of high technology programmable controllers has been both beneficial and confusing to users. The ease and precision with which these devices monitor and control processes such as heat treating make them extremely attractive to industry.

However, until recently there existed no published guidelines for proper application of these controllers to combustion systems. When a programmable controller is used in conjunction with combustion safeguard circuitry on fuel-fired systems, the combustion safety interlocks, listed combustion safeguards, and excess temperature limits shall be wired to directly de-energize the fuel safety shutoff valve(s).

Gas-Pressure Control. Fuel must arrive at the burner in the correct quantity and at the correct time for safe combustion. Fuel pressure thus must be proven within an allowable range. Gas-pressure switches for both high and low gas limits are installed in the main gas lines. Visual pressure gages are also helpful to operators in setting burners and in verifying that the fuel is being supplied within the proper range and that pressure limit switches are not malfunctioning. Mercury-wetted relay pressure switches are recommended for their easy setup and maintenance and for their reliability.

Pressure Regulators. Pressure of gaseous fuel is most commonly regulated by pressure-regulating diaphragms. Good, safe design normally requires one regulator for pilot fuel and one regulator for main-burner fuel. The pilot gas, if taken from the main fuel line, should be drawn from a point between the gas supply and the regulator for the main fuel. Therefore, the pilot and main burner can be set up optimally, safely, and independently. The regulators should be vented to a safe location outside the plant to ensure safety if a regulator diaphragm is damaged in service. Good practice and manufacturers' recommendations show that diaphragm life can be substantial if regulators are shielded from thermal radiation and are used below their maximum design limits. Positive lockup regulators are recommended to prevent downstream pressure buildup during shutdown periods.

Valves. Blocking valves normally are closed valves that are energized only by the combustion-control circuits. The pilot-gas blocking valve is placed downstream of the pressure regulator and a hand-operated gas cock. A pipe union should be inserted just ahead of the electrically operated blocking valve to allow safe removal if repairs are needed. The blocking valve is opened to the pilot assembly only after the furnace is purged.

Purging of Fuel-Fired Furnaces

The furnace must be purged of any possible combustible materials. This is best accomplished by opening the furnace doors, which should be equipped with a limit switch to ensure that they are opened adequately. Once the doors are open, the combustion blower or exhaust fans can be timed to allow for a minimum of 4 standard cubic feet (0.11 m^3) of fresh air per 0.028 m^3 (1 ft^3) of furnace volume. This purge cycle is required for safe startup and is standard practice for all well-managed operations.

Pilot Control

Pilot assemblies can be of either the atmospheric or the blast type. The atmospheric type is similar to an atmospheric burner, in which the air is inspirated from the atmosphere by the gas stream.

In the blast type, air and gas are brought to a mixer under pressure. The gas is then reduced to atmospheric pressure and pulled into the mixer by the pressurized air stream. This is the most positive means of pilot-gas control.

Ignition

For ignition trials, a high-voltage transformer is used in conjunction with a spark plug designed for the pilot or burner assembly. The control circuit opens the pilot valve, and a spark is produced. The spark continues for a short period (normally 15 s) and establishes a flame that can be detected. If the flame is not established because the flame or signal is inadequate, the cycle returns to the purging stage.

The voltages normally employed are approximately 5000 to 6000 V, and the high-voltage transformer is normally mounted on the furnace and grounded to it. The spark in turn is grounded to the pilot assembly and then to the furnace; hence, a well-grounded furnace is an important safety requirement.

Ignition systems have no provisions for providing flame and should not be used in lieu of combustion safeguards. Safety standards specify that spark energy is to provide only a source of ignition.

Flame Detection

A thermocouple junction placed in intimate contact with the pilot flame is perhaps the most common means of flame detection, but thermocouples are useful only on very small pilot assemblies or burners (not to exceed 44 kW, or 150 000 Btu/h). The flame may no longer be present, but a hot burner block or refractory may retain heat and slow the rate of thermocouple cooling. Thus, thermocouple junctions are not recommended except for quench-tank heaters of the constant-pilot, open-grid burner design or for small atmospheric burners.

Flame electrodes, which are small anodes of heat-resisting alloy placed in intimate contact with the normal pilot flame, work on the principle that flame causes ionization within the burner atmosphere and thus allows a circuit to be formed to ground. The flow of a minute amount of current, at low voltage, is sufficient to sense and communicate the presence of a flame.

Flame electrodes are common on all industrial heat-treating furnaces where the flame is kept on ratio or slightly oxidizing. The flame electrode tends to become carbon coated in a reducing flame, a condition that can cause nuisance shutdowns.

Ultraviolet (UV) scanners are the third common device for sensing flame. They are normally dependable if the lens viewing the flame is kept clean. The UV scanners must not be used in any application where ultraviolet light is present from a source other than the burner in question. The UV scanner is a useful and practical device for any clean-flame, clean-furnace operation if it is located and aimed properly. A flow of clean, filtered cooling air across the scanner face aids in keeping it clean and cool, extending scanner life appreciably.

General Comments. Depending on the burner used, the application, and property-insurance requirements, it may be necessary to monitor both the main burner and the pilot flame independently.

Common and serious errors in flame detection are made by operators who circumvent flame-safety equipment rather than correcting the usually minor problems that cause nuisance shutdowns. Flame-safety equipment that uses totally enclosed relays is recommended over types with accessible relays that may be kept open with, for example, a piece of paper. This point, however trivial it may seem, has been profoundly recognized by those firms who have lost operators, furnaces, and product as a result of poorly designed flame-safety equipment that can be circumvented easily. Any employee found tampering with this equipment should receive disciplinary action, and all employees should be trained in the use of flame-safety equipment.

Burner Operation

The main fuel supply for fuel-fired heat-treating furnaces normally is natural gas, propane-air, propane, butane, or one of the fuel oils. Although this discussion centers on natural gas, the same principles apply to the other gases and oils.

The main gas valve may be fully automatic or of the manual-reset type, requiring an operator. The manual type is usually preferred when the furnace is run intermittently or when operators must perform some other function, such as opening doors. When the operator opens the valve, he is in effect making a conscious decision that conditions are ready for the main burner heat. The valve may be made automatic when the furnace is designed and interlocked to preclude an unsafe condition.

For furnaces with capacities greater than 422 MJ/h (400 000 Btu/h), it is recommended that a second blocking valve be inserted into the main gas line. Revised NFPA 86 standards for ovens and furnaces have removed the requirement for the vent valve. IRI (Industrial Risk Insurers) is the only insurance underwriter that requires the installation of a vent valve.

Burner Control. The gas-air ratio ordinarily is controlled to about 10 parts air to 1 part natural gas for good combustion efficiency. There are several devices involved in control of this ratio. Typically, the amount of blower air is varied by a butterfly valve to satisfy the demands of a temperature-control device. A pulse or static pressure line is connected from the combustion air line, downstream of the butterfly valve, to a proportionator valve located in the gas line. The gas is then regulated by the ratio-control valve in proportion to the air flow, and the air-to-gas ratio remains constant throughout the firing range. The devices used to regulate the ratio fall into two broad categories: the diaphragm type, or proportionator, which uses the pulse line to keep air and gas at a specified ratio; and the mechanical-linkage type. Both are effective and common but the diaphragm type is the more positive, because there are no linkages that can slip and require adjustment. Also, if air lines become dirty, resulting in a lessening of air pressure, the gas pressure will follow, maintaining the correct ratio.

Ratio control alone is not sufficient to ensure safe startup of the main burners. It is recommended that the burners be set to a low firing rate when the main burner is started. This can be done either automatically or manually. Once the main burners have been started, the furnace doors can be shut and the furnace brought up to temperature.

Temperature Control

Temperature-control devices fall into two categories: primary controls and process-limiting devices. Safe operation, especially when furnace practices require long cycles and little operator attention, dictates that limits be placed on the process. These limits should alarm and perhaps shut down the operation to prevent destruction of the product, the furnace, or the plant itself. Whether an analog device, a strip chart recorder, a digital readout, or a printout is used is a matter of operator preference and depends on the nature of the product.

The typical temperature sensor is either a thermocouple or a resistive temperature device (RTD). The thermocouple is most common. Several types of thermocouple junctions are available, with the choice depending on such factors as temperature range and furnace atmosphere. They are comparatively inexpensive and can be easily protected from atmospheres with protective wells, which are immersion tubes that project into the furnace zone to be controlled. RTDs, although more accurate than thermocouples by factors ranging from 10 to 1 up to 50 to 1, are expensive and less rugged. For most purposes, thermocouples are satisfactory. Some firms use heat-flow sensing to remotely ascertain interior temperatures and to provide an element of redundancy for protection of furnaces and their contents. Good temperature-sensing devices will detect failure of a thermocouple or RTD, cause the process firing rate to be reduced to its minimum rate, and perhaps provide an alarm.

Furnace temperature can be regulated by one of two very common procedures. Simple high and low firing rates are used when temperature can be allowed to vary within a fairly large range. More common in heat treating is the use of proportional control, wherein the temperature is held nearly constant through the use of a bridge circuit. This circuit balances the signal between the controller and the butterfly valve and holds the latter at the proper opening to maintain the desired temperature. The latter scheme, although more costly, is required for close control.

An excess temperature limit must be applied to all heating systems where it is possible to exceed a safe temperature limit. It shuts down equipment and alarms the operator of this condition.

Waste-Heat Recovery

Recuperative devices used for conserving energy present special problems in safety and control instrumentation. Typically, these recuperators use the products of combustion for preheating the combustion air. Shell and tube heat exchangers are normally used in this type of arrangement. Because preheated air becomes less dense, the air temperature must be sensed, and control of the gas-to-air ratio must be based on this temperature-density function. Experience with these devices has shown that such factors as poor design, poor gasketing, leaks in heat-exchange surfaces, overheating of burner blocks, and failure to allow for expansion and contraction have caused numerous operational problems that constitute safety hazards. Tracking of air-gas ratios can be affected by leakage of mechanical seals, and products of combustion can enter the combustion air. Therefore, it is recommended that oxygen analyzers be used periodically to check the combustion air immediately ahead of the burner block. This analysis will reduce the likelihood of erroneous and perhaps hazardous conditions in the furnace, will give clues to potential design changes needed, and will give warning of part deterioration. Further, it is recommended that heat-treating operators monitor the room atmosphere for carbon monoxide on a periodic basis. Although exhaust may be provided for products of combustion, and sufficient air exchanges may be occurring to satisfy state regulations, there may be a temperature inversion that can cause leaking of products of combustion inside the building, resulting in a potentially dangerous situation.

Supervisory Gas-Cock System

A supervisory gas-cock system is used to ensure a safe lightoff procedure on a manually ignited, multiburner furnace that does not have flame-safety equipment with a programmed sequence of piloting the main burners.

The system consists of specially designed gas valves that have inlet and outlet passages for checking a pressure medium such as air or gas. Air or gas--usually air from a combustion blower--can pass only through the valve when the valve is fully closed. When the individual burner valves and the main gas line valve are closed, the air flow enters a pressure switch that closes and completes an electrical or pneumatic circuit. This allows the main gas valve, usually of the manual-reset type, to be opened. The burners are then individually manually ignited.

Supervisory gas-cock systems are used on radiant-tube furnaces and other furnaces where flame-safety systems are difficult to apply. Fewer of these systems are being used on new furnaces because most burners now are adapted to flame safety and automatic ignition.

Electric Furnaces

Electric-furnace installations are made up of various electrical and mechanical components, many of which are water cooled and equipped with protective devices.

Furnace manufacturers generally issue instructions concerning safe practices, and these instructions should never be ignored. Potential hazards can be avoided by ensuring that operating personnel are trained thoroughly and that installations conform to safety practices and local codes.

Original equipment usually contains devices for preventing overloads and short circuits. In addition, ground detectors and surge detectors protect motor-generator units from faulty coil or transformer installations at heating stations and from breakdown of insulation in the generator windings.

Protective devices commonly used with induction-heating radio-frequency generators are as follows:

- Door interlocks
- Grounding devices to ground high-voltage circuit when furnace doors are open
- Warning lights
- Warning signs
- Circuit breaker for entire unit
- Overload relays
- Water-flow switches
- Water-temperature switches
- Time-delay relays (tube warmup)
- Grid overload relays
- Control-circuit overload relays
- Arc gaps on blocking and tank capacitors
- Surge protection
- Electronic crowbar

Operators should become familiar with these safety devices and should inspect them periodically to ensure their good working condition.

Electrical Power. Although motor generators account for the largest total power output of installed induction-heating equipment, vacuum-tube oscillators probably occur in the greatest number of units. Many small vacuum-tube oscillators are required to account for as many kilowatts as one 1250 kW, 3 kilocycle motor-generator set. Although many vacuum-tube oscillators for induction heating are made in small sizes, 25 kW and 50 kW outputs are also common ratings. Some have been constructed for special applications, with ratings as high as 500 kW. Many small composite (custom-built or homemade) vacuum-tube units are in use also.

Power Interlocks. Most systems produced by reputable manufacturers are designed to be completely fail-safe. These systems also have interlocks that automatically shut down the power supply if a fault develops during operation. The system cannot be restarted until the fault is corrected. Interlocking systems also are used to increase production of induction-heating machines.

Induction-heating machines are expensive; therefore, steps are taken to keep them busy as much of the time as possible. If a hardening process, for example, requires 5 s of heating, followed by 5 s of quenching (before the part is moved from the inductor), and if another 5 s are required on the average for the operator to load and unload the part, then the generator itself is only in use one-third of the time. Production can be increased appreciably by having the same basic equipment supply two or more individual work coils (Fig. 1). This can be done by arranging the control circuit so that if one of the work coils is demanding heat, none of the others can be started. If an operator pushes the start button at one station while another is heating, a relay withholds the actual start of heating until the first station has completed its high-frequency power demand cycle.

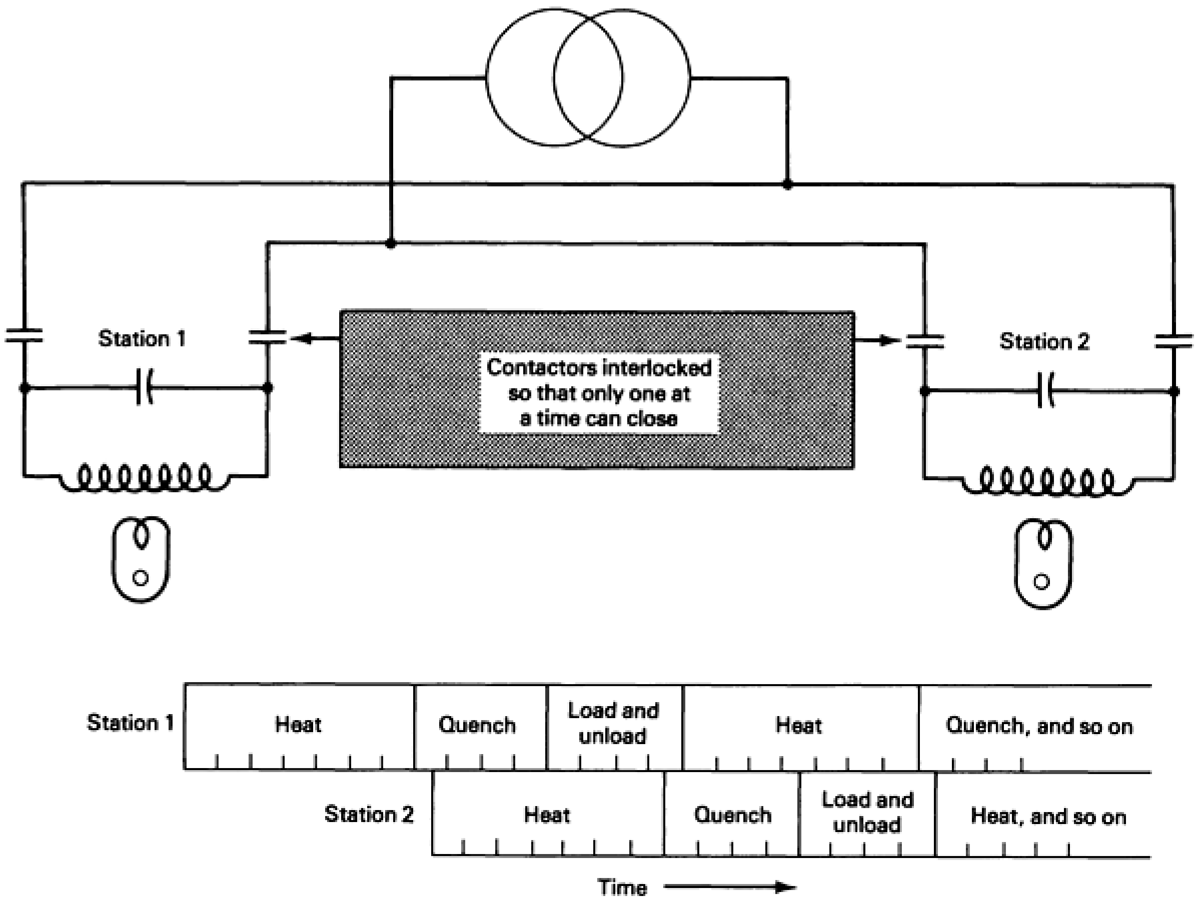


Fig. 1 Interlocked multistation operation of two work coils on an induction-heating machine. Assume that cycle is the same for both stations: heating, 7 s; quenching, 4 s; loading and unloading, 4 s.

It is also customary in the case of interlocked multistation operation of motor-generator equipment to preset the alternator field current for the various stations. Each station has its own field-adjusting autotransformer or potentiometer that is automatically switched into the circuit when that station has the power. This is feasible because with only one station on at a time, it is not necessary to use the same voltage at each.

Fixtures. As introduction of automated systems increases in induction heating, the need for safety controls increases beyond the greater need for such devices as power interlocks.

For example, with highly automated induction-heating machines, a part completely foreign to the part to be treated may enter the automatic feed hopper or bin. If the fixture tries to feed this part into the coil, mechanical jamming and damage may result. If the part does get pushed into the coil itself, assorted problems may result, especially if the unwanted part is larger than the inside diameter of the coil.

The greater the degree of automation, the greater the necessity for safety devices that further complicate the machine. Some automatic induction-heating machines incorporate templates through which the workpiece must pass before being fed to the more delicate parts of the mechanism. If the part touches the template, an electric circuit stops the machine until the error is manually corrected.

Spurious Radiation. Industrial heating equipment using radio-frequency energy is, in many instances, governed by rules of the Federal Communications Commission (FCC). FCC rules apply to induction-heating equipment operating at 10 kHz or above. Any operation whatsoever in frequency bands reserved for international distress equipment is strictly prohibited. One of these bands is from 490 to 510 kHz.

The best way for a user of induction-heating equipment to become familiar with the FCC rules is to acquire a copy of Part 18 of the rules and to study them carefully.

Vacuum-tube oscillators and some motor-generator equipment fall into the FCC-designated categories. The rules state that operation must either be within certain narrow frequency bands (in which any amount of energy may be radiated) or be restricted in field strengths. All such equipment must be certified by a competent engineer, such certification being based upon actual measurements of field strength made around the equipment. In some circumstances, prototype models of industrial high-frequency heating equipment may be tested at the manufacturer's plant and a certificate issued to cover other equipment of the same design. Even though a specific piece of equipment may have been properly certified, and even though its spurious radiation may fall below the prescribed limits, FCC rules state that if it interferes with communications equipment, further corrective action must be taken. The mere existence of a certificate, therefore, does not necessarily absolve the user of further responsibility.

Induction-heating machines sometimes rival the largest communications transmitters in output. The frequencies, and harmonics thereof, used by many induction-heating oscillators fall within the range used by their more delicate counterparts in radio and television services. If only a small portion of the power output of high-frequency heating machines was to be broadcast as unwanted (spurious) radiation, the results would be catastrophic.

Historically, dielectric heating machines have caused more interference than have induction-heating machines; they operate at higher frequencies and are more difficult to shield. However, induction-heating machines, especially vacuum-tube oscillators, have also caused trouble. It is necessary to observe certain precautions in their design and operation to ensure that they do not create interference. Reputable manufacturers of induction-heating equipment take precautions to protect users of their equipment from this type of trouble. They house their equipment in heavy steel cabinets and provide instructions that, if followed, will ensure conformity with FCC rules. However, it must be emphasized that the final legal responsibility for a piece of equipment lies with the user.

Maintenance. Electrical heat-treating equipment is expensive, and standby equipment generally is not maintained. Thus, preventive maintenance is critical, and availability of replacement parts is highly desirable.

Dust, dirt, moisture, and high ambient temperatures are the primary causes of electrical equipment failures; these conditions are commonly present in industrial locations where induction-heating units are installed. In any maintenance program, warnings should be highly visible and clearly stated. The following is a typical warning:

> "If the interlocks are disabled and the main circuit breaker is on with the door open, potentially lethal voltages are exposed. There is always 460 V ac present behind the control circuit breaker and on the line side of the main circuit breaker: care should be exercised at all times when the door is open. Power should be removed by opening the feed breaker or disconnect switch external to supply before working within cabinet. Solid-state circuit breaker board and isolator board are connected directly to 300 V ac. Turn off all breakers and allow one minute for capacitors to discharge before working on these boards."

Special Heat-Treating Processes

Certain special heat-treating processes using such systems as lasers, electron-beam heating, plasma carburizing, and ion nitriding have their own unique safety requirements in addition to standard safeguards associated with high-temperature processing.

Safety of personnel is paramount, but safety of equipment often ensures personnel safety. Thus, proper care and use of equipment cannot be overstressed and frequently becomes almost synonymous with safety.

In this section, ion nitriding and plasma carburizing are used as examples of special processes and the safety precautions related to them. For all heat-treating systems, however, special safety problems can be solved through sound training programs for operators and through effective and regular maintenance.

Plasma (Ion) Nitriding. In this system, also known as glow-discharge nitriding and as ionitriding, parts are connected to the cathode for processing, and the retort is the anode. After the retort is evacuated of atmospheric gases, nitrogen and hydrogen are bled slowly into it. The glow discharge is produced when the parts are heated by electric current to approximately 500 °C (930 °F), although specified temperatures can be as high as 565 °C (1050 °F).

The retort becomes heated by radiation from the parts; additional heat is not required. The glow discharge ionizes the nitrogen, and the electrical potential accelerates the movement of the ionized nitrogen toward the parts.

Although ion nitriding is faster and produces a more ductile and fatigue-resistant case with less white layer, the extra handling and precautions it requires are important factors in overall cost.

Plasma (Ion) Carburizing. The normal range of electrical power used for plasma-arc processing is 25 to 50 kW. Most systems are of fail-safe design and are interlocked to shut down the power supply automatically if a fault develops during operation.

One of the most serious hazards associated with plasma-arc operation is radiation caused by electromagnetic high-electron excitation. Such radiation ranges from radio frequencies to the far ultraviolet, and it includes infrared and visible radiant-energy light rays.

The radiation produced by the plasma is capable of producing severe eye and skin burns. The plasma should never be observed with the naked eye.

Furnace Protection. The primary safety feature of a surface ion-nitriding furnace is the arc-control system. Successful ion processing requires application of 300 to 1000 V dc to the workpiece. In these voltage ranges, the potential for an arc to form between the cathode and the anode is quite high during the initial part of the cycle. These arcs can be quite small; under certain circumstances, however, major arcs can occur that may be powerful enough to rupture vessel walls.

One method of controlling arcing and protecting equipment is to place a large resistance in series between the furnace vessel and the power supply. This prevents overloading of the power supply. An electrical device used to construct a type of arc-shutdown circuit is a silicon-controlled rectifier (SCR), which operates with a low-resistance load at steady voltage.

When an arc begins to form there is an initial rapid increase in current prior to formation of the arc. Upon arc formation, the voltage drops drastically (dv/dt); the SCR senses the voltage change (dv/dt increase) and increases the resistance, thus protecting the power supply. Additionally, the SCR is normally connected to another electrical device, such as a bridge rectifier. Once the change in voltage signifying arc formation is detected, the rectifier damps the current supply. This damping is normally sufficient to shut down the arc by allowing redistribution of the energy on the portion of the part that was arcing.

This type of circuit reacts after the arc has formed, however, and the potential for ruined workpieces or holes in anodes or vessel walls remains. This is a particular problem if the unit requires operators to manually shut down the power supply after observing dead shorts, formed by misloaded parts that create short circuits.

Arc Suppression. Some equipment used in ion nitriding and plasma carburizing does not rely on an arc-shutdown circuit as the primary safety factor. Rather, true arc-suppression circuits are employed. Such a circuit senses the change in current just prior to the formation of an arc and shuts off the power completely, preventing the arc from forming. The power is then proportionally ramped back on, allowing redistribution of energy.

In one system, a counter in the controlling microprocessor tallies the number of times the power is turned off and on.

If the potential for arcing is too large, as determined by the logic preprogrammed into the microprocessor as part of the executive command package, the system shuts down, prints a fault message on both the cathode-ray tube and data logger, sounds an alarm and siren, and activates a warning light. All this occurs automatically without an arc forming and protects both the part and the equipment. The microprocessor detects a dead short by sensing and reporting the rapid frequency of shutdown/startup cycles and prints a different short warning message, also with alarms, siren, and lights. This sequencing is also totally automatic and requires no operator interface. The equipment has a backup system that operates on the dv/dt principle. Additionally, all leads through the vessel wall that could carry current to the power supply are triple protected. As an example, the thermocouple has primary protection through an outer ceramic insulator. This is followed by a second powder ceramic insulator. The third protection is a high-voltage isolating amplifier between the thermocouple and the processor.

Thermocouples. The problems associated with passing a thermocouple, or any other lead, through a vessel wall in ion-processing equipment are as follows:

- The lead can become metallized, creating a pathway for catastrophic arcing. This problem becomes increasingly severe as a function of vessel use

- The material of construction used for seals through the vessel wall is quite critical. The conditions of ion processing can affect the sealing materials, allowing increased leakage as a function of vessel use
- Temperature uniformity throughout the entire workload in the vessel is quite critical. Proper design of thermocouple insulators that are calibrated to give true temperature readings, as well as proper design of fixturing, is necessary to achieve uniform temperatures

Fixture Design. Design of the fixture is critical to the successful application of ion processing. Poorly designed fixtures can allow overheated or underheated parts. If equipment without an arc-suppression circuit is used, parts can be ruined because of poor fixture design. The fixture often allows simple masking, and through proper design, can minimize or eliminate the hollow-cathode effect. This effect is signified by either failure of the glow to uniformly penetrate the interior surface of a hole or cylinder, or overheating and possible melting of the part, caused by overlapping glows.

Atmosphere Furnaces

Atmosphere furnaces must be considered in any discussion of furnace safety because of the potential explosion hazard produced by introduction of special flammable atmospheres.

Although many of these furnaces are supplied with inert gas purging and standby emergency purging, training of operators in manual burnout procedures is extremely important in the event of failure of automatic controls. These emergency instructions may vary with equipment design, and thus the importance of consulting and understanding emergency procedures, as outlined by the furnace manufacturer's instructions, should not be minimized.

Protective Controls. Protective devices should be installed and interlocked and should include the following:

- A safety shutoff valve on the atmosphere supply line to the furnace
- An atmosphere gas-supply-monitoring device that permits the operator to visually determine the adequacy of atmosphere gas flow at all times
- A sufficient number of temperature-monitoring devices to determine temperature in all zones of the furnace; these should be interlocked to prevent opening of the atmosphere-gas-supply safety shutoff valve until all zones are at or above 760 °C (1400 °F)
- An automatic safety shutoff valve for flame curtain burner supply gas; this should be interlocked to prevent opening of the valve when furnace temperature is below 760 °C (1400 °F)
- Audible and/or visual alarms to alert the furnace operator of abnormal conditions
- Manual door-opening facilities to permit operator control in the event of power failure

Operator Training. The most essential safety consideration is the selection of alert and competent operators. Their knowledge and training are vital to continued safe operation. New operators should be instructed thoroughly and required to demonstrate an adequate understanding of the equipment and its operations.

Regular operators should receive scheduled retraining to maintain a high level of proficiency and effectiveness, and all operators should have ready access to operating instructions at all times. An outline of these instructions should be posted near the furnace.

Operating instructions generally are provided by the equipment manufacturer, and these instructions include schematic piping and wiring diagrams. All such instructions should include procedures for lightup, shut-down, emergencies, and maintenance.

Operator training should include instructions in:

- Combustion of air-gas mixtures
- Explosion hazards
- Sources of ignition and ignition temperature
- Atmosphere gas analysis

- Handling of flammable atmosphere gases
- Handling of toxic atmosphere gases
- Functions of control and safety devices
- Purpose and basic principles of atmosphere-gas generators

This listing is intended only to serve as a guideline; specific requirements are covered in the following standard issued for furnaces: "Industrial Furnaces, Special Atmospheres," NFPA 86C, National Fire Protection Association, 1991.

Process Cooling

Heat treating of metals includes controlled cooling or quenching of the heated metal; metals are cooled from the specific treatment temperature in a variety of media that include air, oils, salts, water, and synthetic fluids.

As a general rule, furnace equipment does not include instrumentation for control of the safety aspects of the quench media. Normal practice in layout of plant and facilities will provide for isolation of air-cooling areas, for the usual pedestrian protection at pits, and for the necessary building protection should an uncontrolled conflagration occur because of the quenching operation. However, certain equipment can be specified to ensure safe and controllable operation in specific cooling processes.

The greatest concern exists for fires associated with oil quenching. All of the ingredients for a dangerous fire--fuel, oxygen, and a source of ignition--exist at the surface of an oil tank.

The most common type of fire occurs when movement of a hot workpiece is obstructed as it enters the quench oil. The result is sustained ignition and vaporization that continues as the liquid is locally heated above its flash point. Prompt immersion removes the source of local vaporization, and local flashing is extinguished by normal agitation of the oil.

A second type of fire occurs when the main body of oil is heated above the flash point because of malfunction of heating or cooling equipment, or when the quench load is greater than that for which the system was designed. When an ignition source is supplied, the resultant fire soon reaches full intensity and is very difficult to extinguish.

A third and less likely type of fire occurs because of material-handling accidents that involve spills on or near heated furnaces or cooling equipment.

Equipment is available for detection of fires and release of control media. Automatic water-spray systems are usually recommended in buildings of fire-resistant or non-combustible construction, and areas adjacent to quench-oil tanks can be protected with automatic sprinklers. Quench oil and water should not be mixed, however. High-value oils can be protected with automatic carbon dioxide or dry chemical systems. In general, these automatic systems are specified for centralized large-capacity quench-oil systems.

Special equipment is available for totally enclosed systems that operate in special atmosphere furnaces. However, the incompatibility of water and quench oil can be a source of trouble in these units. Water in oil rapidly turns to steam when locally heated beyond 100 °C (212 °F). This steam can cause violent boilover, increased pressure within the enclosed system, and forcible ejection of burning oil from small openings. Commercial safety equipment capable of detecting even small quantities of water in oil can be arranged to alert the furnace operator and to interrupt the quench process.

Quench-tank heating systems should be equipped with all safety devices normally used in conjunction with the chosen heating method. Overtemperature safety systems are essential. In addition, system interlocks between heating media actuators and both agitators and pumps will prevent local overheating of the bath.

Mechanical Equipment

Material handling cannot be separated from other safety considerations associated with heat-treating operations. Many mechanical operations must be performed before, after, and sometimes during the actual temperature-induced transformation that usually occurs while the work is in the heat-treating furnace. Doors must be opened and closed, conveyors started, rolls advanced, and mechanical handling equipment activated. All of these mechanical operations

constitute hazards of varying degrees of severity that must be evaluated. Some are serious enough to warrant the introduction of safety equipment to preclude serious injury of personnel and damage of expensive furnace equipment.

Furnace doors are often interlocked with other components of a facility through use of limit switches that prevent inappropriate opening or closing. For instance, in an atmosphere furnace, inner doors cannot be opened until proper vestibule ambient conditions have been restored after parts are removed. Interlocks on doors may include complex designs to prevent inadvertent opening during a power failure on a hydrogen atmosphere furnace. There are simpler designs that prevent closing of a door on a simple normalizing furnace before the extractor is removed. Some door interlocks are connected to pressure- or temperature-sensing devices. Such devices are used with vacuum furnaces in which inadvertent exposure of the molybdenum-graphite heating elements to air at high temperature would be disastrous. Moreover, without door interlocks, roller-hearth or walking-beam furnaces could advance workpieces into an unopened discharge-zone door.

Moving parts of furnaces represent potential hazards that can be neutralized rather easily with simple time-delay relays connected to audible alarms, which in turn are connected to the start buttons of electric motors. For instance, the conveyors on some large continuous furnaces cannot be advanced until an alarm has been sounded and a timer has allowed sufficient time for workmen to stand clear.

Charles F. Walton, Consultant

Introduction

CAST IRONS are alloys of iron, carbon, and silicon in which more carbon is present than can be retained in solution in solid metal. In common (unalloyed) cast iron (Fig. 1), the carbon that exceeds the solubility limit (shown by the lower dashed line in Fig. 1) precipitates either as graphitic carbon or as iron carbide.

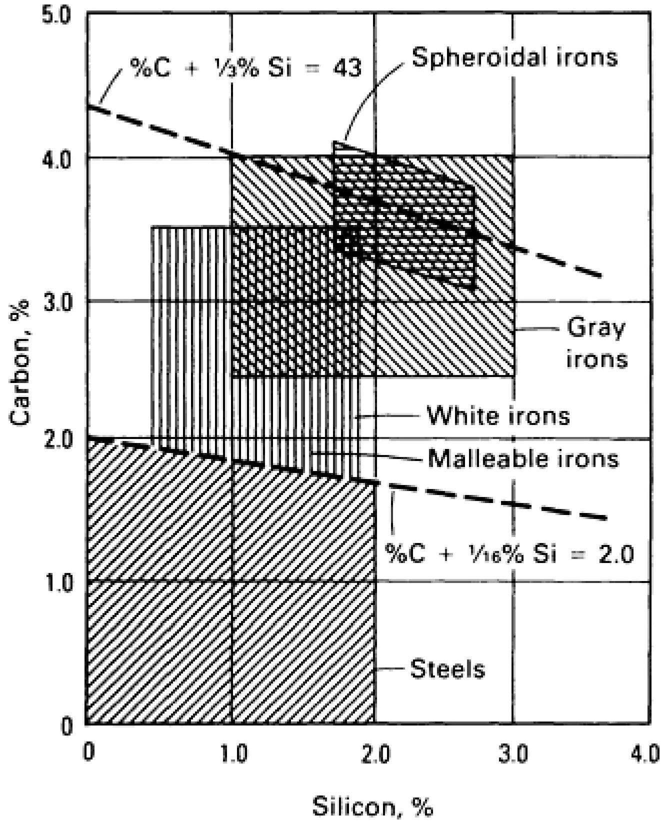


Fig. 1 Carbon and silicon composition ranges of common cast irons and steel. In addition to silicon, other elements may change the maximum solubility of carbon in austenite. Source: Ref 1

Types of Cast Iron. There are six basic types of cast irons and several varieties of each. Dependable heat treating requires information on the kind of material, its proximate composition and what is to be accomplished. The types of iron are classified as to how the excess carbon occurs in the microstructure:

- *White iron* is essentially free of graphite, and most of the carbon content is present as separate grains of hard Fe_3C. White iron exhibits a white, crystalline fracture surface because fracture occurs along the iron carbide plates. It is only stress relieved
- *Malleable iron* contains compact nodules of graphite flakes. These are called "temper carbon" because they form during an extended annealing of white iron of a suitable composition
- *Gray iron* contains carbon in the form of graphite flakes. Gray iron exhibits a gray fracture surface because fracture occurs along the graphite plates (flakes)
- *Ductile iron,* also known as spheroidal graphite iron, contains spherulitic graphite in which the graphite flakes form into balls as do cabbage leaves. Ductile iron is so named because in the as-cast form it exhibits measurable ductility

- *Austempered ductile iron* is a moderately alloyed ductile iron that is austempered for high strength with appreciable ductility. Its microstructure is different from austempered steel, and its heat treatment is a specialty
- *Compacted graphite iron* contains graphite in the form of thick, stubby flakes. Its mechanical properties are between those of gray and ductile iron
- *High-alloy iron* contains over three percent alloy content and is commercially classified separately. High-alloy irons may be a type of white iron, gray iron, or ductile iron. The matrix may be ferritic or austenitic and not have the usual transformation

Differentiating Gray and Ductile Irons. These two types of irons are sometimes confused. Identification is important in heat treating because of the typically lower silicon content and frequent alloy content in the higher strength grades of gray iron.

Ductile iron castings have a definite ring when struck with a hammer, but it is not the clear ring of steel. Gray iron castings have a damped sound. Breathing on a fresh surface (filed, ground, or machined) of ductile iron releases the smell of acetylene gas. It is formed by moisture reacting with the magnesium carbide in ductile iron.

The critical transformation temperature range for iron is mainly influenced by its silicon content. The carbon content, either combined or total, is not important. Silicon raises the transformation temperature range. The lower temperature of the critical range for cast irons can be estimated using the following formulas:

$$\text{Critical temperature, °F} = 1350 + 50\ (\%\text{Si}) - 45\ (\%\text{Mn})$$

$$\text{Critical temperature, °C} = 730 + 28\ (\%\text{Si}) - 25\ (\%\text{Mn})$$

In addition, silicon in iron decreases carbon solubility in austenite and tends to dissociate iron carbide. Thus, the carbon content of pearlite in iron can be appreciably lower than in the plain carbon and low-alloy steels. Depending on the silicon content and the cooling rate, the carbon content of pearlite varies and can be as low as 0.50% with 2.5% Si.

Heat-Treating Effects. The primary microstructure of cast irons can be modified by heat treatment. In the absence of chromium, iron carbide can be dissociated into austenite and graphite at annealing temperatures, but the shape of graphite cannot be changed.

The matrix can be internally decarburized or carburized either by depositing graphite on existing sites or by dissolving carbon from them. At temperatures approaching the critical temperature, silicon can cause the iron carbide (Fe_3C) in pearlite (called the combined carbon content) to dissociate into ferrite and carbon. The carbon diffuses to and deposits on the graphite already present in the microstructure. This reaction could be considered to be internal decarburization. The effect can be reversed by heating to above the critical temperature. In a very short time, austenite becomes saturated with carbon that is dissolved from the graphite.

The following articles in this Section of the Volume discuss the heat treatment of gray irons, ductile irons, malleable irons, and high-alloy irons. Compacted graphite irons are not typically heat treated.

Reference

1. C.F. Walton and T.J. Opar, *Iron Castings Handbook,* Iron Castings Society, 1981

Heating Equipment

Heat-treating furnaces for iron castings should be designed and operated to provide uniform heating throughout the load. The temperature measurement and control should be of the castings, not the furnace. Special programs are usually necessary for castings of complex shape with internal walls. The metallurgy of iron allows only a narrow temperature range for satisfactory results.

Iron tends to form a protective atmosphere in a tight furnace or box. Cast iron chips from the machine shop are used as packing material for other metals because the graphite and silicon in iron react with free oxygen in the atmosphere. A protective atmosphere should be used for finish machined parts. Heavy oxidization is especially undesirable for iron because a subscale of iron silicate is formed in the surface metal. This is not readily removed by grit blasting, especially in internal passages. Only molten salt electrolysis (Kolene process) can clean all casting surfaces.

The flame and induction hardening of surfaces on iron castings can be successfully and consistently accomplished, but the process must be closely controlled because the allowable temperature range is narrow. For example, a small variation in line voltage to the travel motor on a lathe way hardener caused irregular results.

Because of the brief time that the iron is above the critical temperature in surface hardening, it is best if the matrix microstructure of the iron is all pearlite or tempered martensite. A small amount of ferrite adjacent to graphite in the microstructure will cause no problem because it will dissolve carbon from the graphite very rapidly. Alloyed iron is not necessary or desirable for surface hardening because alloys slow the transformation upon heating as well as upon cooling. Alloys are sometimes used to minimize the amount of ferrite in the matrix. This is satisfactory if the time during which the surface metal temperature is above the critical temperature is adequate to allow complete transformation to austenite.

Quenching

Small- and medium-sized castings that do not have a high-stress-inducing shape can be normalized by cooling in open air or with fans. As soon as they have transformed (become magnetic), the castings should be placed in a furnace at 540 to 590 °C (1000 to 1100 °F) for equalization and slow cooling to minimize residual stress. Castings and machined components of suitable shape can be oil quenched and tempered in the usual way. Because of the relatively high hardenability of iron, it is never water quenched except in surface hardening.

Retained Stress in Iron Castings

Most iron castings are essentially free of internal stress as-cast. Molding sand is a very good insulator and retains much of the heat it absorbs from the iron when the iron solidifies at 1090 °C (2000 °F). When the solid iron goes through the critical transformation temperature, an additional amount of heat is liberated from the iron. The additional heat in the casting counteracts undercooling and tends to equalize the temperature throughout the casting. This is commonly referred to as mold stress relieving. Thus most iron castings that are cooled in a sand mold to below 425 °C (800 °F) are essentially free of internal stress.

There are castings, however, in which one section has much thicker metal and cools at a much slower rate than another section. Such castings can retain stress if, due to their shape, the more rapidly cooling portion restrains the contraction of the slower-cooling section. For example, a typical gear blank has a relatively thick outside section in which the teeth are machined. The hub is also comparatively thick, but the web between the two is usually not as thick. If the heat from the two heavy sections keeps the thinner metal between them from cooling too rapidly, the final casting will be essentially stress free. On the other hand, a brake wheel for an elevator is similar in shape to a gear blank except that the exterior rim may be appreciably less massive than the hub. Because the rim can cool more rapidly than the hub, by the time the hub finally cools and contracts, the rim is already cool and firm. Thus, tensile stress is developed in the web between the rim and the hub. This is especially undesirable in a brake wheel because in use the rim is heated by friction. Heat expands the rim and increases the tensile stress in the web. Such a casting should be given a controlled stress-relief heat treatment. The heavy hub must be heated at the same rate as the thinner rim to avoid cracking the casting.

Structural castings for precision machinery often have internal walls (frequently with internal and external walls of comparable thicknesses). This type of casting can be essentially stress free if it is allowed to cool to below 425 °C (800 °F) in the mold. The stress relieving of complex castings requires extended furnace time for both heating and cooling. The furnace program should be established by observing the temperature readings from thermocouples attached to inner and outer portions of the casting. These two temperatures should not differ by 100 °C (200 °F) during heating and by 50 °C (100 °F) during controlled cooling.

Retained Stresses. Evaluation of retained stresses in a casting is usually made when the casting changes dimensions during machining. Stresses in a casting can be accurately evaluated in two ways. A foil strain gage can be applied to the surface of a casting at a critical location. The metal on which the gage is mounted is trepanned or otherwise cut out of the casting. Gage readings before and after removal indicate the retained stress. In the second method, a casting can simply be sawed, and any change in the thickness of the kerf observed. This is more useful for smaller castings.

Stress Relief. The relief of residual stress is accomplished by heating the iron to a temperature at which the stress is relieved by rapid creep. Of course, complex shapes must then be cooled uniformly so that stress is not reintroduced. Vibration has been promoted as a method for providing stress relief to iron castings. This procedure has not been demonstrated to be successful in a valid test.

The temperature at which stresses are relieved within a reasonable time depends on the strength of the iron. Higher-strength irons require higher-stress-relieving temperatures. However, the use of higher temperatures has a limiting factor. As the temperature of the iron is increased above 540 °C (1000 °F), there is an increasing tendency for the combined carbon (pearlite) in the matrix to dissociate into ferrite and carbon. The carbon diffuses to and precipitates on the existing graphite. Thus the combined carbon in the matrix is reduced, and the hardness of the iron is decreased. The rate of precipitation of graphite at a temperature is increased by a higher silicon content and reduced by the presence of alloys. Generally, a successful stress-relief heat treatment decreases the hardness of the iron a small amount.

Hardness Measurement

All cast irons are heterogeneous alloys and have constituents of widely different hardnesses. A test of hardness in iron, except for microhardness, is a weighted average of the hardnesses of the constituents. The commonly used standard Brinell hardness test using a 10 mm diam ball and a 3000 kg load makes an impression that is large enough to provide a good average hardness even on a coarse structure. When other hardness tests with smaller indentation are used, several values should be taken and averaged.

The conversion of hardness values from different methods of testing is influenced by the material being tested. The hardness conversion tables in Volume 8 of *ASM Handbook*, formerly 9th Edition *Metals Handbook* are generally satisfactory. Figure 2 and Table 1 give examples of conversion values and show the deviation from the conversion table for steel.

Table 1 Comparative hardness values for quenched and tempered ductile irons

Iron	HB[(a)]	HRC converted from HB[(b)]	Observed HRC[(c)]	Microhardness, HV[(d)]	HRC converted from HV[(b)]	HRC converted from HV minus observed HRC
1	415	44.5	44.4	527	50.9	6.5
2	444	47.2	45.0	521	50.6	5.6
3	444	47.2	45.7	530	51.1	5.4
4	444	47.2	47.6	593	54.9	7.3
5	461	48.8	46.7	595	55.0	8.3
6	461	48.8	48.3	560	53.0	4.7
7	461	48.8	49.1	581	54.2	5.1
8	477	50.3	49.6	572	53.7	4.1
9	477	50.3	50.1	618	56.2	6.1

10	555	55.6	53.4	637	57.2	3.8

(a) Average of three readings for each iron.

(b) Values based on SAE-ASM-ASTM hardness conversions for steel.

(c) Average of five readings for each iron.

(d) Average of a minimum of five readings for each iron; 100 kg load

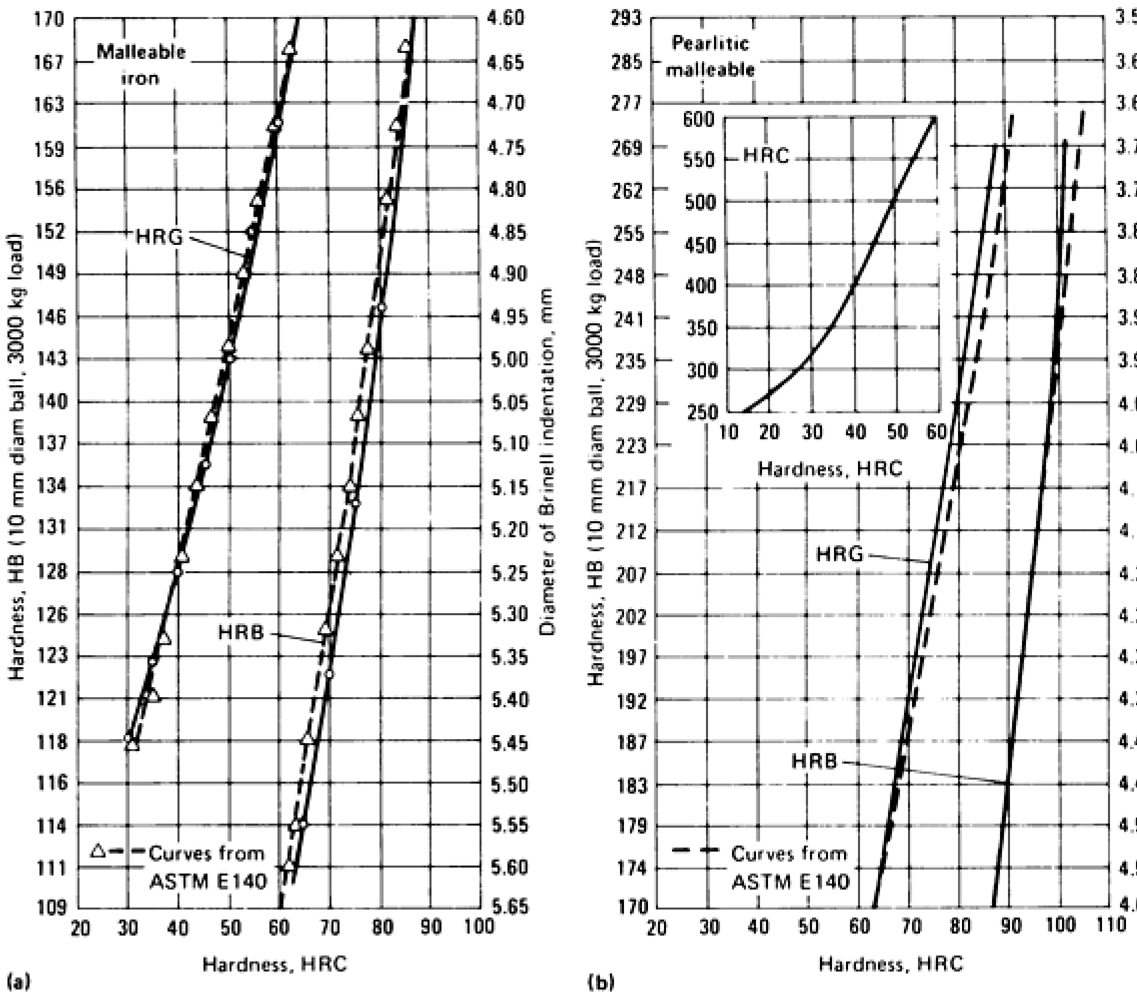


Fig. 2 Hardness conversions. (a) Conversion from HB to HRB and HRG scales for malleable iron. (b) Conversion from HB to HRB, HRC, and HRG scales for pearlitic malleable iron

In a comparison of the hardness of graphite-bearing irons with the hardness of other metals (especially in regard to machinability or wear resistance), the effect of the graphite in lowering the indicated hardness should be noted. Figure 3 shows the influence of the amount of graphite in flake form (gray iron) on the indicated hardness. Although ductile iron contains more graphite than do the machinery grades of gray iron, the graphite in ductile iron is in compact spheres and has less effect on hardness and other properties.

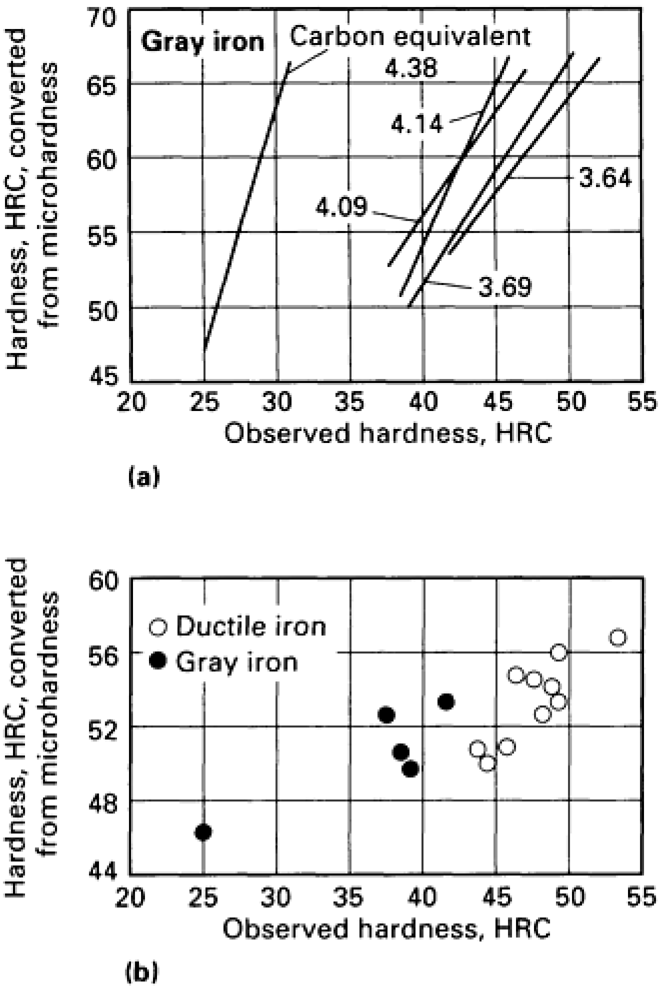


Fig. 3 Relations between observed and converted hardness values for gray and ductile irons. (a) Relation, as influenced by carbon equivalent, for gray iron containing type 3 graphite. (b) Relation for gray and ductile irons quenched in water from 900 °C (1650 °F) and tempered 2 h at 425 °C (800 °F)

Heat Treating of Gray Irons

Revised by Bela Kovacs, Applied Process, Division of the Atmosphere Group, Inc.

Introduction

GRAY IRONS are a group of cast irons that form flake graphite during solidification, in contrast to the spheroidal graphite morphology of ductile irons. The flake graphite in gray irons is dispersed in a matrix with a microstructure that is determined by composition and heat treatment. The usual microstructure of gray iron is a matrix of pearlite with the graphite flakes dispersed throughout. In terms of composition, gray irons usually contain 2.5 to 4% C, 1 to 3% Si, and additions of manganese, depending on the desired microstructure (as low as 0.1% Mn in ferritic gray irons and as high as 1.2% in pearlitic). Other alloying elements include nickel, copper, molybdenum, and chromium.

The heat treatment of gray irons can considerably alter the matrix microstructure with little or no effect on the size and shape of the graphite achieved during casting. The matrix microstructures resulting from heat treatment can vary from ferrite-pearlite to tempered martensite. However, even though gray iron can be hardened by quenching from elevated temperatures, heat treatment is not ordinarily used commercially to increase the overall strength of gray iron castings because the strength of the as-cast metal can be increased at less cost by reducing the silicon and total carbon contents or by adding alloying elements. When gray iron is quenched and tempered, this is usually done to increase resistance to wear

and abrasion by increasing hardness with a structure consisting of graphite embedded in hard martensite. The most common heat treatments of gray iron are annealing and stress relieving.

Although the size of the graphite flakes in gray irons is unaffected by heat treatment, the size does have a marked influence on the carbon kinetics during heat treating. In castings with fine graphite flakes, the carbon diffusion paths are shorter, and ferritization or normalization is achieved in a shorter time than in those castings with large graphite flakes. Castings with fine graphite flakes not only are easier to heat treat, but also display superior mechanical properties. The factors that affect the graphite morphology achieved during casting are discussed in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.*

Chemical composition is another important parameter influencing the heat treatment of gray cast irons. Silicon, for example, decreases carbon solubility, increases the diffusion rate of carbon in austenite, and usually accelerates the various reactions during heat treating. Silicon also raises the austenitizing temperature significantly and reduces the combined carbon content (cementite volume). Manganese, in contrast, lowers the austenitizing temperature and increases hardenability. It also increases carbon solubility, slows carbon diffusion in austenite, and increases the combined carbon content. In addition, manganese alloys and stabilizes pearlitic carbide and thus increases the pearlite content. Further, manganese reduces pearlite spacing and generally slows the heat-treating process.

Annealing

The heat treatment most frequently applied to gray iron, with the possible exception of stress relieving, is annealing. The annealing of gray iron consists of heating the iron to a temperature high enough to soften it and/or to minimize or eliminate massive eutectic carbides, thereby improving its machinability. This heat treatment reduces mechanical properties substantially, however. It reduces the grade level approximately to the next lower grade; for example, the properties of a class 40 gray iron will be diminished to those of a class 30 gray iron. Figure 1 shows the effect of full annealing on the tensile strength of class 30 gray iron arbitration bars. The degree of reduction of properties depends on the annealing temperature, the time at temperature, and the alloy composition of the iron.

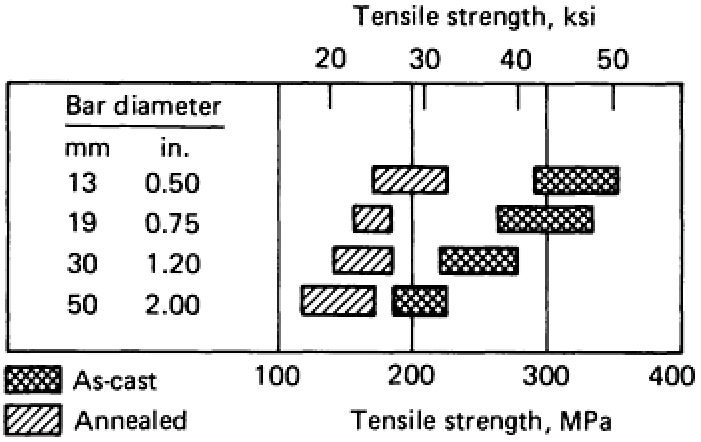


Fig. 1 Effect of annealing on tensile strength of class 30 gray iron. Specimens were arbitration bars from 31 heats. Bars were annealed at 925 °C (1700 °F) for 2 h plus 1 h per 25 mm (1 in.) of section over 25 mm, and cooled at a maximum rate of 160 °C/h (285 °F/h) from 925 to 565 °C (1700 to 1050 °F). Cooling continued from that level at a maximum rate of 130 °C/h (230 °F/h) to 200 °C (390 °F); bars were then air cooled to room temperature.

Gray iron is commonly subjected to one of three annealing treatments, each of which involves heating to a different temperature range. These treatments are ferritizing annealing, medium (or full) annealing, and graphitizing annealing.

Ferritizing Annealing. For an unalloyed or low-alloy cast iron of normal composition, when the only result desired is the conversion of pearlitic carbide to ferrite and graphite for improved machinability, it is generally unnecessary to heat the casting to a temperature above the transformation range. Up to approximately 595 °C (1100 °F), the effect of short times at temperature on the structure of gray iron is insignificant. As the temperature increases above 595 °C (1100 °F),

the rate at which iron carbide decomposes to ferrite plus graphite increases markedly, reaching a maximum at the lower transformation temperature (about 760 °C, or 1400 °F, for unalloyed or low-alloy iron). This is indicated in Fig. 2, which shows the structure of unalloyed gray iron in the as-cast condition (Fig. 2a) and after being held for 1 h at 760 °C (1400 °F) per inch of section (Fig. 2b). Heating to a higher temperature for the same period of time may be detrimental to the annealing process if it causes partial or complete transformation to austenite.

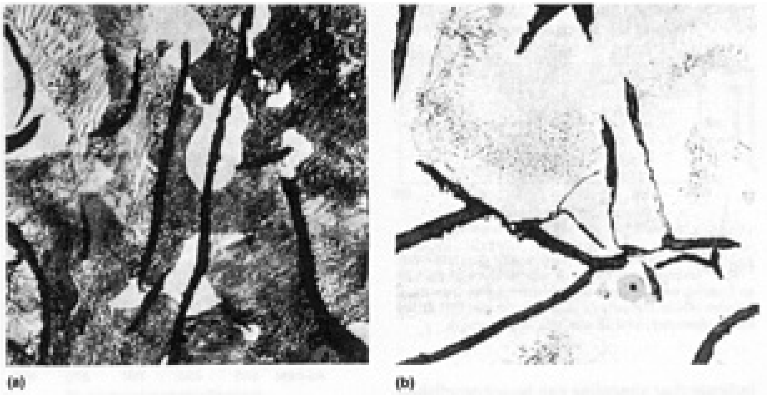


Fig. 2 Conversion of as-cast pearlitic structure of unalloyed gray iron to ferrite and graphite by annealing. (a) As cast; 180 HB. (b) Annealed 1 h at 760 °C (1400 °F); 120 HB. Magnification, 500×

For most gray irons, a ferritizing annealing temperature between 700 and 760 °C (1300 and 1400 °F) is recommended. The furnace temperature profile must be such that castings are sure to reach the set temperatures. Precise temperatures within this range are determined by the exact composition of the iron. When machining properties are of primary importance, it is advisable to anneal several samples at various temperatures between 700 and 760 °C (1300 and 1400 °F) in order to determine the temperature that yields the lowest final hardness.

The casting must be held at temperature long enough to allow the graphitizing process to proceed to completion. At temperatures below 700 °C (1300 °F), an excessively long holding time is usually required. At temperatures between 700 and 760 °C (1300 and 1400 °F), holding time varies with chemical composition, and may be as short as 10 min for unalloyed irons. If an unusually low rate of cooling is used, the time at temperature may be further reduced.

Although the rate of cooling per se is not of great importance to the annealing process, slow cooling is recommended if the stress relief that automatically occurs during annealing is to be retained as the casting cools to room temperature. A cooling rate ranging from as high as 110 °C/h (200 °F/h) to 290 °C (550 °F) is satisfactory for all except the most complex castings.

Medium (full) annealing is usually performed at temperatures between 790 and 900 °C (1450 and 1650 °F). This treatment is used when a ferritizing anneal would be ineffective because of the high alloy content of a particular iron. It is recommended, however, that the efficacy of temperatures at or below 760 °C (1400 °F) be tested before a higher annealing temperature is adopted as part of a standard procedure.

Holding times comparable to those used in ferritizing annealing are usually employed. When the high temperatures of medium annealing are used, however, the casting must be cooled slowly through the transformation range, from about 790 to 675 °C (1450 to 1250 °F).

Graphitizing Annealing. If the microstructure of gray iron contains massive carbide particles, higher annealing temperatures are necessary. Graphitizing annealing may simply serve to convert massive carbide to pearlite and graphite, although in some applications it may be desired to carry out a ferritizing annealing treatment to provide maximum machinability.

The production of free carbide that must later be removed by annealing is, except with pipe and permanent mold castings, almost always an accident resulting from inadequate inoculation or the presence of excess carbide formers, which inhibit normal graphitization; thus, the annealing process is not considered part of the normal production cycle.

To break down massive carbide with reasonable speed, temperatures of at least 870 °C (1600 °F) are required. With each additional 55 °C (100 °F) increment in holding temperature, the rate of carbide decomposition doubles. Consequently, it is general practice to employ holding temperatures of 900 to 955 °C (1650 to 1750 °F). However, at 925 °C (1700 °F) and above, the phosphide eutectic present in irons containing 0.10% P or more may melt.

The holding time at temperature may vary from a few minutes to several hours. The chill carbide (white iron) in some high-silicon, high-carbon irons can be eliminated in as little as 15 min at 940 °C (1720 °F). In all applications, unless a controlled-atmosphere furnace is used, the time at temperature should be as short as possible because at these high temperatures gray iron is susceptible to scaling if moisture is present in the furnace atmosphere.

The cooling rate chosen depends on the final use of the iron. If the principal object of the treatment is to break down carbides and it is desired to retain maximum strength and wear resistance, the casting should be air cooled from the annealing temperature to about 540 °C (1000 °F) to promote the formation of a pearlitic structure. If maximum machinability is the object, the casting should be furnace cooled to 540 °C (1000 °F), and special care should be exerted to ensure slow cooling through the transformation range. In both instances, cooling from 540 °C (1000 °F) to about 290 °C (550 °F) at not more than 110 °C/h (200 °F/h) is recommended to minimize residual stresses.

Effect of Alloy Content on lime at Temperature. Certain elements, such as carbon and silicon, accelerate the decomposition of pearlite and massive carbide at annealing temperatures. Therefore, when these elements are present in sufficient percentages, the time at annealing temperature may be reduced. In an investigation of the decomposition of pearlite at various temperatures in irons containing 1.93 and 2.68% Si, it was determined that the pearlite always broke down more rapidly in the higher-silicon iron and that this iron could be effectively annealed over a greater temperature range. For example, at an annealing temperature of 750 °C (1380 °F), the complete breakdown of pearlite occurred in the higher-silicon iron in 10 min, whereas 45 min were required for the lower-silicon iron. This shows the pronounced effect of silicon as an aid to the diffusion of carbon to the flakes present in the iron.

On the other hand, the pearlite-promoting elements (antimony, tin, vanadium, chromium, manganese, phosphorus, nickel, and copper) delay pearlite decomposition. The percentage increases in the time required to decompose pearlite that are affected by 0.10% additions of five of these elements are:

Element	Increase in time, %
Manganese	60
Nickel	30
Copper	30
Chromium	200
Phosphorus	30

Normalizing

Gray iron is normalized by being heated to a temperature above the transformation range, held at this temperature for a period of about 1 h per inch of maximum section thickness, and cooled in still air to room temperature. Normalizing may be used to enhance mechanical properties, such as hardness and tensile strength, or to restore as-cast properties that have been modified by another heating process, such as graphitizing or the preheating and postheating associated with repair welding.

The temperature range for normalizing gray iron is approximately 885 to 925 °C (1625 to 1700 °F). Austenitizing temperature has a marked effect on microstructure and on mechanical properties such as hardness and tensile strength. The tensile strength and hardness of a normalized gray iron casting depend on the following parameters:

- Combined carbon content
- Pearlite spacing (distance between cementitc plates)
- Graphite morphology

The graphite morphology does not change to any significant extent during normalization, and its effect on hardness and tensile strength is omitted in this discussion on normalizing.

Combined carbon content is determined by the normalizing (austenitizing) temperature and the chemical composition of the casting. Higher normalizing temperatures increase the carbon solubility in austenite (that is, the cementite volume in the resultant pearlite). A higher cementite volume, in turn, increases both the hardness and the tensile strength. The alloy composition of a gray iron casting also influences carbon solubility in austenite. Some elements increase carbon solubility, some decrease it, and others have no effect on it. The carbon content of the matrix is determined by the combined effects of the alloying elements.

Pearlite Spacing. The other parameter affecting hardness and tensile strength in a normalized gray iron casting is the pearlite spacing. Pearlite spacing is determined by the cooling rate of the casting after austenitization and the alloy composition. Fast cooling results in small pearlite spacing, higher hardness, and higher tensile strength. Too high a cooling rate may cause partial or full martensitic transformation. A combination of high normalizing temperature and high cooling rate promote martensitic transformation. Martensite is detrimental to machining. The addition of alloying elements may change hardness and tensile strength significantly. These changes, however, are mainly due to the change in carbon kinetics caused by these elements and not as much to the addition of the elements per se.

Partial control of hardness can be exercised during normalizing by allowing castings to cool in the furnace to a temperature below the normalizing temperature. Figure 3 shows the results obtained with gray iron rings that were heated to 955 °C (1750 °F) and then furnace cooled to different temperatures before being removed from the furnace and cooled in air. These data also indicate that annealing can be accomplished by cooling castings in the furnace to 650 °C (1200 °F) and then air cooling. However, if stress-free castings are desired, they should be cooled in the furnace to below 455 °C (850 °F) before being removed.

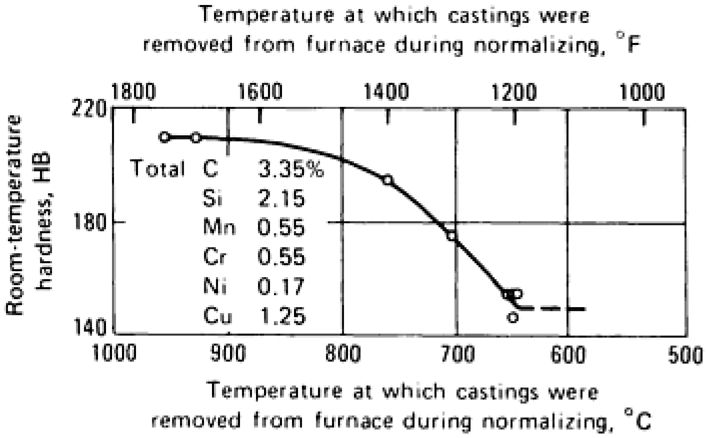


Fig. 3 Room-temperature hardness of gray iron after normalizing. Effect of temperature at start of air cooling on hardness of normalized gray iron rings 120 mm ($4\frac{3}{4}$ in.) in outside diameter, 95 mm ($3\frac{3}{4}$ in.) in inside diameter, and 38 mm ($1\frac{1}{2}$ in.) in length

Additional effects of normalizing, as a function of alloy content and carbon equivalent, are shown in Table 1. Bars 1, 3, 4, 6, and 7 are essentially free of alloying elements, except for residual amounts. Bars 1 and 3, characterized by high as-cast strength and low carbon equivalent, virtually regained their as-cast strength as a result of normalizing for $1\frac{1}{2}$ h at 900 °C (1650 °F), air cooling, and stress relieving at 540 °C (1000 °F). The same treatment lowered the strength of bars 4, 6, and 7, all of which had higher carbon equivalents and relatively low manganese content. Bar 2 showed an increase in strength because of the high stabilizing effect of the molybdenum, nickel, and manganese contents. Bar 5, despite a high carbon equivalent, greatly exceeded as-cast strength because of its manganese, chromium, molybdenum, and nickel contents.

Table 1 Influence of alloy content and carbon equivalent on typical properties of gray irons before and after normalizing

Bar	Composition, %									Carbon equivalent, %	As-cast			Normalized		
											Tensile strength		Hardness, HB	Tensile strength		Hardness, HB
	C	Si	P	S	Mn	Cr	Ni	Mo	Cu		MPa	ksi		MPa	ksi	
1	2.71	2.00	0.13	0.031	0.46	0.076	0.061	0.059	. . .	3.37	405	59	241	380	55	241
2	3.25	2.03	0.02	0.031	0.67	0.085	0.80	0.30	0.22	3.93	380	55	241	425	62	255
3	2.66	1.90	0.03	0.018	0.63	0.063	0.092	0.042	. . .	3.27	400	58	255	385	56	241
4	3.15	2.20	0.38	0.018	0.44	0.074	0.071	0.071	0.39	3.88	295	43	229	235	34.3	179
5	3.45	2.16	0.09	0.077	0.84	0.39	1.21	0.50	0.10	4.17	250	36	248	405	59	311
6	3.31	2.10	0.39	0.070	0.41	0.069	0.08	0.055	0.44	4.01	275	40	212	200	29	163
7	3.42	2.44	0.42	0.058	0.56	0.063	0.058	0.057	0.108	4.23	215	31	187	180	26	143

The effect of alloy content on hardness after normalizing is shown in Fig. 4 for two alloy irons with different carbon equivalents and nickel and chromium contents. Again it is evident that alloy content has a stabilizing effect in the graphitizing annealing range and serves to increase hardness when the austenitizing temperature ranges from about 790 to 980 °C (1450 to 1800 °F). Thus it can be concluded that normalizing serves to restore as-cast properties to gray iron--or, if the carbon equivalent is sufficiently low, even causes these properties to be exceeded--and that the alloying elements chromium, molybdenum, and nickel enhance the strengthening effect of normalizing.

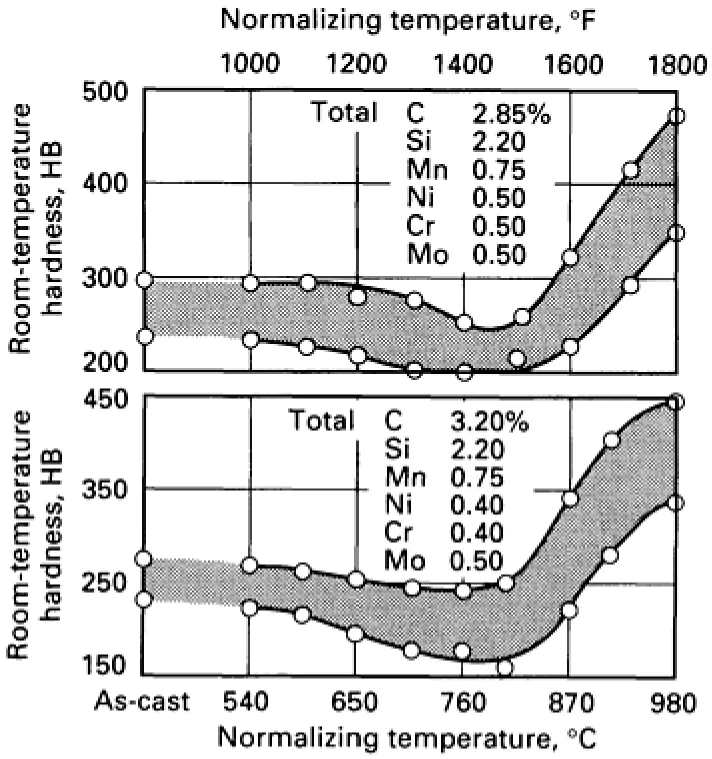


Fig. 4 Room-temperature hardness of two different alloy gray irons held at normalizing temperature 1 h for each 25 mm (1 in.) of thickness and air cooled on wire mesh screen. From production and experimental data

Hardening and Tempering

Gray irons are hardened and tempered to improve their mechanical properties, particularly strength and wear resistance. After being hardened and tempered, these irons usually exhibit wear resistance approximately five times greater than that of pearlitic gray irons.

Furnace or salt bath hardening can be applied to a wider variety of gray irons than can either flame or induction hardening. In flame and induction hardening, a relatively large content of combined carbon is required because of the extremely short period available for the solution of carbon in austenite. In furnace or salt bath hardening, however, a casting can be held at a temperature above the transformation range for as long as is necessary; even an iron initially containing no combined carbon can be hardened.

Unalloyed gray iron of low combined carbon content must be austenitized for a longer time to saturate austenite with carbon. Figure 5 shows the relationship of hardness to holding time for small quenched specimens. With increased time, more carbon is dissolved in austenite, and hardness after quenching is increased.

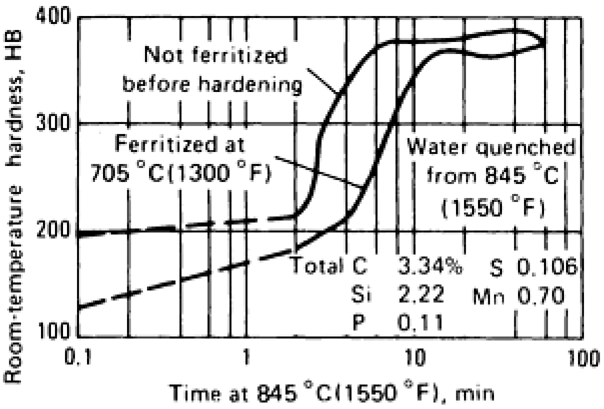
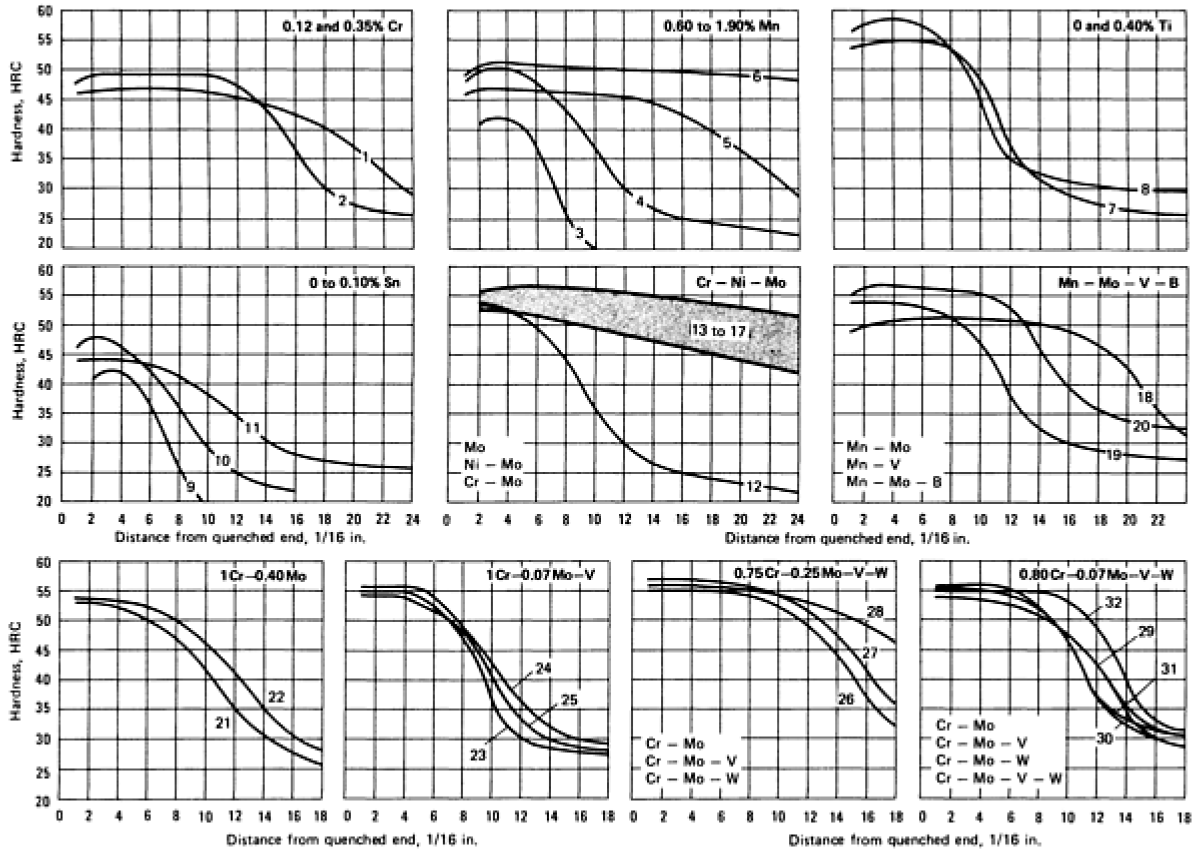


Fig. 5 Effect of austenitizing time on room-temperature hardness of quenched gray iron specimens. Specimens were 32 mm ($1\frac{1}{4}$ in.) in diameter by 19 mm ($\frac{3}{4}$ in.) in thickness.

Because of its higher silicon content, an unalloyed gray iron with a combined carbon content of 0.60% exhibits higher hardenability than a carbon steel with the same carbon content. However, because of the effect of silicon in reducing the solubility of carbon in austenite, unalloyed irons with higher silicon contents necessarily require higher austenitizing temperatures to attain the same hardness.

Manganese increases hardenability. Approximately 1.50% Mn was found to be sufficient for through hardening a 38 mm ($1\frac{1}{2}$ in.) section in oil or for through hardening a 64 mm ($2\frac{1}{2}$ in.) section in water.

Manganese, nickel, copper, and molybdenum are the recognized elements for increasing the hardenability of gray iron. Although chromium, by itself, does not influence the hardenability of gray iron, its contribution to carbide stabilization is important, particularly in flame hardening. Figure 6 shows the effects of various combinations of elements on hardenability.



Iron	Composition, %										Austenitizing temperature	
	Total C	Si	P	S	Mn	Cr	Ni	Mo	V	Other	°C	°F
1	3.30	1.40	0.116	0.10	1.47	0.12	. . .	. . .	. . .	. . .	840	1540
2	3.30	1.90	0.116	0.10	1.43	0.35	. . .	. . .	. . .	. . .	840	1540
3	3.15	2.05	0.124	0.112	0.60	0.06	. . .	. . .	. . .	. . .	840	1540
4	2.97	2.31	0.116	0.116	0.92	0.06	. . .	. . .	. . .	. . .	840	1540
5	3.42	1.90	0.116	0.100	1.47	0.12	. . .	. . .	. . .	. . .	840	1540
6	3.13	2.29	0.116	0.018	1.90	0.08	. . .	. . .	. . .	. . .	840	1540
7	3.00	2.00	0.15	0.10	1.25	. . .	. . .	. . .	. . .	. . .	840	1540

8	3.00	2.00	0.15	0.10	1.25	. . .	. . .	. . .	. . .	0.40 Ti	840	1540
9	3.15	2.05	0.124	0.112	0.60	. . .	. . .	. . .	. . .	. . .	840	1540
10	3.10	2.25	0.120	0.160	0.65	. . .	. . .	. . .	. . .	0.05 Sn	840	1540
11	3.10	2.25	0.120	0.160	0.65	. . .	. . .	. . .	. . .	0.10 Sn	840	1540
12	3.19	1.70	0.216	0.097	0.76	0.03	. . .	0.013	. . .	. . .	855	1575
13	3.22	1.73	0.212	0.089	0.75	0.03	. . .	0.47	. . .	. . .	855	1575
14	3.20	1.76	0.187	0.054	0.64	0.005	Trace	0.48	. . .	. . .	855	1575
15	3.22	2.02	0.114	0.067	0.66	0.02	1.21	0.52	. . .	. . .	855	1575
16	3.21	2.24	0.114	0.071	0.67	0.50	0.06	0.52	. . .	. . .	855	1575
17	3.36	1.96	0.158	0.070	0.74	0.35	0.52	0.47	. . .	. . .	855	1575
18	3.21	2.01	0.15	0.10	1.53	0.40	. . .	0.13	. . .	. . .	840	1540
19	3.20	2.00	0.15	0.10	1.25	0.40	. . .	. . .	0.05	. . .	840	1540
20	3.10	2.09	0.15	0.10	1.46	0.44	. . .	0.14	. . .	0.095 B	840	1540
21	3.22	2.10	0.108	0.088	0.68	0.97	. . .	0.40	. . .	. . .	845	1550
22	3.20	2.15	0.108	0.093	0.70	1.00	. . .	0.41	. . .	. . .	845	1550
23	3.19	2.55	0.092	0.090	0.71	0.96	. . .	0.054	0.16	. . .	845	1550
24	3.17	2.20	0.094	0.092	0.66	0.95	. . .	0.069	0.081	. . .	845	1550
25	3.19	2.20	0.092	0.092	0.68	0.93	. . .	0.075	0.27	. . .	845	1550
26	3.17	1.90	0.080	0.094	0.65	0.73	. . .	0.19	. . .	. . .	845	1550
27	3.25	1.85	0.074	0.092	0.65	0.77	. . .	0.30	0.13	. . .	845	1550

28	3.21	1.90	0.069	0.100	0.70	0.75	. . .	0.28	. . .	0.40 W	845	1550
29	3.20	2.20	0.096	0.090	0.68	0.94	. . .	0.047	0.13	0.75 W	845	1550
30	3.12	1.80	0.074	0.090	0.69	0.75	. . .	0.064	. . .	. . .	845	1550
31	3.18	1.80	0.073	0.090	0.68	0.77	. . .	0.091	0.12	. . .	845	1550
32	3.14	1.70	0.079	0.090	0.69	0.77	. . .	0.071	. . .	0.37 W	845	1550

Fig. 6 Effects of alloying elements on hardenability of gray iron. Irons 1 through 20 were induction furnace melted and poured into standard dry sand molds 30 mm (1.2 in.) in diameter. Alloy constituents for irons 21 through 32 were added to 205 kg (450 lb) ladles, from which the metal was poured into automotive-camshaft production molds. Standard end-quench hardenability specimens were machined from these castings, austenitized for 1 h at the temperatures indicated, and then water quenched.

Treatment Cycle

Austenitizing. In hardening gray iron, the casting is heated to a temperature high enough to promote the formation of austenite, held at that temperature until the desired amount of carbon has been dissolved, and then quenched at a suitable rate. Heating for austenitizing may be accomplished in a salt bath or in an electrically heated, gas-fired or oil-fired furnace.

The temperature to which a casting must be heated is determined by the transformation range of the particular gray iron of which it is made. The transformation range can extend more than 55 °C (100 °F) above the A_1 (transformation-start) temperature. A formula for determining the approximate A_1 transformation temperature of unalloyed gray iron is:

$$°C: 730 + 28.0 (\% Si) - 25.0 (\% Mn)$$
$$°F: 1345 + 50.4 (\% Si) - 45.0 (\% Mn)$$

Chromium raises the transformation range of gray iron. In high-nickel, high-silicon irons, for example, each percent of chromium raises the transformation range by about 10 to 15 °C (20 to 30 °F). Nickel, on the other hand, lowers the critical range. In a gray iron containing from 4 to 5% Ni, the upper limit of the transformation range is about 710 °C (1310 °F).

Provided that recommended limits are not exceeded, the higher the casting is heated above the transformation range, the greater will be the amount of carbon dissolved in the austenite (Fig. 7) and the higher will be the hardness of the casting after quenching (Table 2). In practice, temperatures as much as 95 °C (175 °F) higher than the calculated A_1 transformation temperature are used to ensure full austenitizing. However, excessively high temperatures should be avoided because quenching from such high temperatures increases the danger of distortion and cracking and promotes the retention of austenite, particularly in alloyed irons.

Table 2 Effect of austenitizing temperature on hardness of various oil-quenched gray irons

Composition, %									Hardness, HB, of as-cast iron	Hardness, HB, after oil quenching from			
TC[(a)]	CC[(b)]	Si	P	S	Mn	Cr	Ni	Mo		790 °C (1450 °F)	815 °C (1500 °F)	845 °C (1550 °F)	870 °C (1600 °F)
3.19	0.69	1.70	0.216	0.097	0.76	0.03	. . .	0.013	217	159	269	444	477
3.10	0.70	2.05	. . .	. . .	0.80	0.27	0.37	0.45	255	207	444	514	601
3.20	0.58	1.76	0.187	0.054	0.64	0.005	Trace	0.48	223	311	477	486	529
3.22	0.53	2.02	0.114	0.067	0.66	0.02	1.21	0.52	241	355	469	486	460
3.21	0.60	2.24	0.114	0.071	0.67	0.50	0.06	0.52	235	208	487	520	512
3.36	0.61	1.96	0.158	0.070	0.74	0.35	0.52	0.47	235	370	477	480	465

(a) Total carbon.

(b) Combined carbon

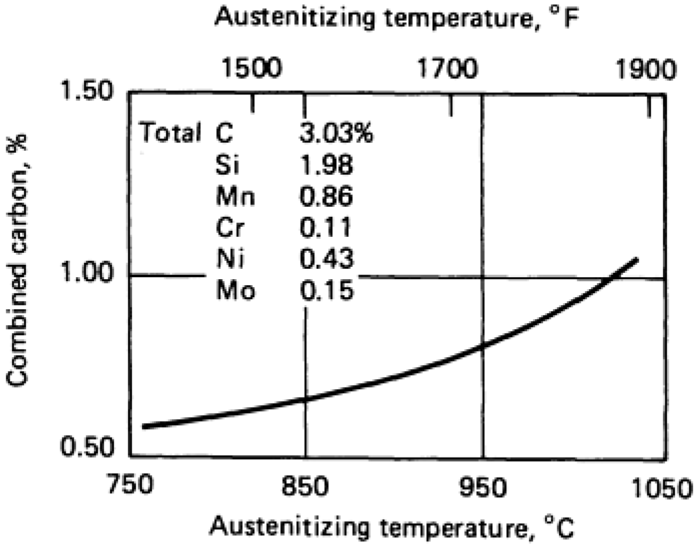


Fig. 7 Increase in combined carbon with increase in austenitizing temperature for gray iron. Specimens were furnace heated and water quenched. Combined carbon by difference

Castings should be treated through the lower temperature range slowly, in order to avoid cracking. Above a range of 595 to 650 °C (1100 to 1200 °F), that is, above the stress-relieving range, heating may be as rapid as desired. In fact, time may be saved by heating the casting slowly to about 650 °C (1200 °F) in one furnace and then transferring it to a second

furnace and bringing it rapidly up to the austenitizing temperature. As little as 20 min per inch of section may be sufficient time at temperature.

Quenching. Molten salt and oil are the quenching media used most frequently for gray iron. Water is not generally a satisfactory quenching medium for furnace-heated gray iron; it extracts heat so rapidly that distortion and cracking are likely in all parts except small ones of simple design. Recently developed water-soluble polymer quenches can provide the convenience of water quenching, along with lower cooling rates, which can minimize thermal shock.

The least severe quenching medium is air. Unalloyed or low-alloy gray iron castings usually cannot be air quenched because the cooling rate is not sufficiently high to form martensite. However, for irons of high alloy content, forced-air quenching is frequently the most desirable cooling method.

A casting of nonuniform section should be quenched in such a way that the heavier section enters the quenching bath first. During quenching, agitation is desirable because it ensures even temperature distribution in the bath and improves quenching efficiency. Because as-quenched castings at room temperature are sensitive to cracking, they should be removed from the quench bath as soon as their temperature falls to about 150 °C (300 °F) and tempered immediately.

Tempering. After quenching, castings are usually tempered at temperatures well below the transformation range for about 1 h per inch of thickest section. As the quenched iron is tempered, its hardness decreases, whereas it usually gains in strength and toughness (Fig. 8 and 9) (Table 3).

Table 3 Composition of gray irons in Fig. 8(d)

Iron	Composition, %					
	TC[(a)]	CC[(b)]	Si	Cr	Ni	Mo
Unalloyed	3.20	0.80	2.43	0.13	0.05	0.17
1	3.23	0.70	2.55	0.58	0.06	0.12
2	3.21	0.83	1.90	0.08	0.78	0.27
3	3.29	0.79	2.58	0.24	0.10	0.55

(a) Total carbon.

(b) Combined carbon

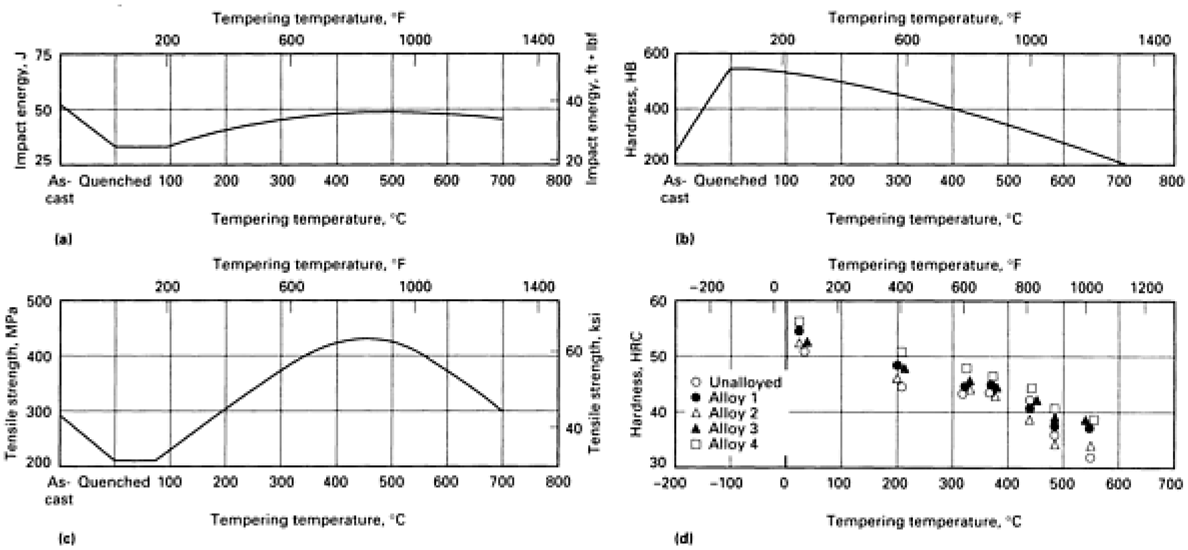


Fig. 8 Effect of tempering temperature on gray iron. (a) to (c) Changes in mechanical properties of hardened low-silicon unalloyed gray iron. (d) Hardness of gray iron specimens quenched in oil from 870 °C (1600 °F) and tempered. Each point on this chart represents an average of five hardness readings. For compositions of irons, see Table 3.

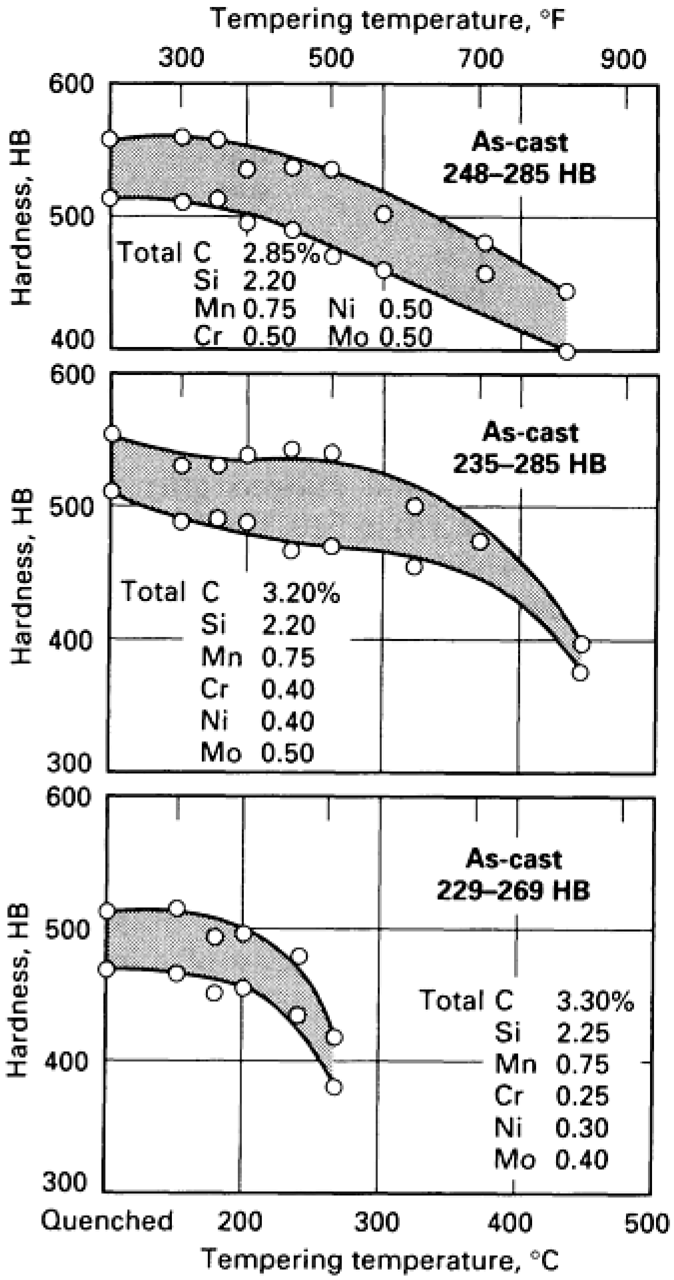


Fig. 9 Influence of alloy content on hardness of quenched and tempered gray iron test castings. Castings were normalized to the same hardness range before being austenitized for hardening and were oil quenched from 850 °C (1560 °F).

Applications

Examples of the quenching and tempering temperatures used and results obtained for four different production parts made of gray iron are discussed below.

Example 1. Unalloyed gray iron valve guides were heated in an atmosphere-controlled furnace and held for 1 h at 885 °C (1625 °F). The guides were then quenched in oil that was maintained at about 60 °C (140 °F). An as-quenched hardness of 45 to 50 HRC was obtained. After tempering at 480 °C (900 °F), hardness was 30 to 34 HRC.

Example 2. Valve guides made of gray iron containing 3.40% C, 2.40% Si, 0.21% Cr, and 0.50% Cu where heated to 870 °C (1600 °F) and held at this temperature for 1h. After being oil quenched from this temperature, the guides were tempered for 1 h at 495 °C (925 °F). Hardness distributions after quenching and after tempering, for 25 guides, are shown in Fig. 10.

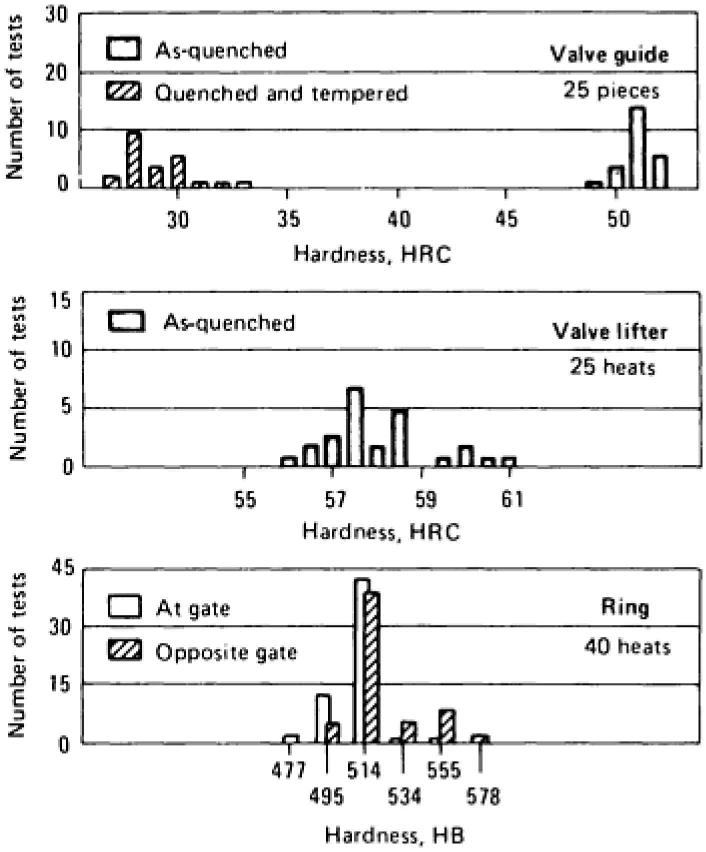


Fig. 10 Distribution of hardness for quenched and tempered production parts made of gray iron

Example 3. Automotive valve lifter castings made of gray iron containing 3.10 to 3.30% C, 2.10 to 2.40% Si, 1.00 to 1.25% Cr, 0.40 to 0.70% Ni, and 0.50 to 0.70% Mo were heated in a gas-fired radiant-tube conveyor furnace. A controlled atmosphere of endothermic generator gas was used to prevent decarburization of the machined surfaces. The castings were held for 45 min at 855 °C (1570 °F), quenched in oil at 55 °C (130 °F), and tempered for 3 h at 150 °C (300 °F) to a hardness of 55 to 61 HRC. The hardness readings were made 1.6 mm ($\frac{1}{16}$ in.) off center from the tappet face. A distribution of hardness values representing castings from 25 heats is given in Fig. 10.

Example 4. Ring-shape castings 65 mm (2.5 in.) in outside diameter by 20 mm (0.75 in.) high by 6.4 to 13 mm (0.25 to 0.5 in.) in wall thickness, made of a hardenable gray iron, were heat treated in groups and sampled for response to heat treatment. These castings were heat treated by holding for $\frac{1}{2}$h at 850 °C (1560 °F) and then oil quenching. Hardness data for 20 consecutive lots representing 40 heats are shown in Fig. 10. Each casting was tested at and opposite the gate.

Properties

The sections below describe some of the effects of tempering on properties. Additional information on the properties of gray irons is contained in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.*

Strength. Tempering increases the tensile strength of hardened gray iron. Although the tempering temperature that yields maximum strength depends on chemical composition and increases with higher alloy content, the high-strength tempering range for both unalloyed and alloyed gray irons is approximately 370 to 510 °C (700 to 950 °F).

Other Properties. Tempering temperatures near 370 °C (700 °F) increase the impact resistance of hardened, low-silicon, unalloyed gray iron (Fig. 8). If alloying elements are present, higher tempering temperatures may be necessary.

Although considerable improvement in tensile strength may result from hardening and tempering, proportional improvements in fatigue properties are rarely obtained.

The modulus of elasticity of a low-alloy (1.32% Ni, 0.44% Cr) gray iron was found to be moderately improved by quench hardening and tempering:

Condition	**Modulus of elasticity**	
	GPa	**ksi**
As-cast	122	17,700
Oil quenched	112	16,200

The modulus of rupture increased markedly with the use of higher tempering temperatures. A similar increase was noted for the transverse breaking load and deflection. In an alloy iron containing 4.5% Ni and 1.5% Cr, the transverse breaking load was increased substantially, even with tempering temperatures as low as 200 °C (400 °F).

Austempering

In austempering, the microstructural end-product of the gray iron matrix formed below the pearlite range but above the martensite range is an acicular or bainitic ferrite, plus varying amounts of austenite, depending on the transformation temperature. The iron is quenched from a temperature above the transformation range in a hot quenching bath and is maintained in the bath at constant temperature until the austempering transformation is complete.

In all hot quenching processes, the temperatures to which castings must be heated for austenitizing and the required holding times at temperature prior to quenching in the hot bath correspond to the temperatures and times used in conventional hardening, that is, temperatures between 840 and 900 °C (1550 and 1650 °F). The holding time depends on the size and chemical composition of the casting. A characteristic curve for hardness as related to isothermal transformation temperature is shown in Fig. 11.

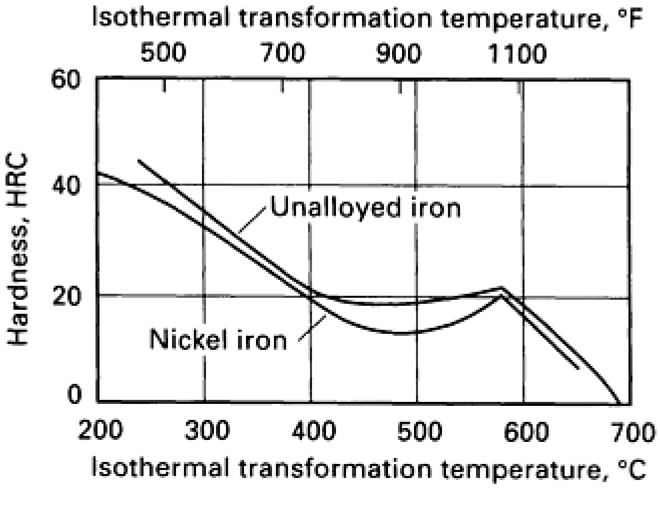


Fig. 11 Effect of isothermal transformation temperature on hardness of austempered gray irons. Holding times were sufficient to complete transformation.

Gray iron is usually quenched in salt, oil, or lead baths at 230 to 425 °C (450 to 800 °F) for austempering. When high hardness and wear resistance are the ultimate aim of this treatment, the temperature of the quench bath is usually held between 230 and 290 °C (450 and 550 °F).

The holding time required for maximum transformation is determined by the temperature of the quenching bath and the composition of the iron. The effect of iron composition on the holding time may be considerable. Alloy additions, such as nickel, chromium, and molybdenum, increase the time required for transformation.

The section thickness and shape of the casting determine the amounts of the added hardenability agents (Ni, Cu, Mo), because cooling must be fast enough to prevent any transformation of austenite until the casting reaches the temperature of the bath. Gray iron cylinder liners containing a minimum of 1.5% total chromium, nickel, molybdenum, and copper have been austempered at about 260 °C (500 °F).

Martempering

Martempering is used to produce martensite without developing the high stresses that usually accompany its formation. It is similar to conventional hardening except that distortion is minimized. Nevertheless, the characteristic brittleness of the martensite remains in a gray iron casting after martempering, and martempered castings are almost always tempered. The casting is quenched from above the transformation range in a salt, oil, or lead bath; held in the bath at a temperature slightly above the range at which martensite forms (200 to 260 °C, or 400 to 500 °F, for unalloyed irons) only until the casting has reached the bath temperature; and then cooled to room temperature.

If a wholly martensitic structure is desired, the casting must be held in the hot quench bath only long enough to permit it to reach the temperature of the bath. Thus, the size and shape of the casting dictate the duration of martempering.

The example below illustrates the use of martempering.

Example 5. Cylinder liners (sleeves) for diesel and heavy-duty gasoline engines, made of gray iron containing 3.25 to 3.50% C, 2.00 to 2.25% Si, 0.25% P (max), 0.12% S (max), 0.55 to 0.80% Mn, and 0.30 to 0.40% Cr, were fully annealed at 870 °C (1600 °F), rough machined, and then austenitized for martempering at 870 °C (1600 °F) in a neutral atmosphere for a total of 1 h (see Table 4 and Fig. 12). They were quenched for 1 min in molten nitrate-nitrite salt at 245 °C (475 °F) and air cooled for 30 min. After being washed to remove adhering salt, the castings were tempered for 2 h at 200 °C (400 °F).

Table 4 Equipment requirements for martempering cast iron cylinder liners

Requirements	Value
Production	
Weight of each piece, kg (lb)	3.8 (8.3)
Number of pieces per push	16
Number of pushes per hour	11
Weight of empty rack, kg (lb)	32 (70)

Total weight of material heated and quenched per hour, kg (lb)	1010 (2231)
Martempering furnace	
Salt pot, 1.83 × 1.98 × 1.83 m (72 × 78 × 72 in.)	Immersion heated, 6.6 m^3 (234 ft^3)[(a)]
Type of salt	Nitrate-nitrite[(b)]
Operating temperature of salt, °C (°F)	245 (475)
Agitation, by 230 mm (9 in.) diam propeller[(c)]	One $7\frac{1}{2}$ hp variable-speed motor
Cooling system	Three $\frac{1}{2}$ hp fans[(d)]

Note: Cylinder liners were austenitized in a radiant tube, gas-fired, single-row pusher furnace containing 27 U-type radiant tubes and accommodating 13 trays per cycle. Each tray measured 610 × 710 mm (24 × 28 in.). Austenitizing temperature was 870 °C (1600 °F). An endothermic atmosphere of 34 m^3/h (1200 ft^3/h) was controlled to 0.2 to 0.4% CO_2 by Orsat analysis.

(a) Pot, containing about 12 Mg (13 tons) of molten salt, was heated by 24 immersion rods, each rated at 5 kW.

(b) Melting point of salt, 145 °C (290 °F). No chloride separation chamber was required because parts were transferred to salt from a controlled-atmosphere hardening furnace.

(c) Propeller was in a 255 mm (10 in.) diam pipe connected to the quench funnel.

(d) Fans force outdoor air through ducts in furnace walls.

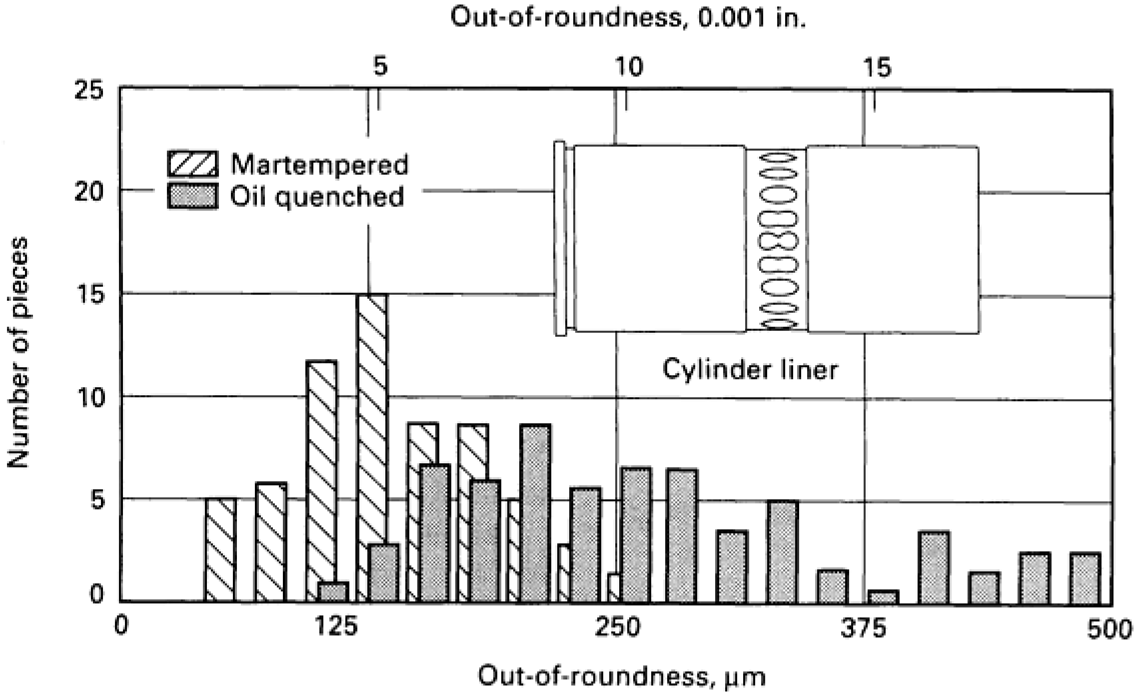


Fig. 12 Distortion in gray iron cylinder liners after martempering and after conventional oil quenching. Before being measured, liners were furnace tempered for 2 h at 200 °C (400 °F).

Austenitizing for martempering was accomplished in a pusher-type continuous furnace. Sixteen sleeves were loaded on each track, which rested on a furnace tray. Upon emerging from the furnace, the rack was pushed from the tray onto a quench elevator that immediately descended into the salt bath; thus, the furnace tray did not come in contact with the molten salt. The sleeves and rack were automatically raised from the salt and remained above the bath for drainage until the next rack was pushed into position, at which point the drained rack was pushed into a slowly moving conveyor for the 30-min cooling cycle. After cooling, the rack and sleeves were moved onto the washer conveyor and, after being washed, were deposited on the tempering-furnace conveyor. Equipment details are summarized in Table 4.

The as-cast sleeves had a graphitic structure predominantly of type A and a graphite flake size of 4 to 6. During the hardening cycle, the matrix dissolved about 0.70% C, and a martensitic structure resulted. The hardness range after hardening was 45 to 50 HRC; the microhardness of the matrix was more than 60 HRC.

Martempering replaced conventional oil quenching, during which each cylinder liner had been placed on a mandrel in order to preserve shape. Despite the use of the mandrel, out-of-roundness after hardening (Fig. 12) and size variations were about twice as great for oil-quenched liners as for those that were martempered. Martempering also eliminated the small percentage of cracked sleeves previously encountered and reduced the amount of grinding stock required for finishing.

Dimensional Accuracy and Distortion. If final dimensional accuracy is important for martempered parts, allowance for growth must be made prior to heat treatment. The uniformity of growth and the allowance required depend on the condition of the iron before hardening. Annealing the cylinder sleeves discussed in Example 5 at 870 °C (1600 °F) and furnace cooling prior to martempering resulted in a linear growth of 0.0010 to 0.0015 mm/mm (0.0010 to 0.0015 in./in.). This was twice as much growth as was encountered when as-cast or normalized pearlitic structures were martempered. A ferritic matrix, which absorbs more carbon during austenitizing than does a pearlitic matrix, causes more expansion (growth).

Some distortion, as differentiated from growth, occurs during martempering. Conditions that may promote excessive distortion are residual stresses from casting, machining, or rapid cooling during previous heat treatments; insufficient time for establishing equilibrium at the austenitizing temperature; and drafts during air cooling after the castings have been removed from the quench bath.

Austempering Versus Martempering. The maximum hardness obtainable by austempering is usually less than that obtainable by martempering, although this difference may be largely canceled during the tempering treatment that is usually necessary following martempering. Both austempering and martempering can result in less distortion and growth than conventional oil quenching and tempering.

Example 6. A high-strength, low-silicon processed iron martempered for 1 min at 260 °C (500 °F) exhibited a hardness of 555 HB, whereas the same iron austempered for 30 min at 275 °C (530 °F) showed a hardness of only 444 HB. After being tempered for 30 min at 390 °C (730 °F), the martempered material had about the same hardness as the austempered material, but its Charpy impact resistance, with a 15 mm (0.6 in.) square specimen and knife edges 70 mm (2.75 in.) apart, was only 14.2 J (10.5 ft · lbf), whereas that of the austempered material was 23.7 J (17.5 ft · lbf). The as-cast material had an impact resistance of 19.7 J (14.5 ft · lbf) and a hardness of 255 HB.

Example 7. When quenched in oil at 95 °C (200 °F) and tempered at 290 °C (550 °F), diesel engine cylinder liners exhibited an average distortion of 0.26 mm (0.0101 in.) and cracked occasionally. When austempered, the same liners had an average distortion of 0.066 mm (0.0026 in.) and when martempered, they displayed an average distortion of 0.06 mm (0.0025 in.). The average maximum growth for these liners was:

Heat treatment	Average maximum growth	
	mm	in.
Oil quenched and tempered	0.71	0.0279
Austempered	0.25	0.0099

The austempering cycle consisted of pre-heating for 5 min at 650 °C (1200 °F), austenitizing for 8 min at 870 °C (1600 °F), quenching to 250 °C (480 °F) and holding for 20 min, and cooling in air. The martempering cycle comprised preheating for 5 min at 650 °C (1200 °F), austenitizing for 8 min at 855 °C (1575 °F), quenching for 1 min in agitated salt at 345 °C (650 °F), cooling in air for a minimum of 1 h, and tempering at 175 °C (350 °F).

Flame Hardening

Flame hardening is the method of surface hardening most commonly applied to gray iron. The mechanics of the process are dealt with in the article "Flame Hardening" in this Volume.

After flame hardening, a gray iron casting consists of a hard, wear-resistant outer layer of martensite and a core of softer gray iron, which during treatment does not reach the A_1 transformation temperature (in fact, the unhardened metal immediately below the hardened case, which has been heated by the flame to some extent, may even be partially annealed during flame hardening if it is unalloyed).

Recommended Composition. Both unalloyed and alloyed gray irons can be successfully flame hardened. However, some compositions yield much better results than do others. One of the most important aspects of composition is the combined carbon content, which should be in the range of 0.50 to 0.70%, although irons with as little as 0.40% combined carbon can be flame hardened. In general, flame hardening is not recommended for irons that contain more than 0.80% combined carbon because such irons (mottled or white irons) may crack in surface hardening.

The stability of the microconstituents from which the carbon precipitates is a factor in determining the hardness of the flame-hardened iron. One user observed that the stability of microconstituents containing combined carbon is indicated by the hardness of test specimens annealed at 845 °C (1550 °F). A test of four pearlitic irons from different sources, containing 3.30% C max, 1.40 to 1.60% Si, 0.80 to 1.10% Mn, and 0.15 to 0.20% Cr, gave the results:

Iron	**Hardness, HB**		**Hardness[(a)], HRC**
	As-cast	**Annealed**	
A	220	200	47-50
B	190	180	47-50
C	200	140	35-38

(a) After flame hardening as-cast iron

For maximum hardness, it is advisable to use an iron containing as small an amount of total carbon as is consistent with the production of sound castings free from any danger of cracking. The coarse graphite flakes typical of high-carbon irons should be avoided because they may be burned out during flame heating, thereby producing a porous and unattractive surface.

Because silicon promotes the formation of graphite and of a low combined carbon content, a relatively low silicon content is also advisable. Several users report that silicon content should not exceed 2% in any iron submitted to a flame-hardening operation, although alloy irons containing 2.4% Si can be hardened successfully. They also recommend that manganese content be held in the range of 0.80 to 1.00% to increase carbon solubility in austenite.

Gray iron to be flame hardened should be as free as possible from porosity and from foreign matter such as sand or slag because porosity and even small inclusions of foreign matter can produce a rough surface or result in cracking after hardening. Rough casting surfaces should be sand or shot blasted prior to heat treatment because skin or scale on the surface acts as a heat insulator and reduces the effectiveness of flame hardening.

Effects of Alloying Elements. In general, alloyed gray irons can be flame hardened with greater ease than can unalloyed irons, partly because alloyed gray irons have increased hardenability. Final hardness also may be increased by alloying additions. The maximum hardness obtainable by flame hardening an unalloyed gray iron containing approximately 3% total carbon, 1.7% Si, and 0.60 to 0.80% Mn ranges from 400 to 500 HB. This is because the Brinell hardness value for gray iron is an average of the hardness of the matrix and that of the relatively soft graphite flakes. Actually, the matrix hardness on which wear resistance depends approximates 600 HB. With the addition of 2.5% Ni and 0.5% Cr, an average surface hardness of 550 HB can be obtained. The same result has been achieved using 1.0 to 1.5% Ni and 0.25% Mo. Small additions of chromium are particularly valuable in preventing softening and ensuring the retention of a high content of combined carbon during austenitizing for hardening. Automotive camshafts containing 1% Cr, 0.50% Mo, and 0.8% Mn are easily flame hardened to 52 HRC to a required depth. These parts are not tempered or stress relieved.

Stress Relieving. Whenever practicable or economically feasible, flame-hardened castings should be stress relieved at 150 to 200 °C (300 to 400 °F) in a furnace, in hot oil, or by passing a flame over the hardened surface. Such a treatment will minimize distortion or cracking and will increase the toughness of the hardened layer.

Stress relieving at 150 °C (300 °F) for 7 h was found to remove 25 to 40% of the residual stresses in a flame-hardened casting, while reducing the hardness of the surface by only 2 to 5 points on the HRA scale. Although stress relieving is desirable, it can often be safely omitted.

Hardness. The surface of flame-hardened gray iron typically has a somewhat lower hardness than the metal immediately below the surface (Fig. 13). This decrease in hardness may be caused by the retention of relatively soft austenite at the surface. Surface hardness often can be raised by heating in the range from 195 to 250 °C (380 to 480 °F).

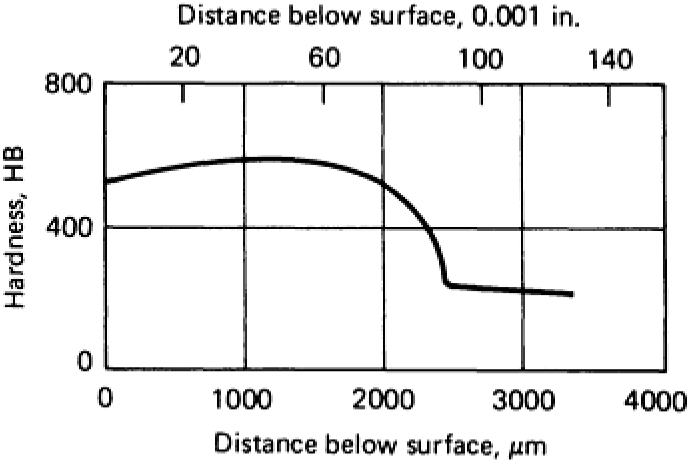


Fig. 13 Typical hardness gradient produced in gray iron by flame hardening

The depth and microstructure of the hardened layer depend on two other factors in addition to temperature: the amount of carbon and alloying elements in solution when the flame-hardened surface is quenched, and the efficiency of quenching. If softness is due to the presence of austenite in the microstructure, subjecting the part to -40 °C (-40 °F) for 1 h will transform the austenite and increase the hardness.

Fatigue strength is usually increased by surface hardening because the treatment induces compressive stresses at the surface. For example, flame or induction heating followed by water quenching induces high compressive stresses (>205 MPa, or 30 ksi) in the fillet areas of crankshafts; however, if self-quenching instead of water quenching is used, undesirable tensile stresses may result at the surface. The degree of improvement in fatigue strength by flame hardening cannot be produced by through hardening.

Quenching. The various methods of flame hardening influence the selection of the quenching medium. In the progressive method, only nonflammable media such as water, soluble-oil mixtures, and solutions of polyvinyl alcohol in water can be employed. Conventional oil cannot be used because of the fire hazard. In spot hardening or spinning methods, in which the flame head is withdrawn from the part before quenching, parts are quenched conventionally by immersion in hot oil.

When quenching is done with water, the water should be at about 30 °C (90 °F) for best results. Lower quenching rates, such as those obtained with 5 to 15% soluble-oil mixtures, compressed air, or compressed air and water at low pressure, are used to prevent cracking. Air quenching is especially suited to highly alloyed cast irons because of their susceptibility to cracking.

Induction Hardening

Gray iron castings can be surface hardened by the induction method when the number of castings to be processed is large enough to warrant the relatively high equipment cost and the need for special induction coils. Considerable variation in

the hardness of the cast irons may be expected because of a variation in the combined carbon content. A minimum combined carbon content of 0.40 to 0.50% C (as pearlite) is recommended for cast iron to be hardened by induction, with the short heating cycles that are characteristic of this process. Heating castings with lower combined carbon content to high hardening temperatures for relatively long periods of time may dissolve some free graphite, but such a procedure is likely to coarsen the grain structure at the surface and will result in undesirably large amounts of retained austenite in the surface layers. The recommended minimum induction hardening temperature for gray iron is 870 to 925 °C (1600 to 1700 °F).

The surface hardness attained from the induction hardening of gray iron is influenced by the carbon equivalent (%C + $\frac{1}{3}$% Si) when this hardness is measured by conventional Rockwell tests. The more graphite that is present in the microstructure, the lower the surface hardness will appear to be after hardening. Table 5 shows the surface hardness of induction-hardened gray iron castings of various carbon equivalents from 3.63 to 4.23. The microstructure of these castings, which were cast in the same manner and cooled at similar rates, contained more and larger graphite flakes as the carbon equivalent increased. This resulted in lower apparent surface hardness after hardening, yet the hardened matrix was consistently 57 to 61 HRC (converted from microhardness).

Table 5 Effect of carbon equivalent on surface hardness of induction-hardened gray irons

Composition, %[(a)]		Carbon equivalent[(b)]	Hardness HRC, converted from		
C	Si		As read	Rockwell 30-N	Microhardness
3.13	1.50	3.63	50	50	61
3.14	1.68	3.70	49	50	57
3.19	1.64	3.74	48	50	61
3.34	1.59	3.87	47	49	58
3.42	1.80	4.02	46	47	61
3.46	2.00	4.13	43	45	59
3.52	2.14	4.23	36	38	61

(a) Each iron also contained 0.50 to 0.90 Mn, 0.35 to 0.55 Ni, 0.08 to 0.15 Cr, and 0.15 to 0.30 Mo.

(b) Carbon equivalent = %C + $\frac{1}{3}$% Si.

Distortion. Induction hardening causes less distortion than would a similar quenching treatment from a furnace. The maximum warpage in a 560 mm (22 in.) length of bar was found to be 0.03 mm (0.0015 in.) after induction hardening, compared with 0.17 to 0.25 mm (0.007 to 0.010 in.) for the same bars quenched from a furnace. For thin-walled cylinders, distortion is not a problem unless the thickness of the induction-hardened layer exceeds 20% of the wall thickness.

For selective hardening, in place or by scanning, to depths up to 3.8 mm (0.150 in.), water quenching can be used safely. However, the hardening of keyways, cross-drilled holes, or extremely thin walls may require the use of oil to prevent excessive distortion or cracking.

Example 8. A cast frame for a baler knotter had a nominal composition of 3.30 to 3.50% C, 0.50 to 0.70% Mn, 0.30 to 0.40% P, 0.15% S max, and about 2.40 to 2.60% Si. A 10.9 mm ($\frac{7}{16}$ in.) section of the frame was heated for 12 s with a 14 kW, 10 kHz unit using a modified hairpin-type inductor. After being water quenched for 4 s, it developed an apparent hardness of approximately 45 HRC (not indicative of the true hardness of the matrix, which can harden to 61 HRC or higher).

Stress Relieving

Gray iron in the as-cast condition contains residual stresses (unless the iron is cooled in the mold, in which case much of the solidification stress is removed)because cooling (and therefore contraction) proceeds at different rates in various sections of a casting. The resultant residual stresses may reduce strength, cause distortion, and in extreme cases even result in failure or cracking. The magnitudes of these stresses depend on the shape and section size of the casting, on the casting technique employed, on the composition and properties of the cast material, and on whether the casting has been stress relieved.

Temperature of stress relieving is usually well below the range for the transformation of pearlite to austenite.

The effects of stress relieving at 650 °C (1200 °F) for 6 h on the tensile strength and hardness of gray irons of classes 25, 35, and 50 are plotted in Fig. 14. As indicated, the properties of the class 25 iron were affected considerably more than were those of the class 35 and class 50 irons. Figure 15 shows the effect of stress-relieving temperature on the hardness of unalloyed and alloyed gray irons.

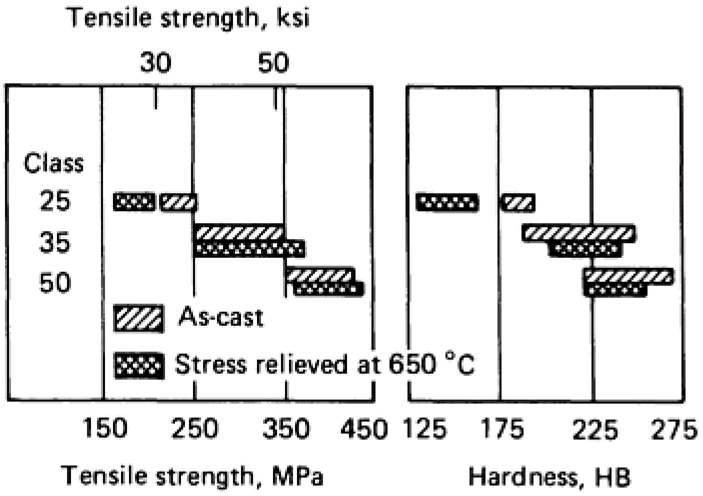
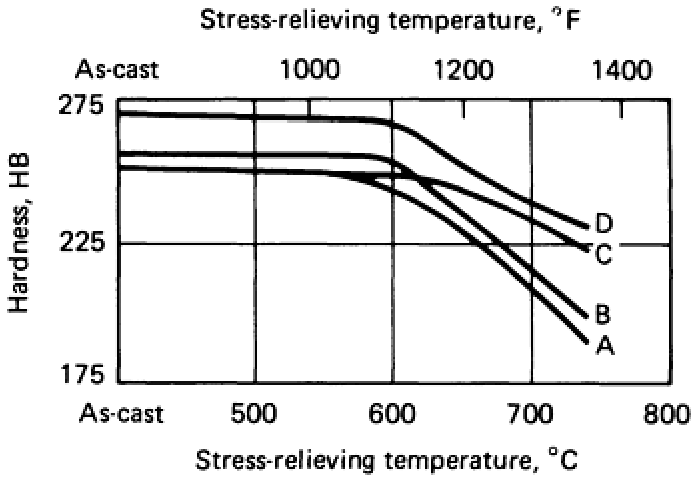


Fig. 14 Effects of stress relieving on tensile strength and hardness of gray iron. Gray iron bars, 30 mm (1.2 in.) in diameter, were stress relieved for 6 h at 650 °C (1200 °F) in a car bottom furnace approximately 13 × 4 × 3 m (42 × 13 × 9 ft); total furnace time was 43$\frac{3}{4}$ h.



Iron	Composition, %					
	TC[a]	CC[b]	Si	Cr	Ni	Mo
A	3.20	0.80	2.43	0.13	0.05	0.17
B	3.29	0.79	2.58	0.24	0.10	0.55
C	3.23	0.70	2.55	0.58	0.06	0.12

(a) Total carbon.

(b) Combined carbon

Fig. 15 Effect of stress-relieving temperature on hardness of gray irons. Bar specimens 30 mm (1.2 in.) in diameter were held for 1 h at indicated temperatures and then air cooled.

For a maximum relief of stress with a minimum of decomposition of carbide in unalloyed irons, a temperature range of 540 to 565 °C (1000 to 1050 °F) is desirable. Figure 16 indicates that from 75 to 85% of the residual stress can be removed by holding for 1 h in this range. Other investigations (for example, see Fig. 17) indicate that the curves in Fig. 16 are applicable to gray irons over a wide range of compositions.

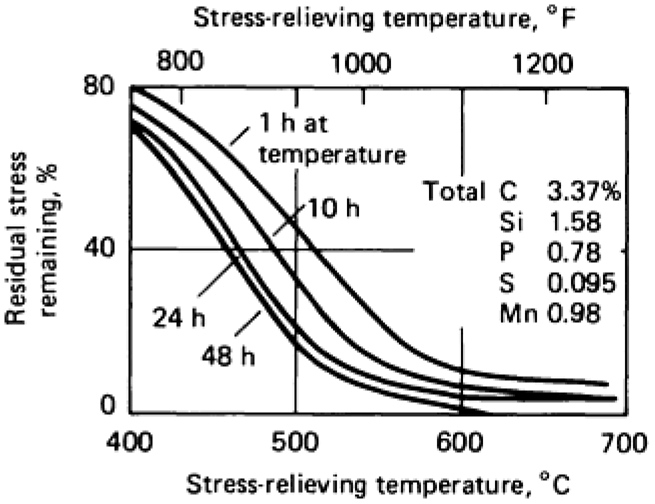


Fig. 16 Effect of stress-relieving temperature on residual stress in gray iron

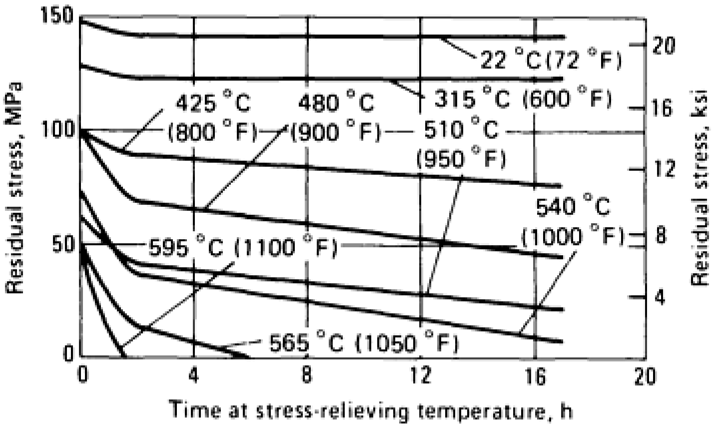
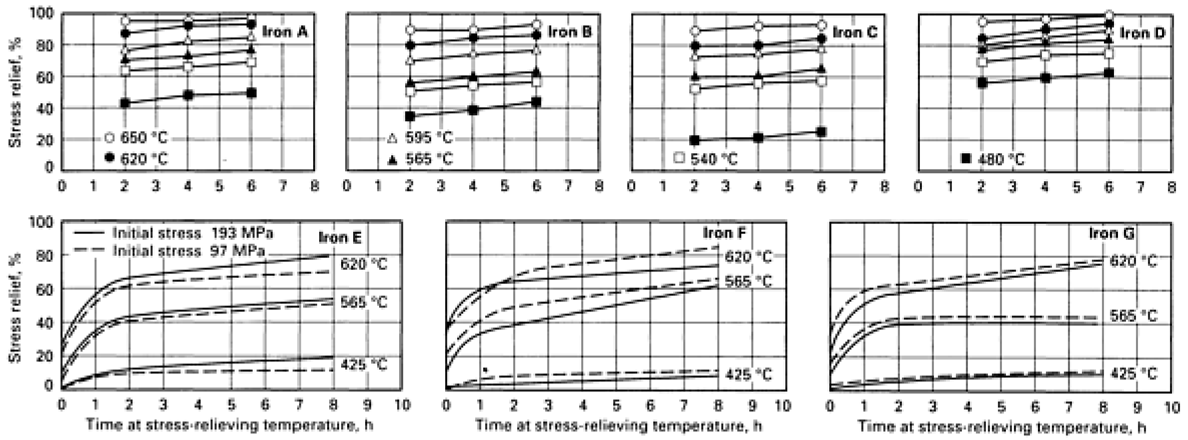


Fig. 17 Effect of stress-relieving temperature and time on residual stress in gray iron. Composition of iron: 2.72% C, 1.97% Si, 0.141% P, 0.080% S, 0.51% Mn

When almost complete stress relief (>85%) is required in unalloyed iron, a minimum temperature of 595 °C (1100 °F) can be employed; however, some sacrifice in strength, hardness, and wear resistance is likely. Fortunately, the soft irons of higher carbon equivalent normally exhibit a lower level of residual stress and comparatively low creep resistance, facilitating stress relief. In fact, irons of high carbon equivalent can be satisfactorily stress relieved at the lower end of the suggested temperature range, that is, at about 510 °C (950 °F). Low-alloy gray irons usually require higher stress-relieving temperatures--on the order of 595 to 650 °C (1100 to 1200 °F), depending on alloy content.

Quantitative data concerning the effects of alloying elements on the optimum stress-relieving temperature are meager. However, it has been reported that in one instance the addition of as little as 0.14% Cr to a 3.20C-2.01Si iron permitted exposure of the iron to a temperature of about 650 °C (1200 °F) for 1 h without sacrifice in room-temperature tensile strength. Figure 18 shows the effect of temperature and time on the relief of stresses for seven low-alloy irons, and the tabulation below the graphs indicates that these irons, depending on shakeout time, can be stress relieved for 8 h at 620 °C (1150 °F) with no adverse effect on hardness.



Iron	Composition, %										Hardness, HRB	
	C	Si	P	S	Mn	Ni	Cr	Mo	Cu	V	Before stress relieving	After stress relieving for 8 h at 620 °C (1150 °F)
A	2.93	2.14	0.110	0.57	0.47	0.35	0.10	. . .	. . .	. . .	98	94
B	3.43	2.12	0.104	0.70	0.81	0.34	0.18	0.23	. . .	. . .	98	94
C	3.24	2.55	0.107	0.62	0.87	0.51	0.20	0.22	. . .	. . .	95	95
D	3.91	1.43	0.54	0.25	0.32	1.56	0.06	. . .	. . .	. . .	82	80
E	3.18	2.13	0.73	0.125	0.70	1.03	0.33	0.65	. . .	. . .	98	98
F	3.12	1.76	0.075	0.097	0.78	1.02	0.41	0.58	. . .	. . .	94	95

Fig. 18 Effect of stress-relieving time and temperature on degree of stress relief obtained in low-alloy gray irons. Table shows compositions and negligible effect of maximum stress-relieving conditions on hardness.

Recommended stress-relieving temperatures, based on normal shakeout times in the foundry, are:

Iron	Temperature	
	°C	°F
Unalloyed, or alloyed without Cr	510-565	950-1050
0.15-0.30% Cr	595-620	1100-1150
>0.30% Cr	620-650	1150-1200

If the service requirements of a casting demand a particularly low residual stress, temperatures about 30 °C (50 °F) above those listed may be used. When these higher temperatures are used, it is advisable to check the hardness of the stress-relieved casting, if hardness and strength are critical, to determine whether an unacceptable decrease in hardness or strength has taken place.

Rate of Heating. The rate at which gray iron castings are heated for stress relief depends on the shape and size of the part but, except for the most complex shapes, is not especially critical. When a batch-type furnace is employed, it is of the utmost importance that furnace temperature not exceed 95 °C (200 °F) at the time of loading. After the furnace is loaded, the heating rate may be fairly high. For example, it is common practice to heat to 620 °C (1150 °F) in about 3 h, hold at temperature for 1 h, and cool to 315 °C (600 °F) in about 4 h before removing castings from the furnace and permitting them to cool in air. These conditions also apply to continuous furnaces in which the various temperature zones can be controlled to avoid introducing additional thermal stress in the castings. It is imperative that flame impingement on castings, which may result in variations in hardness, be avoided.

Rate of Cooling. If a casting is allowed to cool rapidly from the stress-relieving temperature to room temperature, new stresses may be developed and the goal of maximum stress elimination will not be fully achieved. For this reason, slow cooling from the stress-relieving temperature, at least in the upper temperature range, is an essential part of stress relieving.

It is generally recommended that castings be furnace cooled to 315 °C (600 °F) or lower before being allowed to cool in air; for castings of intricate design, it may even be advisable to continue furnace cooling until a temperature of about 95 °C (200 °F) has been reached. Most commercial furnaces cool slowly enough to meet all requirements.

Reduction of Distortion and Elimination of Cracking. The following examples illustrate the use of stress relieving to eliminate distortion and cracking.

Other examples of castings that require stress relief are pump volutes, scrolls, and casings. These parts require two stress-relieving treatments: first, in the as-cast condition, to minimize distortion during machining; and second, after rough machining, to minimize distortion during final machining.

Example 9. A flatness tolerance of 0.1 mm (0.004 in.) could not be maintained after machining as-cast clutch plates. These parts were made of gray iron containing 3.40% C (0.70 to 0.90 combined carbon), 1.30 to 1.80% Si, 0.25 to 0.40% Cr, 0.30 to 0.40% Mo, and nickel and copper as required for a minimum tensile strength of 275 MPa (40 ksi) and a hardness of 207 to 255 HB. After these clutch plates were stress relieved at 620 °C (1150 °F) for 2 h, the tolerance could be held.

Example 10. Necessitated by a rush order, a change in procedure from a slow cool in the mold to a fast shakeout resulted in high residual stress in cast transmission cases. These parts were made of gray iron containing 3.10 to 3.40% C, 2.15 to 2.35% Si, and 0.20 to 0.40% Cr. Some of the first castings produced after the change in procedure developed cracks up to 1.3 mm (0.050 in.) wide during machining; others, although they survived machining without cracking, developed cracks during a final hot washing operation. This problem was eliminated for the remaining pieces from this order by stress relieving them at 620 °C (1150 °F) for 2 h. A return to the original cooling and shakeout practice with subsequent orders eliminated cracking and the need for stress relieving.

Example 11. Hot tears and out-of-roundness occurred in as-cast rings, and additional distortion in the flat plane of these rings occurred during machining. A change in the method of gating these castings equalized temperature differentials and controlled shrinkage distribution, thereby eliminating the hot tears and as-cast distortion. The distortion occurring during machining was eliminated by stress relieving the rings at 370 °C (700 °F) for 2 h.

Example 12. Table 6 shows the results of an evaluation of different cooling methods and stress-relieving treatments on residual stresses in 225 kg (500 lb) diesel engine cylinder blocks. These blocks were made of gray iron containing 3.25% C, 2.20% Si, and 0.30% Cr and having a tensile strength of 240 MPa (35 ksi).

Table 6 Effect of shakeout practice and stress relieving on residual stress in 225 kg (500 lb) diesel engine cylinder blocks

Practice	Close-in		Stress relief, %
	mm	in.	
1. Shakeout after 6 h; cores in place while cooling to 27 °C (80 °F); total time, 16 h	4.1	0.160	Basis for evaluation
2. Practice 1, except cores also shaken out at 6 h	1.9	0.076	52
3. Cooled in mold 16 h before shakeout	1.6	0.064	60
4. Practice 1, followed by stress relieving at 540 °C (1000 °F) for 2 h, furnace cooling to 370 °C (700 °F)	1.5-1.9	0.060-0.076	52-62
5. Practice 1, followed by stress relieving at 620 °C (1150 °F) for 2 h, furnace cooling to 370	0.3-	0.012-	91

Two vertical lines were scribed on one end of each block after shakeout. The distance between these lines was measured before and after vertical saw cuts (parallel to the scribed lines) were made through the end of each block to the first cylinder bore. The amount of close-in between the two vertical lines after sawing was a relative measure of the residual stress.

The results (see Table 6) indicate that the complete shakeout (including cores), allowing inner sections to cool faster, materially reduced stresses, as did the procedure of leaving the casting in the mold to slow the cooling of external sections. This latter procedure is effective if the mass of metal is sufficient to keep the external sections at a high temperature throughout--620 °C (1150 °F) or higher--while equilibrium between outer and inner sections is taking place. As indicated, stress relieving at 540 °C (1000 °F) was substantially less effective than stress relieving at 620 °C (1150 °F).

Heat Treating of Ductile Irons

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Introduction

DUCTILE CAST IRONS (also known as nodular or spheroidal graphite iron), are primarily heat treated to create matrix microstructures and associated mechanical properties not readily obtained in the as-cast condition. As-cast matrix microstructures usually consist of ferrite or pearlite or combinations of both, depending on cast section size and/or alloy composition. These and other factors that affect the casting of ductile irons are discussed in the article "Classification and

Basic Metallurgy of Cast Iron" in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.* The purpose of this article is to discuss the heat treatment of ductile irons.

The most important heat treatments and their purposes are:

- Stress relieving, a low-temperature treatment, to reduce or relieve internal stresses remaining after casting
- Annealing, to improve ductility and toughness, to reduce hardness, and to remove carbides
- Normalizing, to improve strength with some ductility
- Hardening and tempering, to increase hardness or to improve strength and raise proof stress ratio
- Austempering, to yield a microstructure of high strength, with some ductility and good wear resistance
- Surface hardening, by induction, flame, or laser, to produce a locally selected wear-resistant hard surface

The normalizing, hardening, and austempering heat treatment, which involve austenitization followed by controlled cooling or isothermal reaction, or a combination of the two, can produce a variety of microstructures and greatly extend the limits on the mechanical properties of ductile cast iron. These microstructures can be separated into two broad classes:

- Those in which the major iron-bearing matrix phase is the thermodynamically stable body-centered cubic (ferrite) structure
- Those with a matrix phase that is a metastable face-centered cubic (austenite) structure

The former are usually generated by the annealing, normalizing, normalizing and tempering, or quenching and tempering processes. The latter are generated by austempering, an isothermal reaction process resulting in a product called austempered ductile iron (ADI).

Other heat treatments in common industrial use include stress-relief annealing and selective surface heat treatment. Stress-relief annealing does not involve major microstructural transformations, whereas selective surface treatment (such as flame and induction surface hardening) does involve microstructural transformations, but only in selectively controlled parts of the casting.

General Characteristics

The basic structural differences between the ferritic and austenitic classes are explained in Fig. 1 and 2. Figure 1 shows a continuous cooling transformation (CCT) diagram and cooling curves for furnace cooling, air cooling, and quenching. It can be seen from Fig. 1 that slow furnace cooling results in a ferritic matrix (the desired product of annealing), whereas the cooling curve for air cooling, or normalizing, results in a pearlitic matrix, and quenching produces a matrix microstructure consisting mostly of martensite with some retained austenite. Tempering softens the normalized and quenched conditions, resulting in microstructures consisting of the matrix ferrite with small particles of iron carbide (or secondary graphite). Examples of furnace-cooled, air-cooled, and water-quenched microstructures are shown in Fig. 3. Actual annealing cycles usually involve more than just furnace cooling, depending on alloy content and prior structure. These processes will be detailed in the next section.

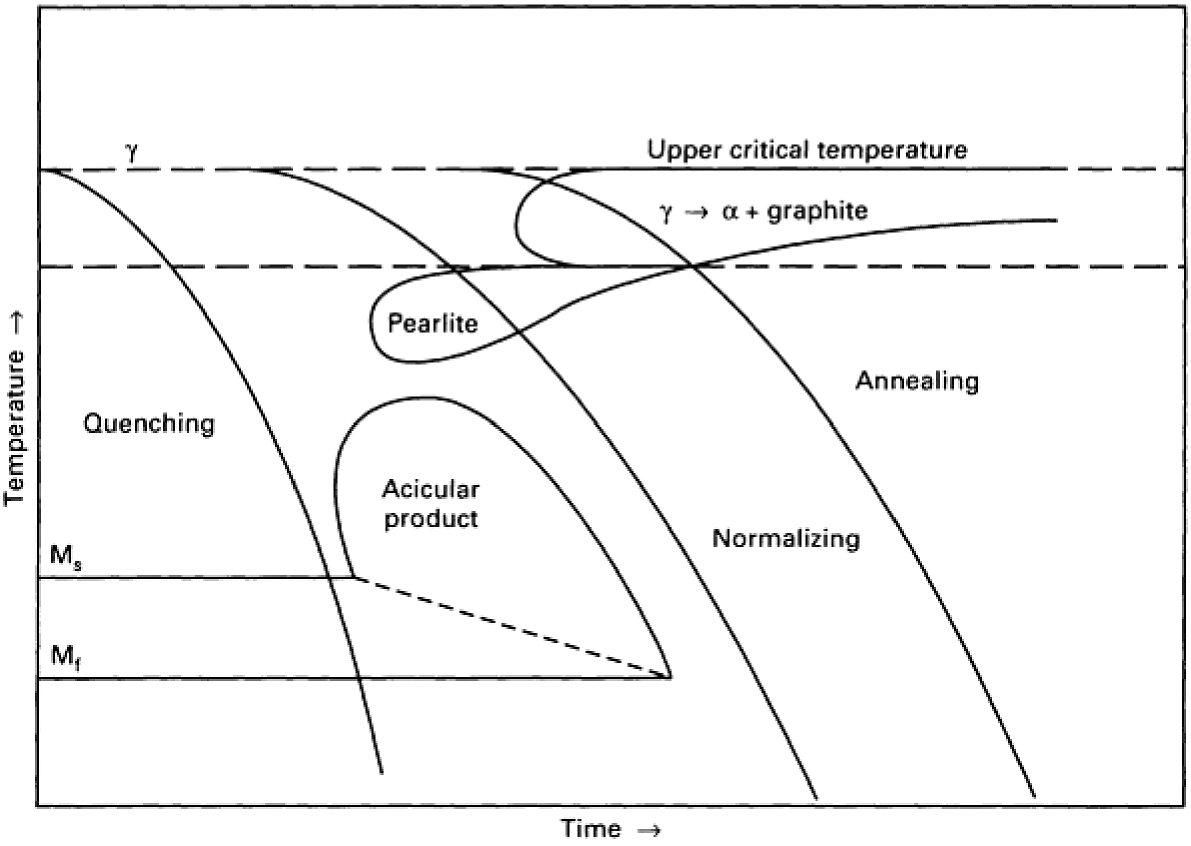


Fig. 1 CCT diagram showing annealing, normalizing, and quenching. M_s, martensite start; M_f, martensite finish

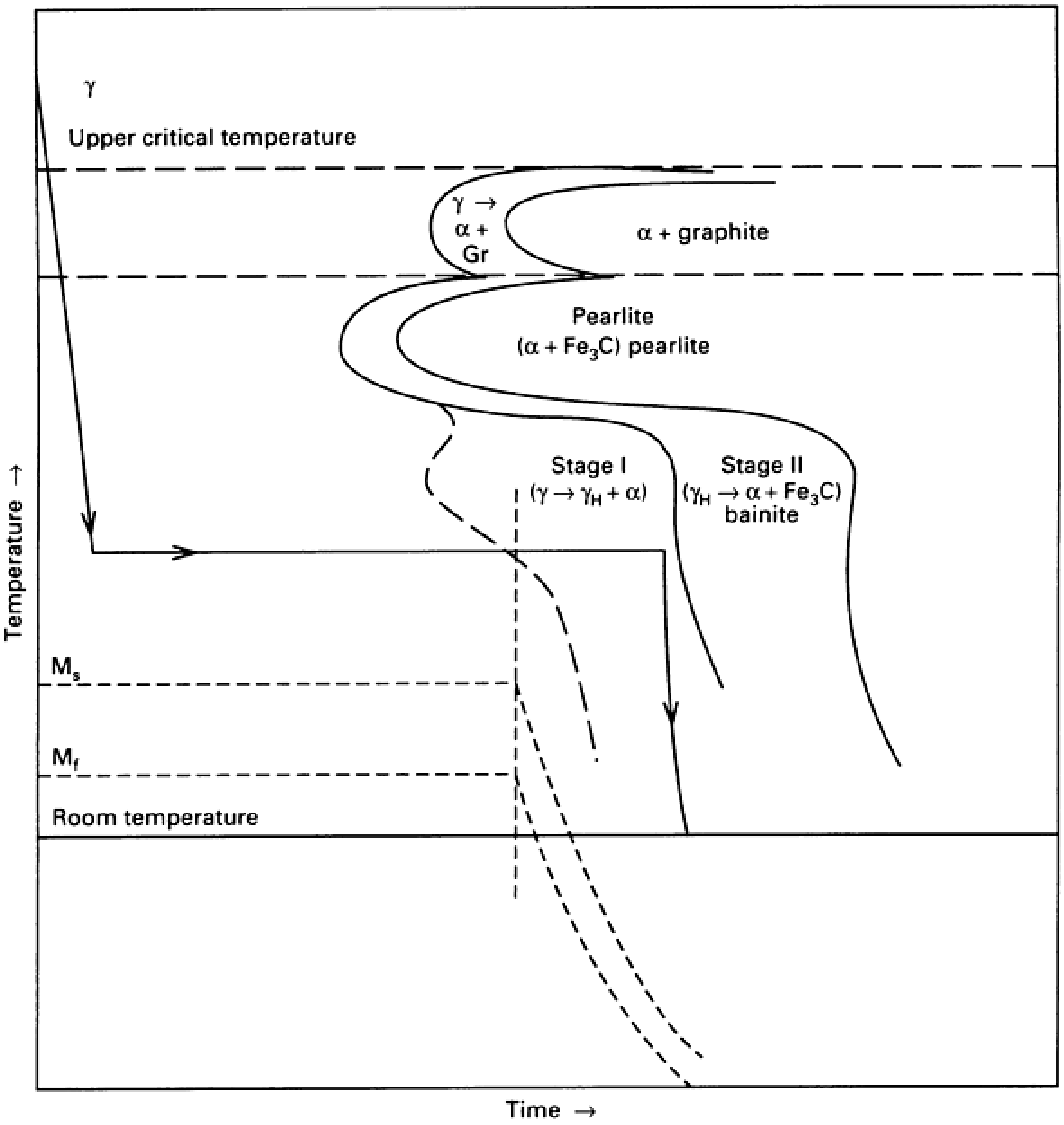


Fig. 2 IT diagram of a processing sequence for austempering, with the M_s and M_f decreasing as the γ is enriched with carbon during stage I

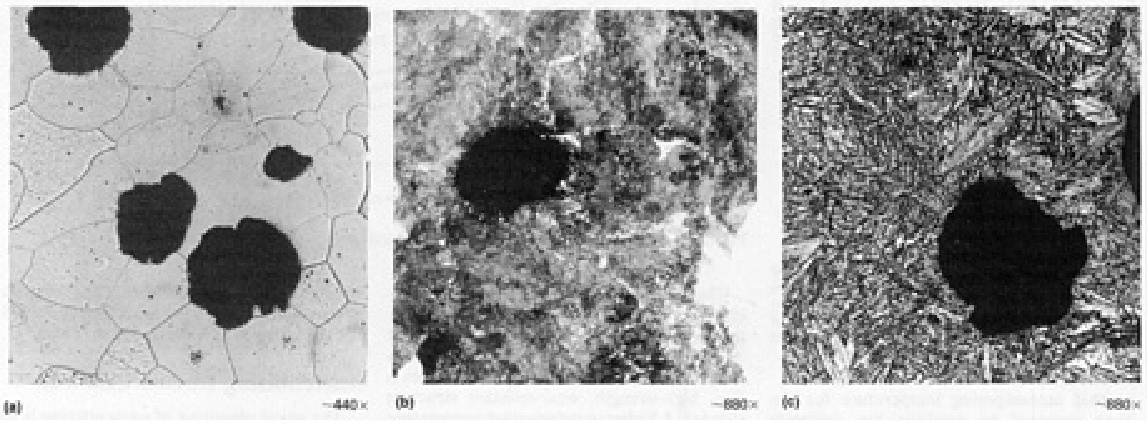
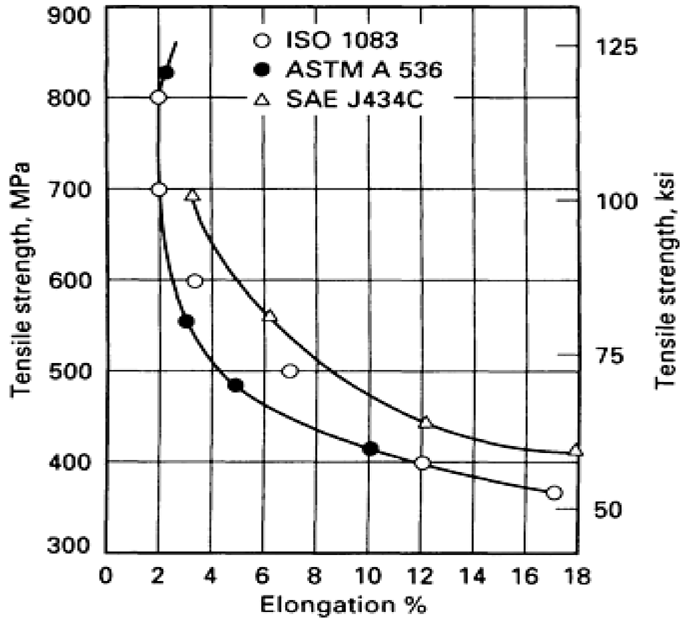


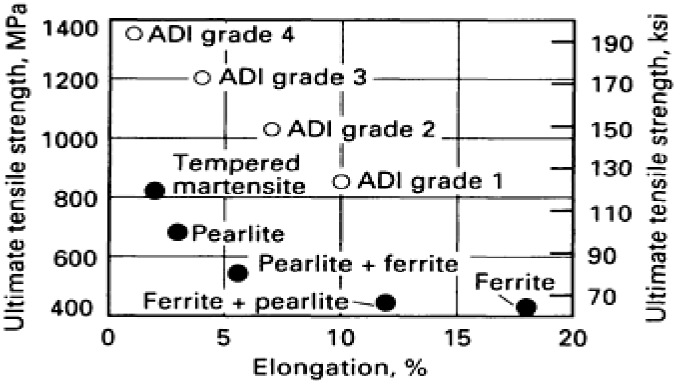
Fig. 3 Optical micrographs of ductile iron with (a) a ferritic matrix in an annealed casting, (b) fine pearlitic matrix in a normalized casting, and (c) a martensitic matrix in a quenched casting. Etched in nital; approximate magnifications shown

Figure 2 shows an isothermal transformation (IT) diagram for a ductile cast iron, together with a processing sequence depicting the production of ADI. In this process, austenitizing is followed by rapid quenching (usually in molten salt) to an intermediate temperature range for a time that allows the unique metastable carbon-rich (~2% C) austenitic matrix (γ_H) to evolve simultaneously with nucleation and growth of a plate-like ferrite (α) or of ferrite plus carbide, depending on the austempering temperature and time at temperature. This austempering reaction progresses to a point at which the entire matrix has been transformed to the metastable product (stage I in Fig. 2), and then that product is "frozen in" by cooling to room temperature *before* the true bainitic ferrite plus carbide phases can appear (stage II in Fig. 2). In ductile cast irons the presence of 2 to 3 wt% Si prevents the rapid formation of iron carbide (Fe_3C). Hence the carbon rejected during ferrite formation in the first stage of the reaction (stage I in Fig. 2) enters the matrix austenite, enriching it and stabilizing it thermally to prevent martensite formation upon subsequent cooling. Thus the processing sequence in Fig. 2 shows that the austempering reaction is terminated before stage II begins and illustrates the decrease in the martensite start (M_s) and martensite finish (M_f) temperatures as γ_H forms in stage I. The kinetics of stage I and stage II have been described in detail in the literature (Ref 1, 2, 3, 4). Typical austempering times range from 1 to 4 h, depending on alloy content and section size. If the part is austempered too long, undesirable bainite will form. Unlike steel, bainite in cast iron microstructures exhibits lower toughness and ductility.

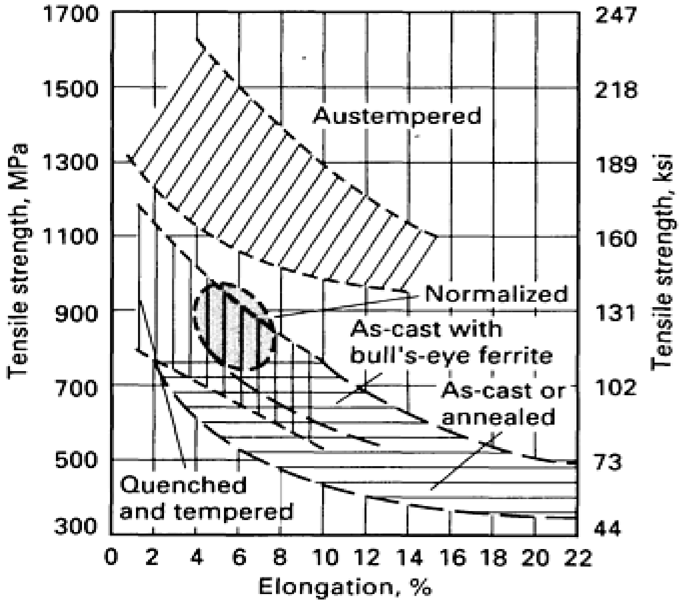
Tensile Properties. Figure 4(a) shows the relationship between minimum specified values for tensile strength and elongation representing the range of values covered by the ISO, ASTM, and SAE specifications. Figure 4(b) shows the difference between minimum values for ASTM grades of austempered and other types of ductile iron. The actual values of properties to be expected from good-quality ductile irons produced to meet any given specified grade will normally cover a range, as shown in Fig. 4(c) and 5.


ISO 1083
ASTM A 536
SAE J434C
Tensile strength, MPa
Tensile strength, ksi
Elongation %

(a)


ADI grade 4
ADI grade 3
ADI grade 2
ADI grade 1
Tempered martensite
Pearlite
Pearlite + ferrite
Ferrite + pearlite
Ferrite
Ultimate tensile strength, MPa
Ultimate tensile strength, ksi
Elongation, %

(b)


Austempered
Normalized
As-cast with bull's-eye ferrite
As-cast or annealed
Quenched and tempered
Tensile strength, MPa
Tensile strength, ksi
Elongation, %

(c)

Fig. 4 Tensile strength versus elongation of ductile iron. (a) Minimum values given in various standards. (b) Minimum values of austempered ductile iron grades specified in ASTM A 897. (c) Range of tensile strength and elongation values with different heat treatments

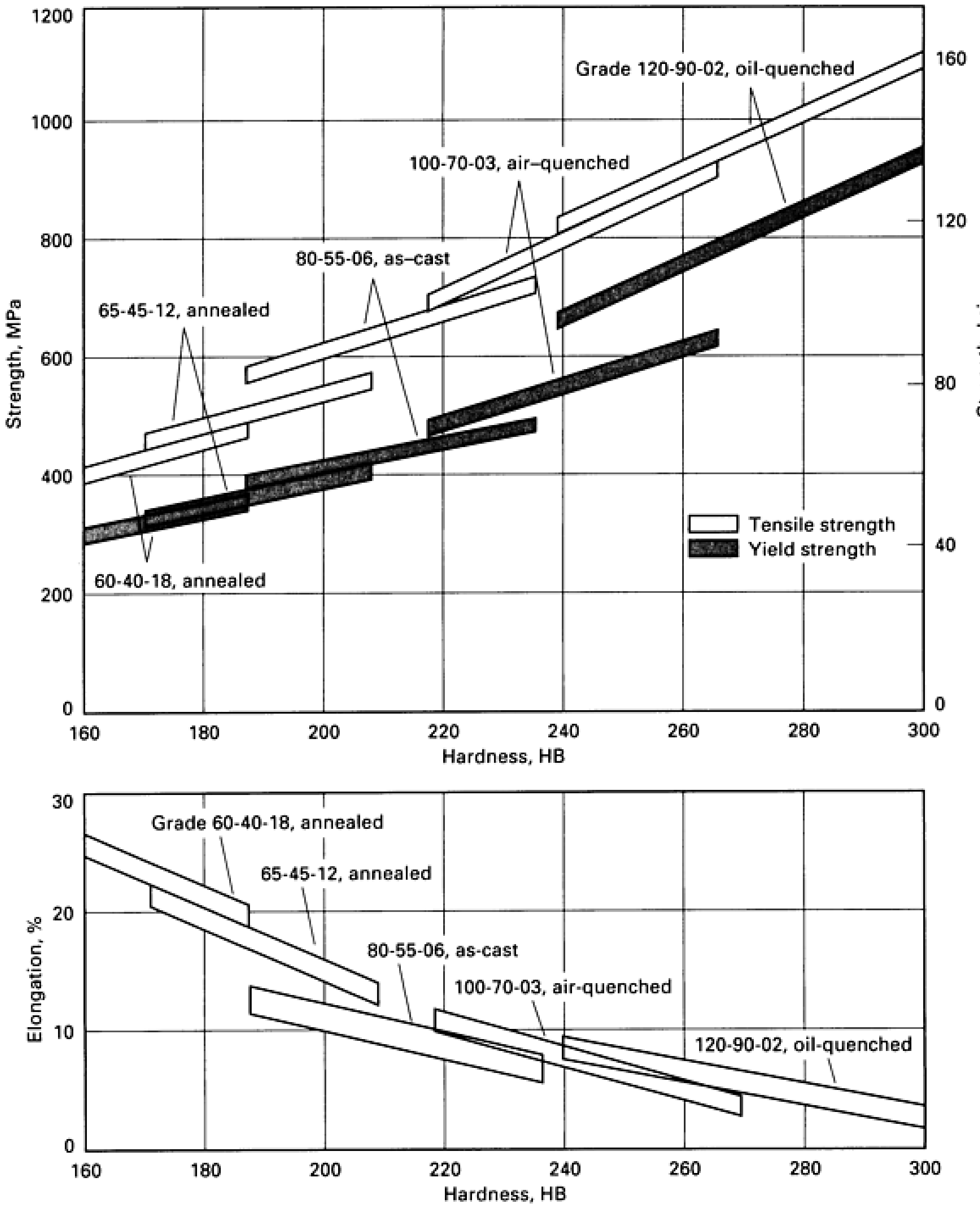


Fig. 5 Strength and ductility versus hardness for ductile iron

Austempered Ductile Iron. It is obvious from Fig. 4(b) and 4(c) that ADI is a unique cast iron material with tensile properties attributable to γ_H. with the fine dispersion of ferrite. As outlined above, austempering is accomplished by heating the casting to a temperature in the austenite-phase range (usually 815 to 925 °C, or 1500 to 1700 °F), holding for the time required to saturate the austenite with carbon, cooling to a temperature above the M_s temperature at a rate

sufficient to avoid the formation of pearlite or other mixed structures, and then holding at that austempering temperature for the time required to produce the optimum structure of acicular ferrite and carbon-enriched austenite.

The properties of ADI can be varied by changing the austempering temperature (see the section "Austempering Temperature and Time" in this article). A lower transformation temperature (260 °C, or 500 °F) produces a fine, high-strength, wear-resistant structure (Fig. 6a). A higher transformation temperature (370 °C, or 700 °F) results in a coarser structure (Fig. 6b) that exhibits high fatigue strength and good ductility. The various grades of ADI have been quantified in ASTM specifications A 897 and A 897M (Table 1).

Table 1 Hardness, toughness, and tensile properties at room temperature for austempered ductile iron grades specified in ASTM A 897 and A 897M (metric)

Grade	Minimum tensile strength		Minimum yield strength		Minimum elongation, %	Unnotched Charpy impact energy		Typical hardness, HB
	MPa	ksi	MPa	ksi		J	ft · lbf	
1	850	125	550	80	10	100	75	269-321
2	1050	150	700	100	7	80	60	302-363
3	1200	175	850	125	4	60	45	341-444
4	1400	200	1100	155	1	35	25	388-477

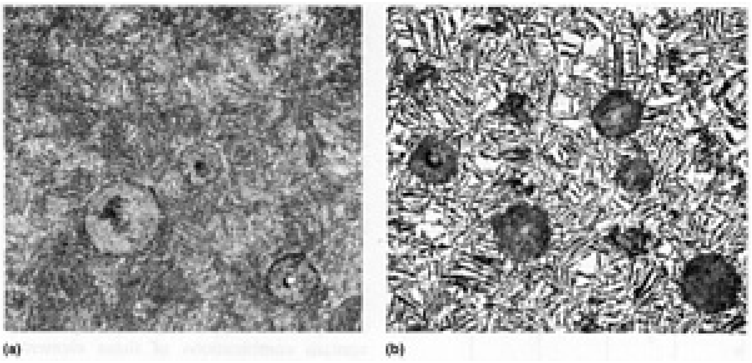


Fig. 6 Micrographs of ductile iron treated at different austempering temperatures. (a) Ductile iron austempered at 260 °C (500 °F) exhibits a fine acicular structure with the following properties: tensile strength, 1585 MPa (230 ksi); yield strength, 1380 MPa (200 ksi); elongation, 3%; unnotched impact, 54 J (40 ft · lbf); hardness, 475 HB. (b) Same iron as in (a) austempered at 370 °C (700 °F) exhibits a coarse acicular structure with the following properties: tensile strength, 1035 MPa (150 ksi); yield strength, 825 MPa (120 ksi); elongation, 11%; unnotched impact, 130 J (95 ft · lbf); hardness, 321 HB. Both etched with 3% nital. 300×. Courtesy of Applied Process, Inc.

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3. E. Dorazil, B. Barta, E. Munsterova, L. Stransky, and A. Huvar, High Strength Bainitic Ductile Iron, *Int. Cast. Met. J.,* June 1982, p 52-62
4. T.N. Rouns and K.B. Rundman, Constitution of Austempered Ductile Iron and Kinetics of Austempering, *Trans. AFS,* Vol 95, 1987, p 851-874

Austenitizing Ductile Cast Iron

The usual objective of austenitizing is to produce an austenitic matrix with as uniform a carbon content as possible prior to thermal processing. Figure 7 is the 2% Si section of the iron-carbon-silicon phase diagram. For a typical hypereutectic ductile cast iron, an upper critical temperature must be exceeded so that the austenitizing temperature is in the two-phase (austenite and graphite) field. This temperature varies with alloy content. It is also clear from Fig. 7 that the "equilibrium" austenite carbon content in equilibrium with graphite increases with an increase in austenitizing temperature. This ability to select (within limits) the matrix austenite carbon content makes austenitizing temperature control important in processes that depend on carbon in the matrix to drive a reaction. This is particularly true in structures to be austempered, in which the hardenability (or austemperability) depends to a significant degree on matrix carbon content. In general, alloy content, the original microstructure, and the section size determine the time required for austenitizing. The sections to follow on annealing, normalizing, quenching and tempering, and austempering discuss austenitizing when it is of concern.

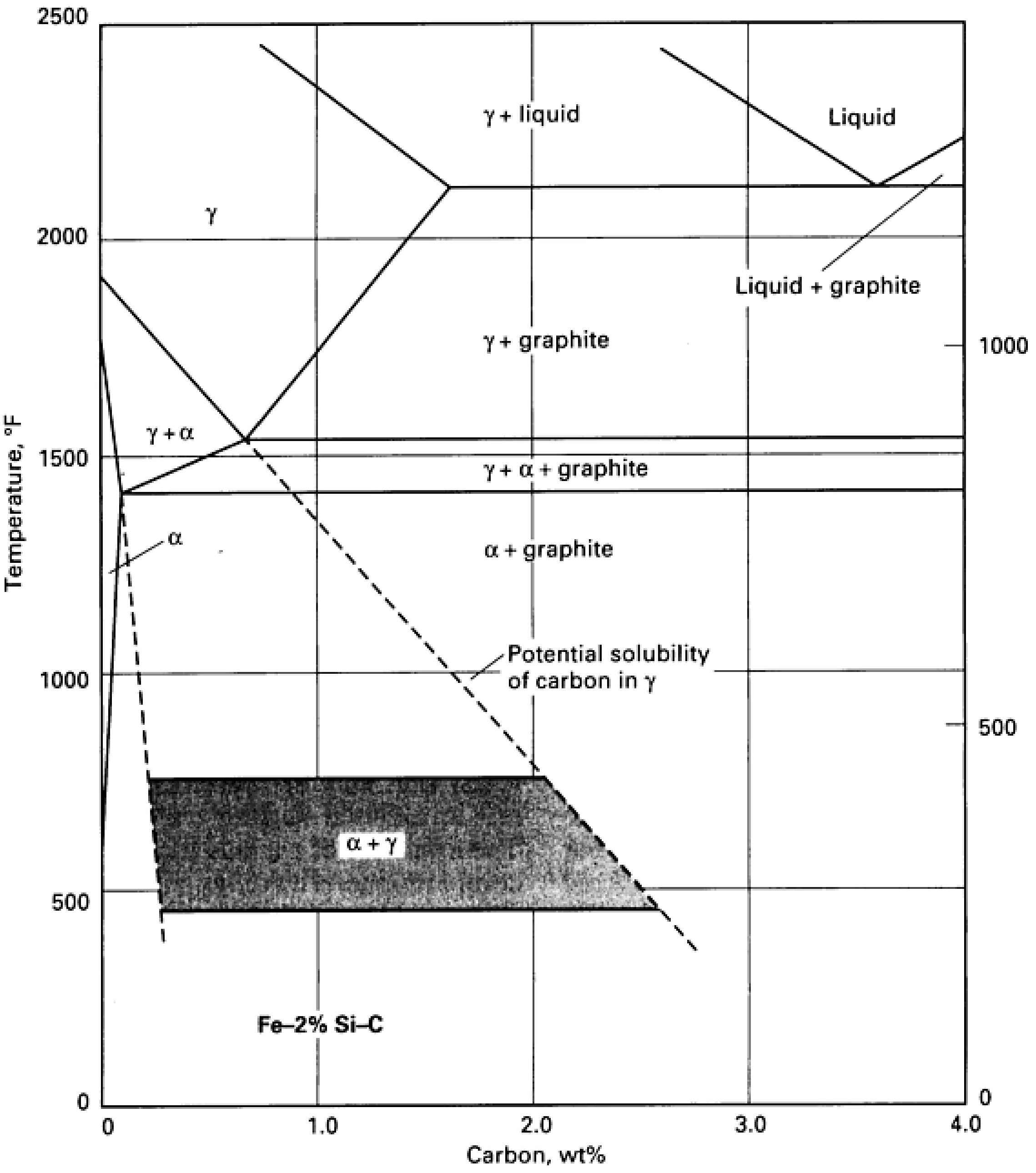

Fig. 7 Section of the Fe-C-2% Si equilibrium phase diagram showing a metastable projection of the α +γ two-phase field into the bainitic transformation temperature range

Annealing Ductile Iron

When maximum ductility and good machinability are desired and high strength is not required, ductile iron castings are generally given a full ferritizing anneal. The microstructure is thus converted to ferrite, and the excess carbon is deposited on the existing nodules (Fig. 3a). This treatment produces ASTM grade 60-40-18. Amounts of manganese, phosphorus, and alloying elements such as chromium and molybdenum should be as low as possible if superior machinability is desired because these elements retard the annealing process.

Recommended practice for annealing ductile iron castings is given below for different alloy contents and for castings with and without eutectic carbides (Ref 5):

- *Full anneal for unalloyed 2 to 3% Si iron with no eutectic carbide:* Heat and hold at 870 to 900 °C (1600 to 1650 °F) for 1 h per inch of section. Furnace cool at 55 °C/h (100 °F/h) to 345 °C (650 °F). Air

cool

- *Full anneal with carbides present:* Heat and hold at 900 to 925 °C (1650 to 1700 °F) for 2 h minimum, longer for heavier sections. Furnace cool at 110 °C/h (200 °F/h) to 700 °C (1300 °F). Hold 2 h at 700 °C (1300 °F). Furnace cool at 55 °C/h (100 °F/h) to 345 °C (650 °F). Air cool
- *Subcritical anneal to convert pearlite to ferrite:* Heat and hold at 705 to 720 °C (1300 to 1330 °F), 1 h per inch of section. Furnace cool at 55 °C/h (100 °F/h) to 345 °C (650 °F). Air cool. Figure 8 shows the influence of subcritical annealing at 705 °C (1300 °F) for various periods of time on the hardness of four ductile irons. When alloys are present, controlled cooling times through the critical temperature range down to 400 °C (750 °F) must be reduced to below 55 °C/h (100 °F/h)

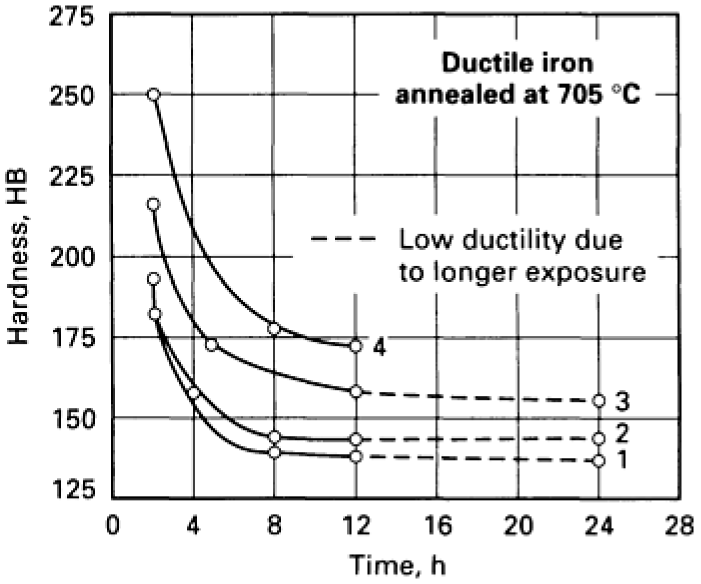

Fig. 8 Influence of time at subcritical annealing temperature on hardness

The effect of time at temperature on the decomposition of primary carbide (Fe_3C) for 6 mm ($\frac{1}{4}$ in.) plate castings is given in Fig. 9. It can be seen from Fig. 9 that these iron carbides break down quite readily; the time required at 900 °C (1650 °F) is approximately 2.5 h. However, certain carbide-forming elements, mainly chromium, form primary carbides that are very difficult, if not impossible, to decompose. For example, the presence of 0.25% Cr results in primary intercellular carbides that cannot be broken down in 2 to 20 h heat treatments at 925 °C (1700 °F). The resulting matrix after pearlite breakdown is carbides in ferrite with only 5% elongation. Other examples of carbide stabilizers are molybdenum contents greater than 0.3%, and vanadium and tungsten contents exceeding 0.05%.

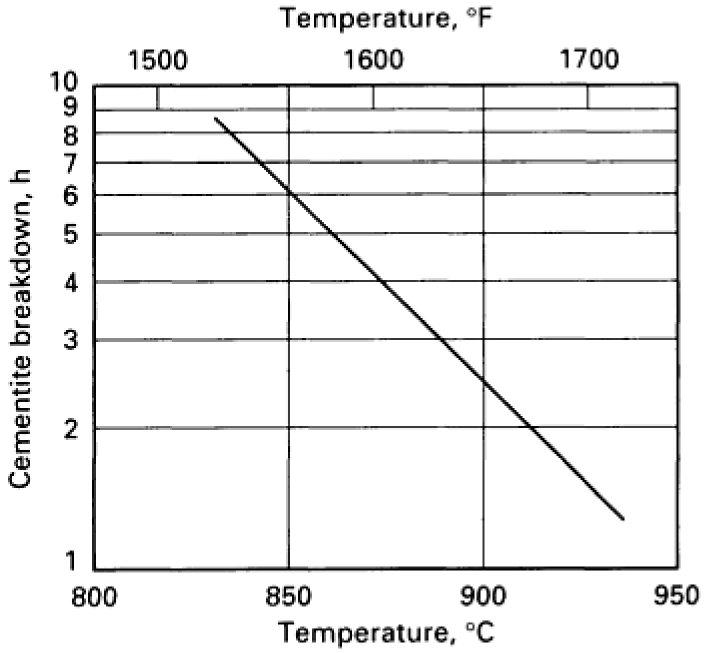

Fig. 9 Effect of time at temperature on decomposition of primary carbide (Fe_3C). Graph is based on an iron with a composition of 3.15% total carbon and 2.66% Si, which is outside the carbon-silicon range for commercial ductile iron.

Reference cited in this section

5. *Iron Castings Handbook,* Iron Casting Society, Inc., 1981, p 550

Hardenability of Ductile Cast Iron

The hardenability of ductile cast iron is an important parameter for determining the response of a specific iron to normalizing, quenching and tempering, or austempering. Hardenability is normally measured by the Jominy test, in which a standard-sized bar (1 in. diam by 4 in. in length) is austenitized and water quenched from one end. The variation in cooling rate results in microstructural variations, giving hardness changes that are measured and recorded. Figure 10 shows Jominy curves from an unalloyed ductile iron (3.9% C, 2.2% Si, 0.04% Mg, and residual Mn, Ni, Cu, Cr, V, Ti) that has been austenitized at 870 and 925 °C (1600 and 1700 °F). The higher matrix carbon content resulting from the higher austenitizing temperature results in an increased hardenability (the Jominy curve is shifted to larger distances from the quenched end) and a greater maximum hardness. The purpose of adding alloy elements to ductile cast irons is to increase hardenability. Figure 11 shows Jominy curves for ductile irons containing variable quantities of manganese, molybdenum, nickel, and copper (Ref 7). It is clear from Fig. 11 that manganese and molybdenum are much more effective in increasing hardenability, per weight percent added, than nickel or copper. However, as is the case with steel, combinations of nickel and molybdenum, or copper and molybdenum, or copper, nickel, and manganese are more effective than the separate elements. The synergistic effects of nickel and molybdenum are shown in the Jominy curves in Fig. 12. Thus heavy-section castings that require through hardening or austempering usually contain combinations of these elements. Silicon, apart from its effect on matrix carbon content, does not have a large effect on hardenability.

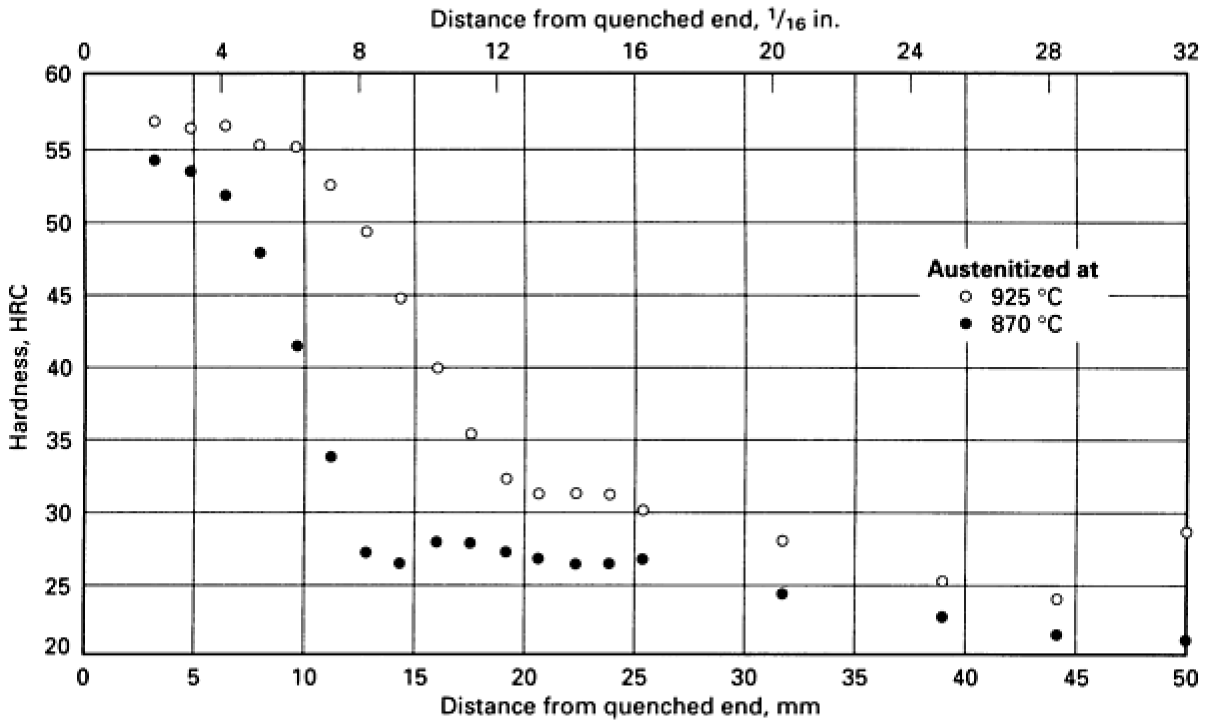

Fig. 10 Jominy curves from a ductile iron (3.9% C, 2.2% Si, 0.04% Mg, residual Mn, Ni, Cu, Cr, V, Ti), austenitized at 870 and 925 °C (1600 and 1700 °F). Source: Ref 6

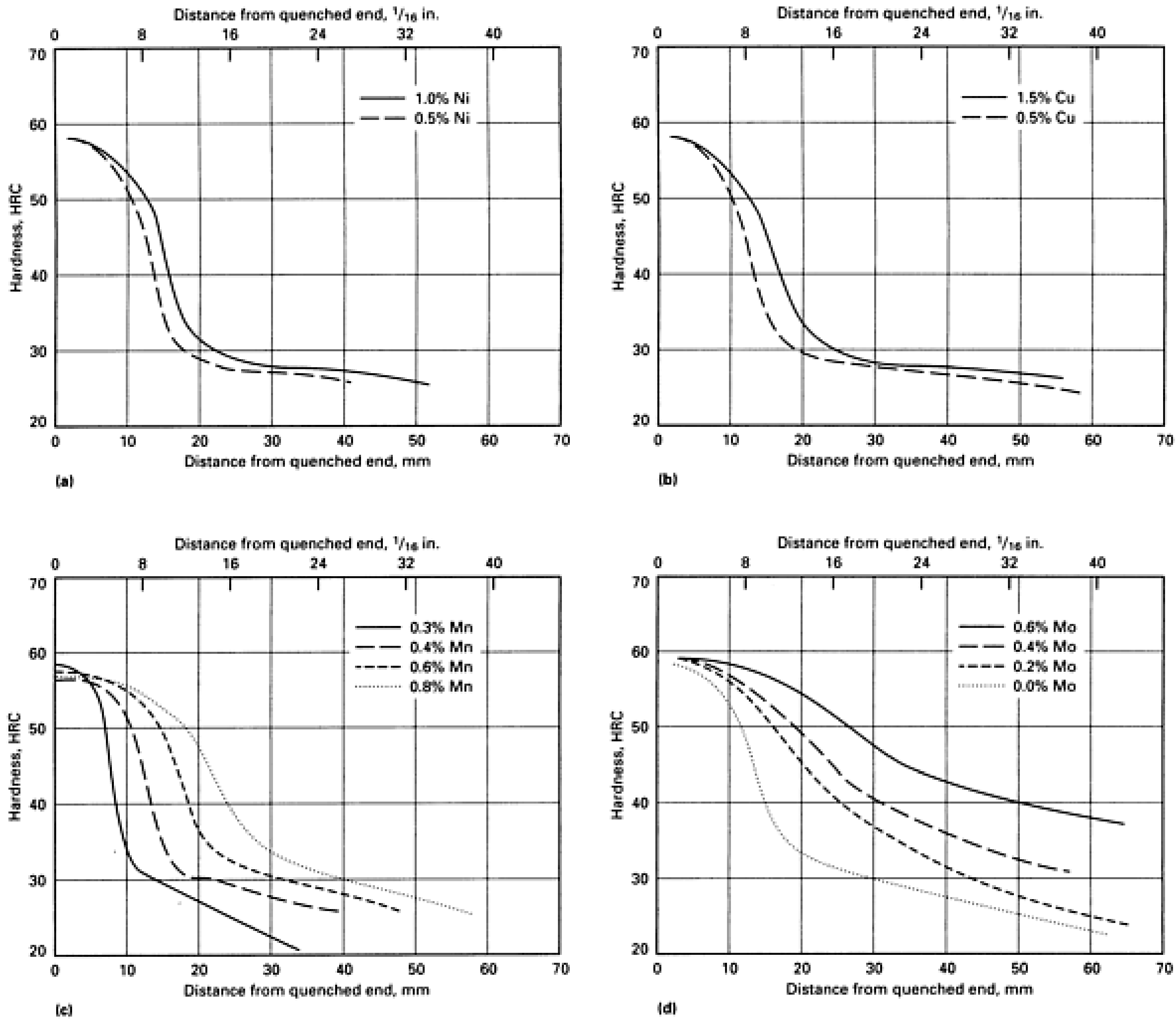

Fig. 11 Jominy curves for ductile irons containing variable quantities of (a) Ni, (b) Cu, (c) Mn, and (d) Mo, austenitized at 870 °C (1600 °F). Source: Ref 7

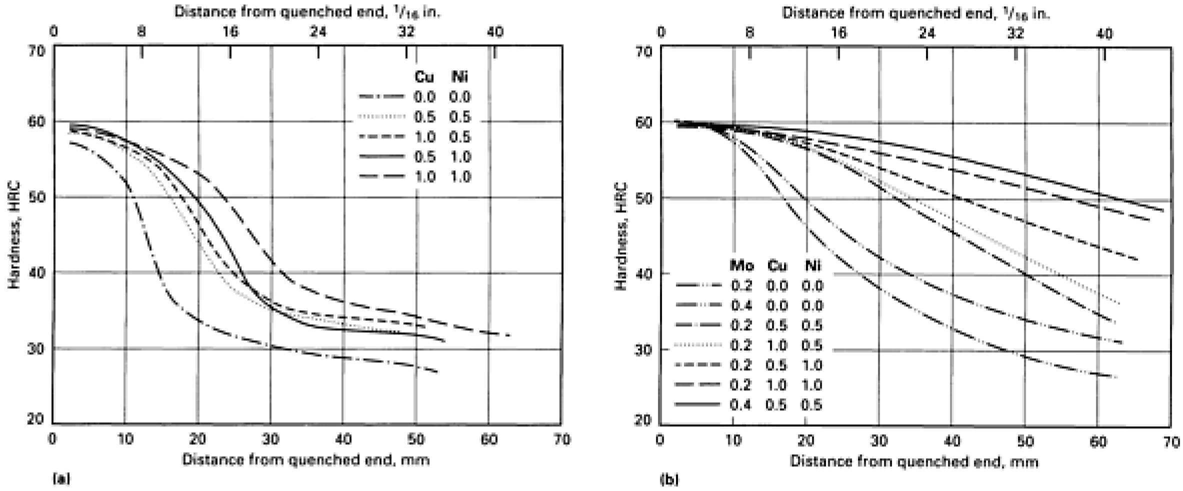

Fig. 12 Jominy curves for ductile irons containing variable combinations of (a) Cu and Ni and (b) Mo, Cu, and Ni, austenitized at 870 °C (1600 °F). Source: Ref 7

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Normalizing Ductile Iron

Normalizing (air cooling following austenitizing) can result in a considerable improvement in tensile strength and may be used in the production of ductile iron of ASTM type 100-70-03 (Fig. 5). The microstructure obtained by normalizing depends on the composition of the castings and the cooling rate. The composition of the casting dictates its hardenability, that is, the relative position of the fields in the time-temperature CCT diagram. The cooling rate depends on the mass of the casting, but it also may be influenced by the temperature and movement of the surrounding air during cooling. Normalizing generally produces a homogeneous structure of fine pearlite (Fig. 3b), if the iron is not too high in silicon content and has at least a moderate manganese content (0.3 to 0.5% or higher). Heavier castings that require normalizing usually contain alloying elements such as nickel, molybdenum, and additional manganese, for higher hardenability to ensure the development of a fully pearlitic structure after normalizing. Lighter castings made of alloyed iron may be martensitic or may contain an acicular structure after normalizing. The influence of various nickel contents and combinations of alloying elements on hardnesses after normalizing different section thicknesses is shown in Fig. 13.

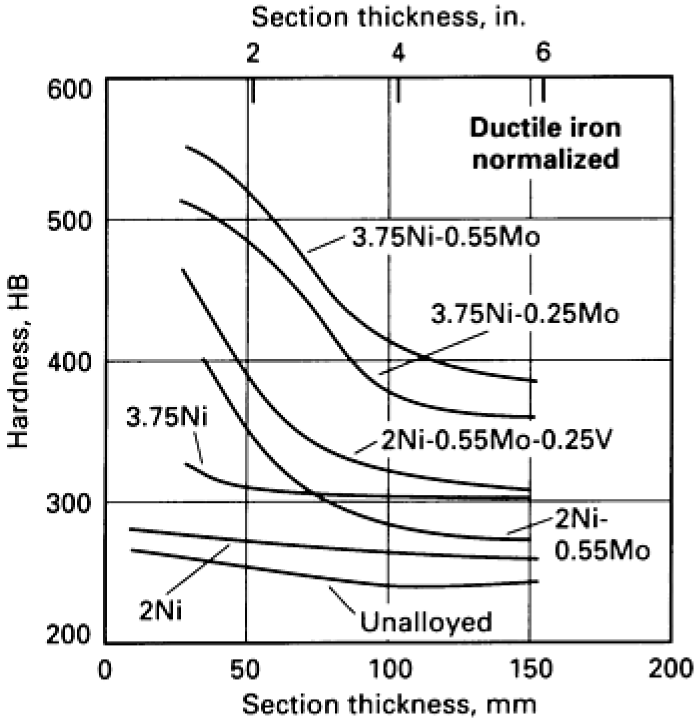

Fig. 13 Effect of alloy content and section thickness on hardness after normalizing

The normalizing temperature is usually between 870 and 940 °C (1600 and 1725 °F). The standard time at temperature of 1 h per inch of section thickness or 1 h minimum is usually satisfactory. Longer times may be required for alloys containing elements that retard carbon diffusion in the austenite. For example, tin and antimony segregate to the nodules, effectively preventing the solution of carbon from the nodule sites (Ref 8).

Normalizing is sometimes followed by tempering to attain the desired hardness and relieve residual stresses that develop upon air cooling when various parts of a casting with different section sizes cool at different rates. Tempering after normalizing is also used to obtain high toughness and impact resistance. The effect of tempering on hardness and tensile properties depends on the composition of the iron and the hardness level obtained in normalizing. Tempering usually consists of reheating to temperatures of 425 to 650 °C (800 to 1200 °F) and holding at the desired temperature for 1 h per

inch of cross section. These temperatures are varied within the above range to meet specification limits. Figure 14 shows the effect of tempering temperature on the hardness of normalized ductile iron.

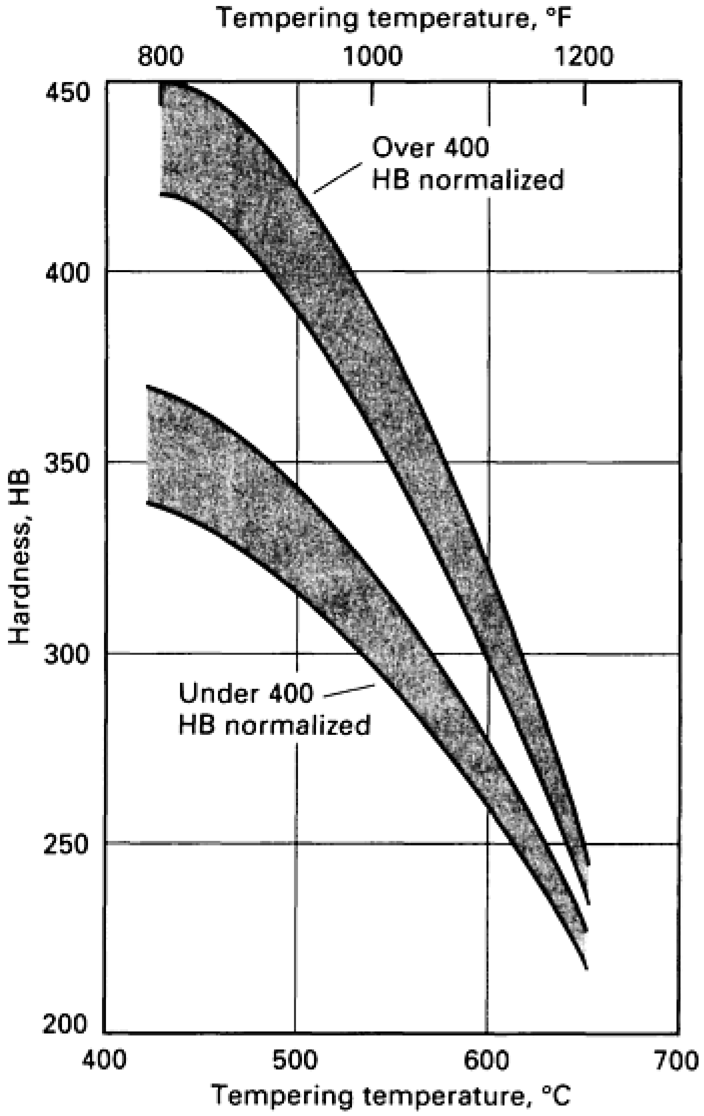

Fig. 14 Hardness of normalized ductile iron tempered at various temperatures

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Quenching and Tempering Ductile Iron

An austenitizing temperature of 845 to 925 °C (1550 to 1700 °F) is normally used for austenitizing commercial castings prior to quenching and tempering. Oil is preferred as a quenching medium to minimize stresses and quench cracking, but water or brine may be used for simple shapes. Complicated castings may have to be oil quenched at 80 to 100 °C (180 to 210 °F) to avoid cracks.

The influence of the austenitizing temperature on the hardness of water-quenched 13 mm ($\frac{1}{2}$ in.) cubes of ductile iron is shown in Fig. 15. These data show that the highest range of hardness (55 to 57 HRC) was obtained with austenitizing temperatures between 845 and 870 °C (1550 and 1600 °F). At temperatures above 870 °C (1600 °F), the higher matrix carbon content resulted in a greater percentage of retained austenite and therefore a lower hardness.

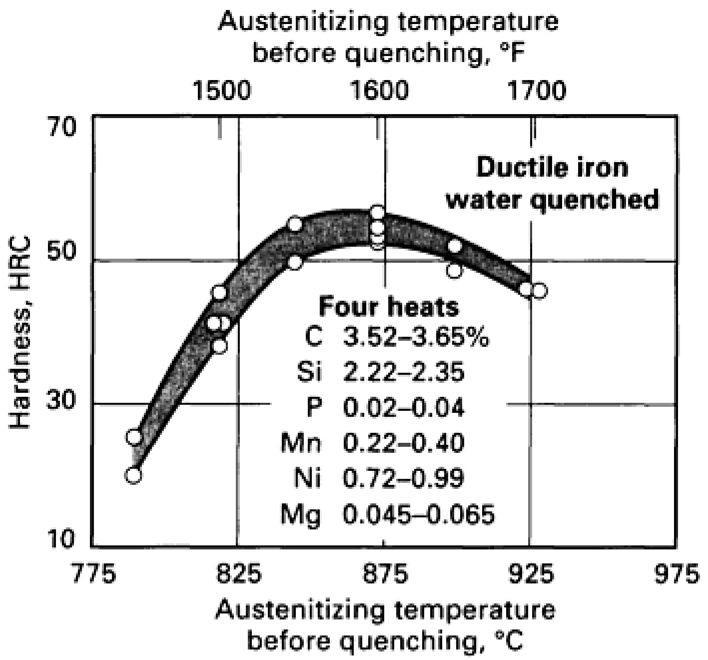


Fig. 15 Influence of austenitizing temperature on hardness of ductile iron. Each value represents the average of three hardness readings. Specimens (13 mm, or $\frac{1}{2}$ in., cubes) were heated in air for 1 h and water quenched.

Castings should be tempered immediately after quenching to relieve quenching stresses. Tempered hardness depends on asquenched hardness level, alloy content, and tempering temperature, as well as time. Tempering in the range from 425 to 600 °C (800 to 1100 °F) results in a decrease in hardness, the magnitude of which depends upon alloy content, initial hardness, and time. Figure 16 shows the change in the Vickers hardness of two quenched ductile iron alloys with tempering temperature and time (Ref 9). Tempering ductile iron in this temperature range is a two-stage process. The first involves the precipitation of carbides similar to the process in steels. The second stage (shown in Fig. 16 by the drop in hardness at longer times) involves nucleation and the growth of small, secondary graphite nodules at the expense of the carbides. The drop in hardness accompanying secondary graphitization produces a corresponding reduction in tensile and fatigue strength as well. Because alloy content affects the rate of secondary graphitization, each alloy will have a unique range of useful tempering temperatures. The influence of tempering temperature between 425 and 700 °C (800 and 1300 °F) for tensile and hardness specimens tempered for 2 h is shown in Fig. 17.

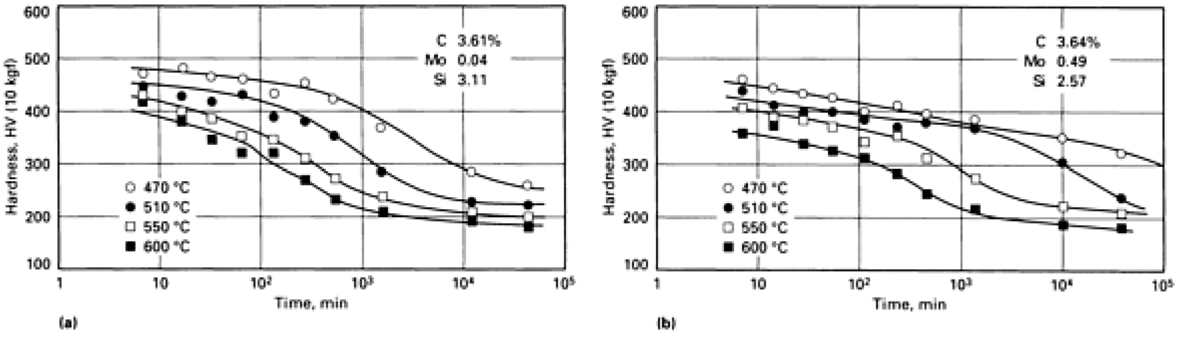
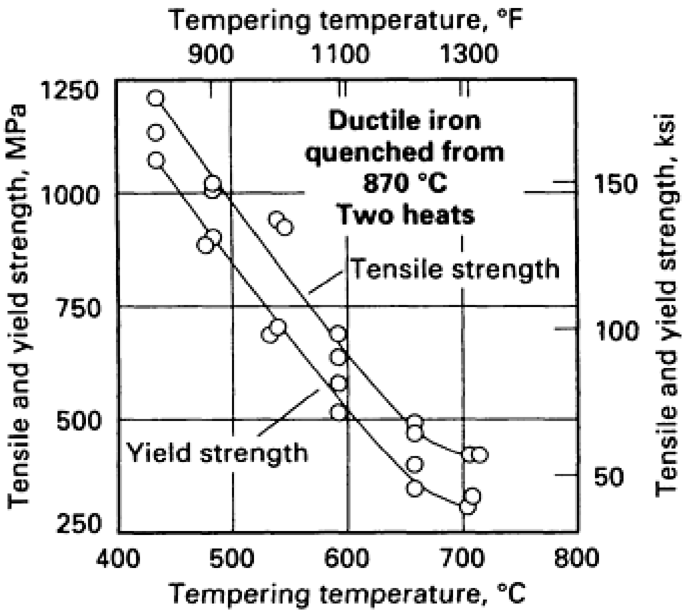
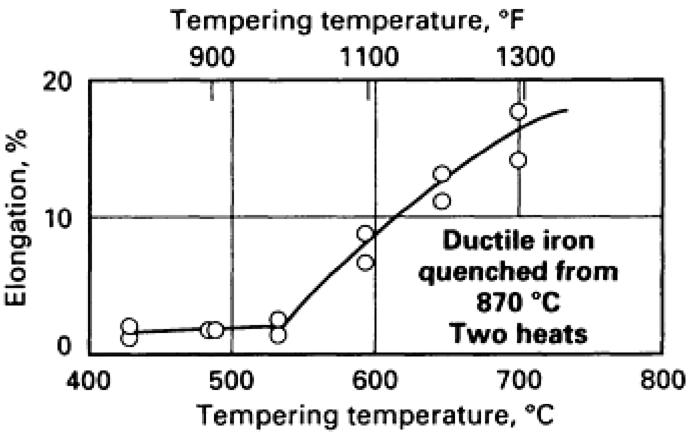


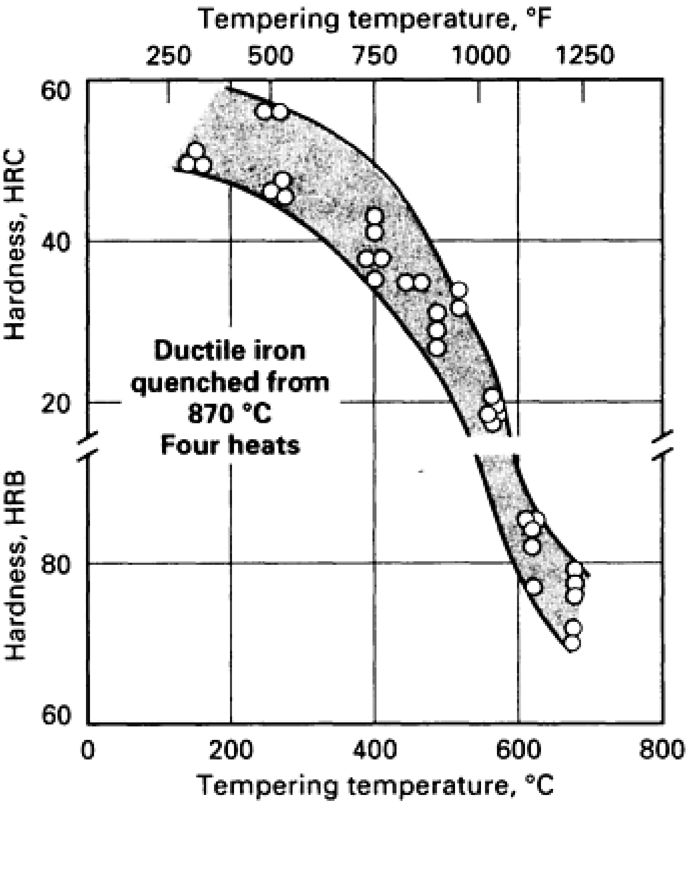
Fig. 16 Vickers hardness (10 kg load) versus tempering time at several tempering temperatures for (a) an alloy with 3.61% C, 3.11% Si, 0.04% Mo and (b) an alloy with 3.64% C, 2.57% Si, 0.49% Mo. Source: Ref 9



Tempering temperature, °F
900
1100
1300
1250
1000
750
500
250
Tensile and yield strength, MPa
Ductile iron
quenched from
870 °C
Two heats
Tensile strength
Yield strength
150
100
50
Tensile and yield strength, ksi
400
500
600
700
800
Tempering temperature, °C



Tempering temperature, °F
900
1100
1300
20
10
0
Elongation, %
Ductile iron
quenched from
870 °C
Two heats
400
500
600
700
800
Tempering temperature, °C



Tempering temperature, °F
250
500
750
1000
1250
60
40
20
Hardness, HRC
Ductile iron
quenched from
870 °C
Four heats
80
60
Hardness, HRB
0
200
400
600
800
Tempering temperature, °C

Fig. 17 Influence of tempering temperature on mechanical properties of ductile iron quenched from 870 °C (1600 °F) and tempered 2 h. Data represent irons from four heats with composition ranges of: 3.52 to 3.68% C, 2.28 to 2.35% Si, 0.02 to 0.04% P, 0.22 to 0.41% Mn, 0.69 to 0.99% Ni, and 0.045 to 0.065% Mg. Data for tensile strength, tensile yield strength, and elongation are for irons (from two of these heats) that contained 0.91 and 0.99% Ni.

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9. K.B. Rundman and T.N. Rouns, On the Effects of Molybdenum on the Kinetics of Secondary Graphitization in Quenched and Tempered Ductile Irons, *Trans. AFS,* Vol 90, 1982, p 487-497

Austempering Ductile Iron

When optimum strength and ductility are required, the heat treater has the opportunity to produce an austempered structure of austenite and ferrite. As shown previously in Fig. 4, the austempered matrix is responsible for a significantly better tensile strength-to-ductility ratio than is possible with any other grade of ductile cast iron. The production of these desirable properties requires careful attention to section size and the time-temperature exposure during austenitizing and austempering.

Section Size and Alloying. As section size increases, the rate of temperature change between the austenitizing temperature and austempering temperature decreases. Quenching and austempering techniques include the hot-oil quench (≤240 °C, or 460 °F, only); nitrate/nitrite salt quenches; fluidizedbed method (for thin, small parts only); and, in tool-type applications, lead baths.

In order to avoid high-temperature reaction products (such as pearlite in larger section sizes), salt bath quench severities can be increased with water additions (Ref 10) or with alloying elements (such as copper, nickel, manganese, or molybdenum) that enhance pearlite hardenability (Ref 3). It is important to understand that these alloying elements tend to segregate during solidification so that a nonuniform distribution exists throughout the matrix. This has a potentially detrimental effect on the austempering reaction and therefore on mechanical properties. Ductility and impact toughness are the most severely affected.

Manganese and molybdenum have the most powerful effect upon pearlite hardenability but will also segregate and freeze into intercellular regions of the casting to promote iron or alloy carbides. While nickel and copper do not affect hardenability nearly as much, they segregate to graphite nodule sites and do not form detrimental carbides. Combinations of these elements, which segregate in opposite fashions, are selected for their synergistic effect on hardenability.

Austenitizing Temperature and Time. The schematic phase diagram of Fig. 7 shows that as austenitizing temperature increases, so does the matrix carbon content; the actual matrix carbon content depends in a complex way on the alloy elements present, their amount, and their location (segregation) within the matrix.

The most important determinant of matrix carbon content in ductile irons is the silicon content; as silicon content increases for a given austenitizing temperature, the carbon content in the matrix decreases. Austenitizing temperatures between 845 and 925 °C (1550 and 1700 °F) are normal, and austenitizing times of approximately 2 h have been shown to be sufficient to recarburize the matrix fully. Figure 10 shows that the austenitizing temperature, through its effect upon matrix carbon, has a significant effect on hardenability. The higher austenitizing temperature with its higher carbon content promotes increased hardenability, which causes a slower rate of isothermal austenite transformation. This reduced rate of austenite reaction to all transformation products is shown in the beginning portions of the IT diagrams in Fig. 18.

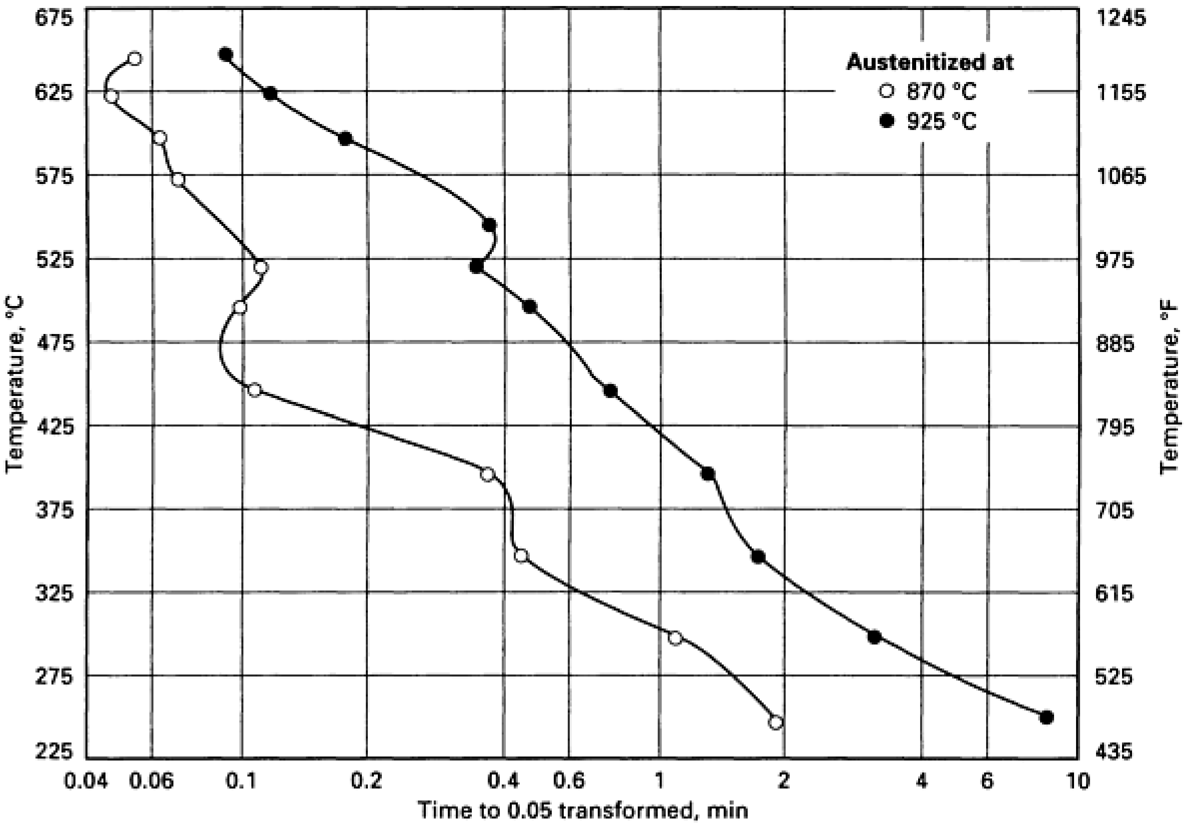

Fig. 18 Time to 5% transformed for a low-alloy ductile iron austenitized at 870 and 925 °C (1600 and 1700 °F). Source: Ref 6

Austempering Temperature and Time. The austempering temperature is the primary determinant of the final microstructure and therefore the hardness and strength of the austempered product. As the austempering temperature increases, the strength and impact toughness vary as shown in Fig. 19 for irons with two levels of manganese. The attainment of maximum ductility at any given austempering temperature is a sensitive function of time, as shown in Fig. 20 for a number of ductile cast iron alloys (Ref 12). The initial increase in elongation occurs as stage I (Fig. 2) and elongation progresses to completion, at which point the fraction of austenite is a maximum. Further austempering merely serves to reduce ductility as the stage II reaction causes decomposition to the equilibrium bainite product. Typical austempering times vary from 1 to 4 h. Micrographs of ASTM ADI grades 5 and 2 (Table 1) are shown in Fig. 6(a) and 6(b), respectively.

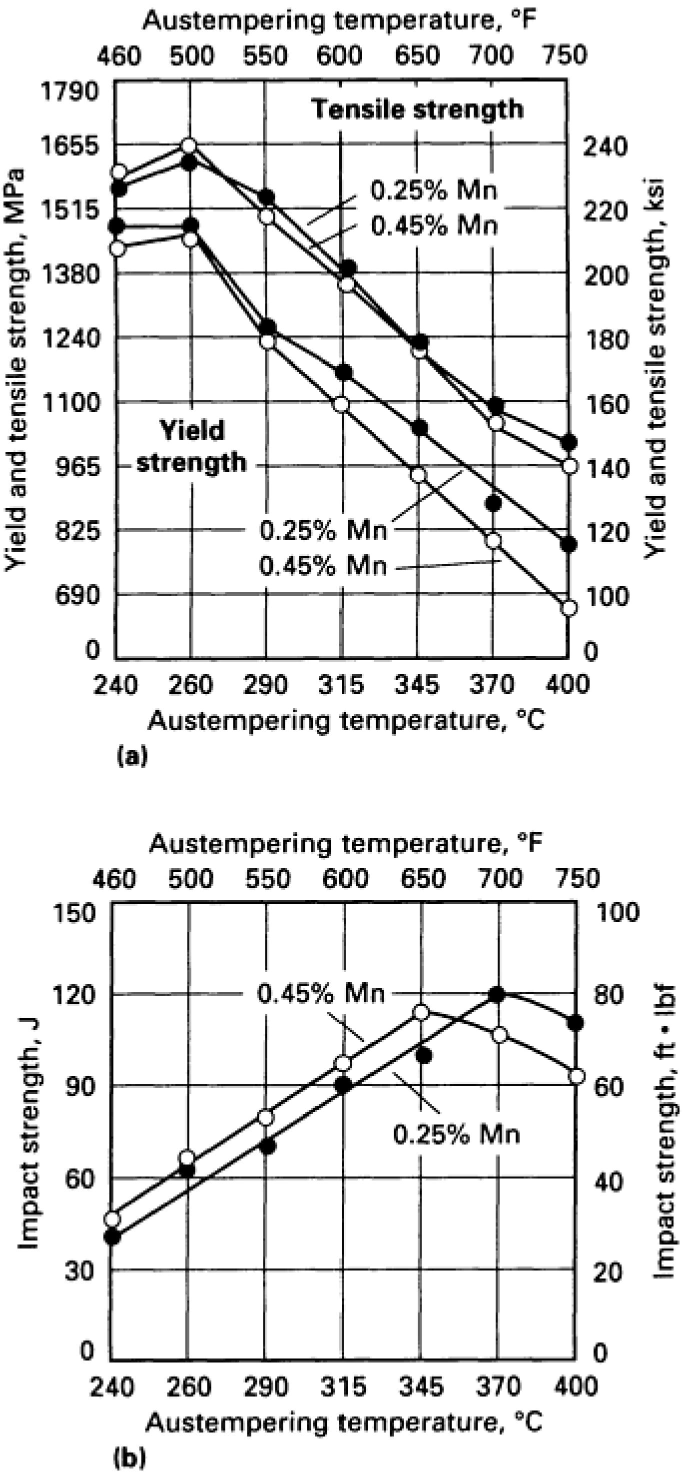

Fig. 19 Effect of austempering temperature on properties of ductile iron. (a) Yield strength and tensile strength versus austempering temperature. (b) Impact strength versus austempering temperature. Source: Ref 11

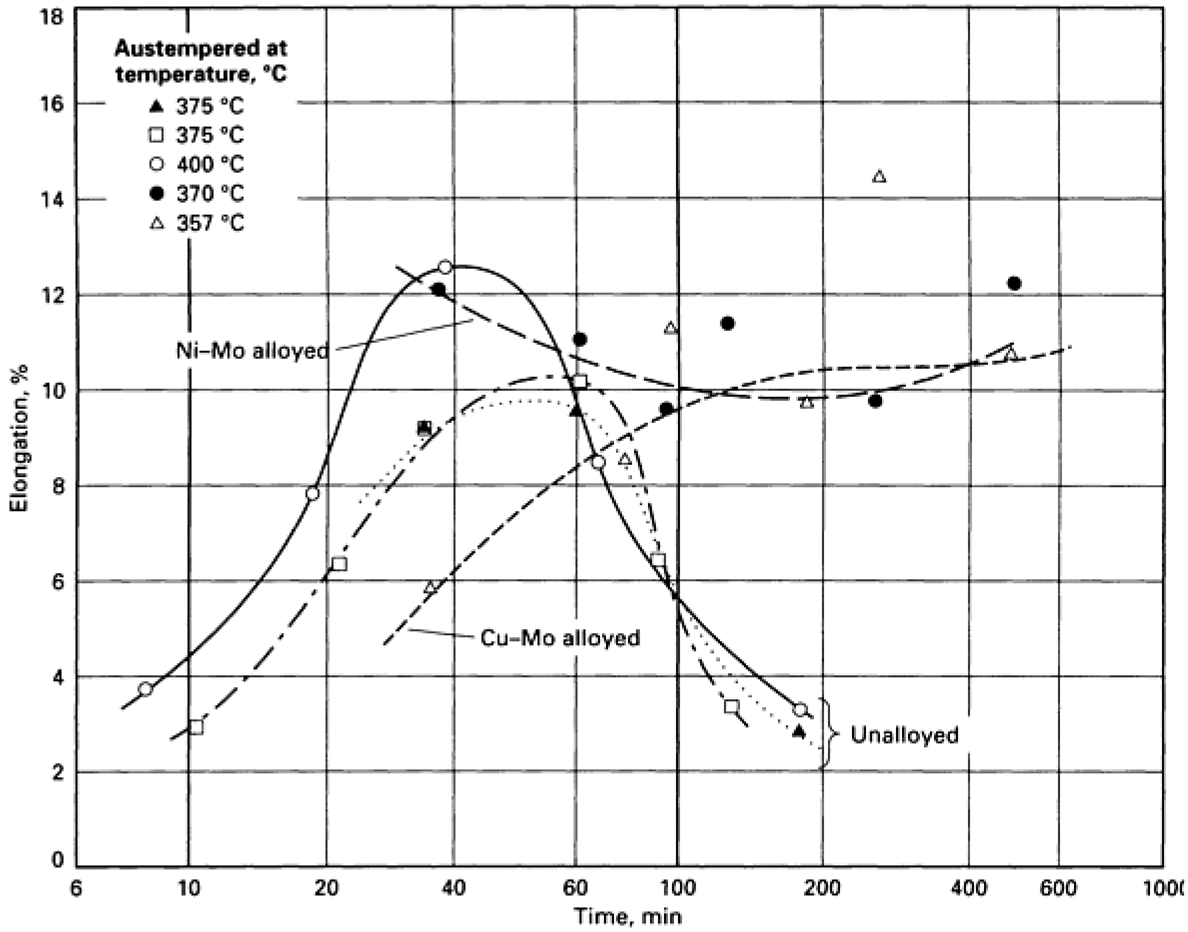

Fig. 20 Elongation versus austempering time for a group of ductile iron alloys. Source: Ref 12

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Surface Hardening of Ductile Iron

Ductile iron responds readily to surface hardening by flame, induction, or laser heating. Because of the short heating cycle in these processes, the pearlitic types of ductile iron ASTM 80-60-03 and 100-70-03 are preferred. Irons without free ferrite in their microstructure respond almost instantly to flame or induction heating and require very little holding time at the austenitizing temperature in order to be fully hardened.

With a moderate amount of free ferrite, the response may be satisfactory, but an entirely ferritic matrix, typical of the grades with high ductility, requires several minutes at 870 °C (1600 °F) to be fully hardened by subsequent cooling. A

matrix microstructure of fine pearlite, readily obtained by normalizing, has a rapid response to surface hardening and provides excellent core support for the hardened case.

With proper technique and the control of temperature between 845 and 900 °C (1550 and 1650 °F), the ranges of surface hardness for ductile iron with different matrices expected in commercial production are:

- Ductile iron, fully annealed (ferritic), water quenched behind the flame or induction coil, 35 to 45 HRC
- Ductile iron, predominantly ferritic (partly pearlitic), stress relieved prior to heating, self quenched, 40 to 45 HRC
- Ductile iron, predominantly ferritic (partly pearlitic), stress relieved prior to heating, water quenched, 50 to 55 HRC
- Ductile iron, mostly pearlitic, stress relieved before heating, water quenched, 58 to 62 HRC

Heating time and temperature, amount of dissolved carbon, section size, and rate of quench help to determine final hardness values. Often soluble-oil or polymer quench media are used to minimize quench cracking where the casting section changes.

Flame or induction-hardened ductile iron castings have been used for heavy-duty applications such as foils for cold working titanium, ring gears for paper-mill drives, crankshafts, and large sprockets for chain drives. Induction hardening is discussed below; flame hardening is discussed in a separate so-named article in this Volume.

The response of ductile iron to induction hardening is dependent on the amount of pearlite in the matrix of as-cast, normalized, and normalized and tempered prior structures (Ref 13). In quenched and tempered iron, the secondary graphite nodules formed during tempering are close enough together to supply sufficient carbon to the matrix by re-solution during induction heating.

In the as-cast condition, a minimum of 50% pearlite is considered necessary for satisfactory hardening with induction heating cycles of 3.5 s and longer and hardening temperatures of 955 to 980 °C (1750 to 1800 °F). Structures containing less pearlite can be hardened by using higher temperatures, but at the risk of retaining austenite, forming ledeburite, and damaging the surface. With more than 50% pearlite, hardening temperatures may be reduced to within the range of 900 to 925 °C (1650 to 1700 °F).

In the Normalized Condition. For heating cycles of 3.5 s and longer, at temperatures of 955 to 980 °C (1750 to 1800 °F), 50% pearlite in a prior structure would be considered a minimum. Normalized and tempered irons exhibit a poor response with lower pearlite content because of the depletion of the matrix carbon. In the tempering operation, the carbon migrates from the pearlite matrix to the graphite nodules. In the heating cycle, carbon is reabsorbed in the matrix from the nodule; however, there is insufficient time for it to migrate throughout the ferritic areas. Another factor in the response of ductile iron is the graphite nodule count; the greater the number of nodules per unit area, the deeper the hardening for any given heat cycle. This effect is more evident as the percentage of ferrite increases (Fig. 21).

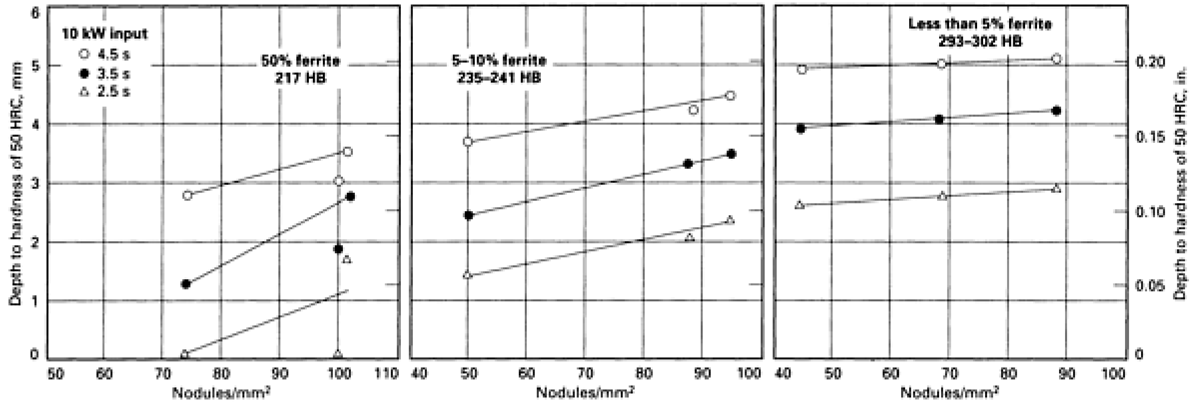

Fig. 21 Relationship between depth of induction hardening to 50 HRC and graphite nodule count in normalized

and tempered ductile (nodular) iron

Quenched and Tempered. The response of quenched and tempered nodular iron to induction hardening is excellent over a wide range of microstructures containing up to 95% ferrite. As a prior treatment, quenching and tempering has the advantage of permitting a lower prior hardness; there is a risk of distortion and quench cracking, however.

Example 1: Response of a Quenched and Tempered Ductile Iron to Induction Surface Hardening.

A quenched and tempered structure that provided good response to induction hardening was obtained by oil quenching from 900 °C (1650 °F) and tempering at 620 °C (1150 °F) for 1 h. This treatment produced a hardness of 262 HB, which could have been lowered, if necessary, by increasing the tempering temperature to 675 °C (1250 °F). By induction heating to a depth of 4.7 mm (0.184 in.), a surface hardness of 54 to 56 HRC was developed, and a depth of hardness to 50 HRC of 4.2 mm (0.164 in.) was obtained.

Nitriding is a case-hardening process that involves the diffusion of nitrogen into the surface at a temperature of about 550 to 600 °C (1020 to 1110 °F). Usually the source of nitrogen is ammonia, and the process produces a surface layer about 0.1 mm (0.004 in.) deep with a surface hardness approaching 1100 HV. The surface layer is typically white and featureless in an etched microstructure, but nitride needles can be found just below it. Alloying elements can be used to increase case hardness, and 0.5 to 1% Al, Ni, and Mo have been reported to achieve useful results. Nitrided cases provide, in addition to very high hardness, increased wear resistance and antiscuffing properties, improved fatigue life, and improved corrosion resistance. Typical applications are for cylinder liners, bearing pins, and small shafts.

Nitriding can also be carried out in liquid salt baths based on cyanide salts. Such processes have lower temperatures of treatment, although case depth may be decreased. More recently, processes for nitriding in a plasma have been developed and applied with success to ductile iron, but the process may be more restricted because of the special equipment and cost likely to be involved.

Remelt Hardening. With the very high local heating achievable with plasma torches or lasers, it is possible to produce a very small melted area on the surface of a ductile iron component. This area then rapidly resolidifies because of the self-quenching effect of the casting mass. The remelted and resolidified region has a structure of white iron that is substantially graphite free and therefore has high hardness and wear resistance. The area that is remelted by a 2 kW laser is very small, typically 1.5 mm (0.06 in.) in diameter and 0.5 to 2 mm (0.02 to 0.08 in.) in depth, and having a hardness of about 900 HV without cracking. By traversing the casting surface, the area hardened by this method can be of useful size and is likely to find application in tappets, cams, and other small components subjected to sliding wear. Figure 22 shows the microstructure of a pearlitic iron traversed by a 1.5 kW laser at 456 mm/s (18.25 in./s).

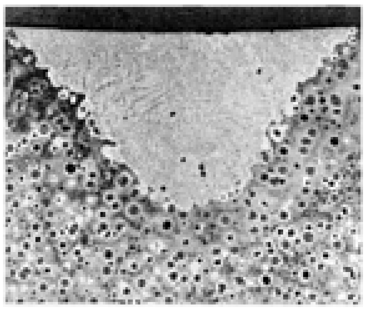

Fig. 22 Remelt-hardened and transition zones in a pearlitic iron after treatment with a 1.6 kW, 1.5 mm (0.06 in.) diam laser beam of 4.56 mm/s (0.18 in./s). Etched in picral. 50×

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Stress Relieving of Ductile Iron

When not otherwise heat treated, complex engineering castings of ductile iron may be stress relieved at 510 to 675 °C (950 to 1250 °F). Temperatures at the lower end of this range are satisfactory for many applications; temperatures at the higher end will eliminate virtually all residual stress (Fig. 23) but will also effect some reduction in hardness and tensile strength. Recommended ranges of stress-relieving temperature for various types of ductile iron are as follows:

- *Unalloyed:* 510 to 565 °C (950 to 1050 °F)
- *Low-alloy:* 565 to 595 °C (1050 to 1100 °F)
- *High-alloy:* 595 to 650 °C (1100 to 1200 °F)
- *Austenitic:* 620 to 675 °C (1150 to 1250 °F)

The required time at temperature will depend on the temperature used, the complexity of the casting, and the completeness of stress relief desired (Fig. 22), but 1 h plus 1 h per inch of section thickness is recommended general practice.

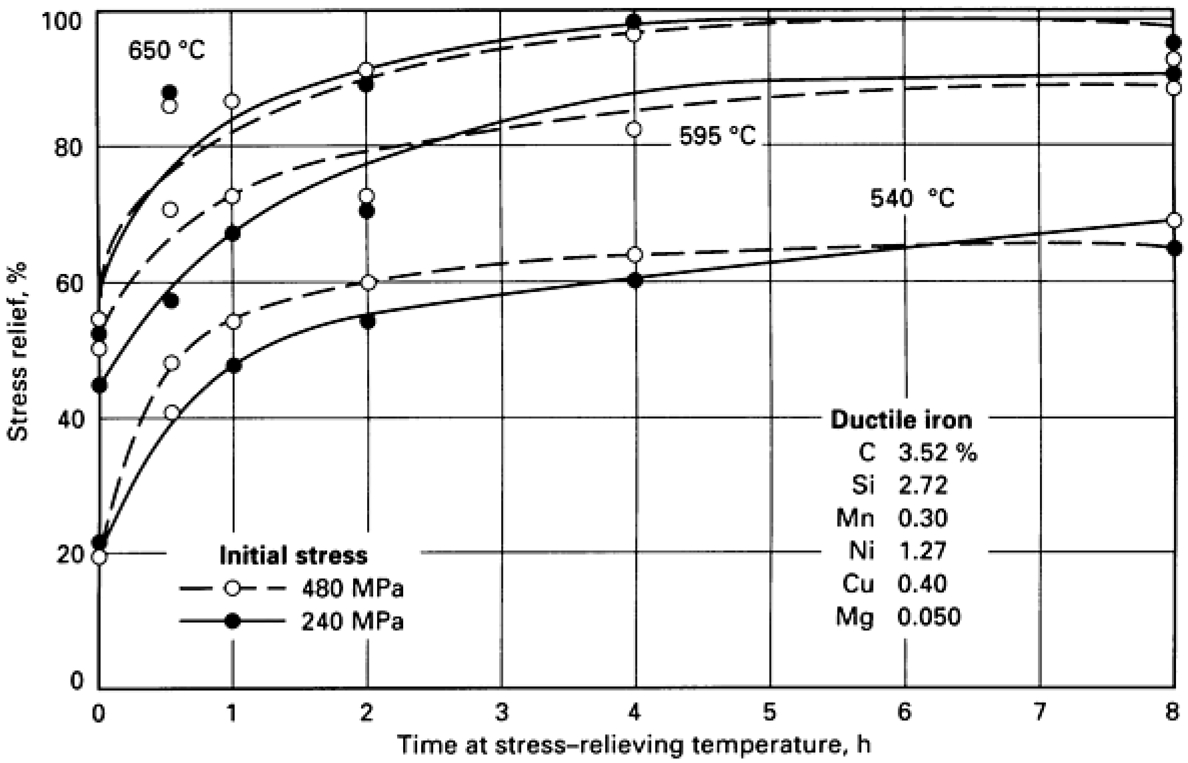

Fig. 23 Stress relief obtained in ductile iron held at three temperatures for $\frac{1}{2}$ to 8 h. Initial hardness was 102 to 103 HRB. Hardness after holding at 540, 595, and 650 °C (1000, 1100, and 1200 °F) for 8 h was 102 to 104, 101 to 103, and 90 to 93 HRB.

Cooling should be uniform to avoid reintroducing stresses. Castings should be furnace cooled to 290 °C (550 °F), after which they can be air cooled. In most instances, however, austenitic iron can be uniformly air cooled from the stress-relieving temperature.

Effect of Heat Treatment on Fatigue Strength

In heat treating to improve fatigue properties, the proper composition and temperature must be selected to ensure the greatest improvement, and it is essential to have an optimum-quality cast microstructure (that is, high nodule count, excellent nodularity, and freedom from defects). For example, one cause of low fatigue strength in quenched and tempered ductile irons results from the precipitation of secondary graphite throughout the matrix upon tempering. The softening that accompanies this event results in reduced fatigue strength as well (see rapid hardness decrease in Fig. 16). The amount of secondary graphite can be controlled by composition (primarily carbon and silicon) and tempering temperature (the incidence of secondary graphite increases with temperature). Naturally as the amount of carbon increases so will the quantity of secondary graphite. An increased silicon content will increase the rate of secondary graphitization (Ref 9).

The fatigue properties of as-cast ductile irons can be improved significantly by heat treatment, but not in the same proportion as can the static tensile properties. Fatigue strength at 20×10^6 cycles (rotary bending) has been shown to increase with matrix hardness as a result of heat treatment (Ref 14), with fatigue strengths ranging from 170 to 200 MPa (25 to 30 ksi) in annealed irons and from 310 to 345 MPa (45 to 50 ksi) in austempered or quenched and tempered irons. Recently rotary bending fatigue strengths (at 20×10^6 cycles) in austempered irons of approximately 480 MPa (70 ksi) have been reported (Ref 15), and fatigue strengths on the order of 690 MPa (100 ksi) can be attained with rolling or peening after austempering. Of course, fatigue strength will be optimal when the matrix structure is homogeneous throughout and no defects are present. The nature of ductile cast iron is such that there are many microstructural sources that can reduce fatigue strength; these include increasing nodule size, microporosity, eutectic carbides in intercellular regions, and slag or other inclusions. All of these problems tend to be exaggerated in heavy-section castings.

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Introduction

FERRITIC AND PEARLITIC malleable irons are both produced by annealing white iron of controlled composition. Thus, annealing is an essential part of the manufacturing process for these irons and, as such, is discussed in detail in the article entitled "Malleable Iron" in *Properties and Selection: Irons, Steels, and High-Performance Alloys,* Volume 1 of *ASM Handbook*

Malleable irons have largely been replaced by ductile iron in many applications. This is due in part to the necessity of lengthy heat treatments for malleable iron and the difficulty in cooling thick sections rapidly enough to produce white iron. Malleable iron is still often preferred for thin-section castings and parts that require maximum machinability and wear resistance. Figure 1 compares mechanical strengths of nodular and malleable irons.

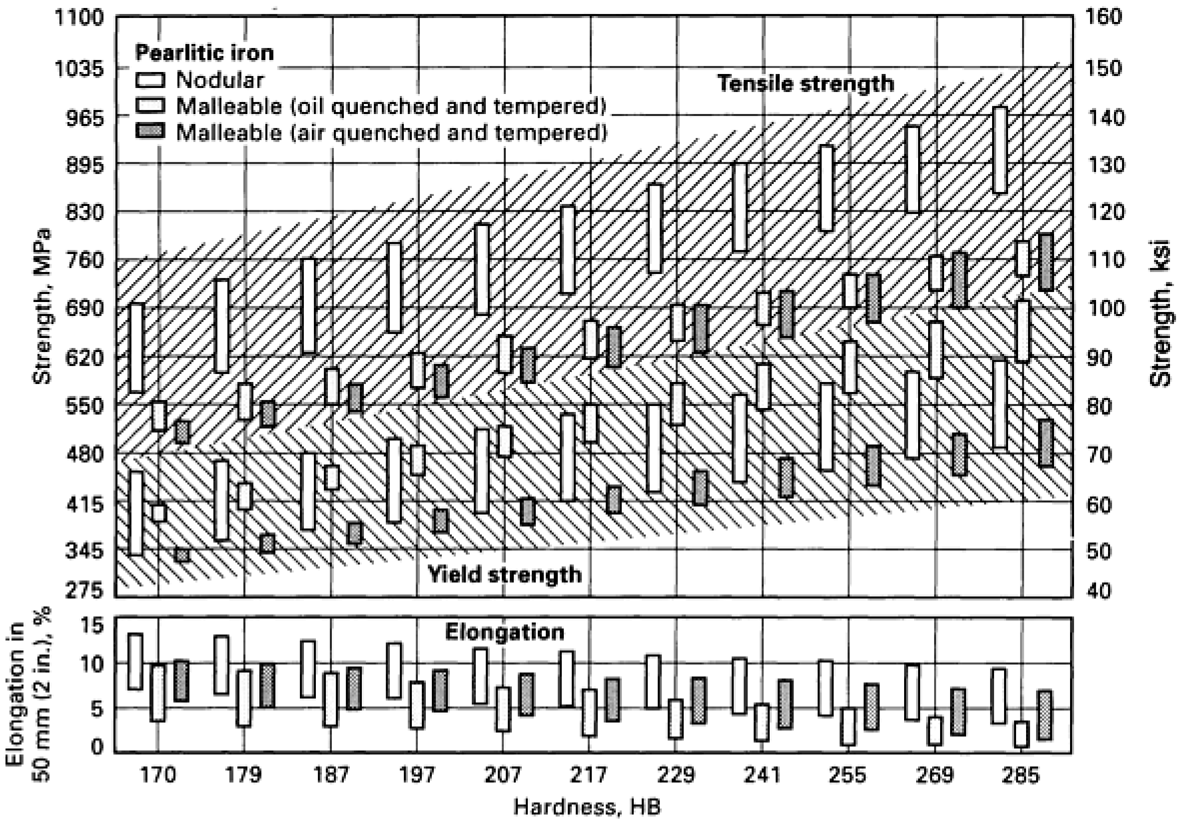


Fig. 1 Tensile properties versus hardness of pearlitic nodular and malleable iron

The annealing of malleable iron should be done in a furnace with a controlled atmosphere of dry nitrogen, hydrogen (1.5%), and carbon monoxide (1.5%). The dew point of this mixture should be between -40 and-7 °C (-40 and -20 °F). These conditions eliminate the possibility of decarburization and loss of temper carbon nodules below the casting surface.

The annealing treatment involves three important steps. The first causes nucleation of temper carbon. It is initiated during heating to a high holding temperature and occurs very early during the holding period.

The second step consists of holding at 900 to 970 °C (1650 to 1780 °F); this step is called first-stage graphitization (FSG). During FSG, massive carbides are eliminated from the iron structure. Long holding periods at 955 °C (1750 °F) will reduce the solubility of nitrogen in iron (which should be kept at 80 to 120 ppm), thereby reducing the mechanical properties of the iron. This occurrence should be kept in mind for long, or "weekend," holding periods. When the carbides are eliminated, the iron is rapidly cooled to 740 °C (1365 °F) prior to entering second-stage graphitization.

The third step in the annealing treatment consists of slow cooling through the allotropic transformation range of the iron; this step is called second-stage graphitization (SSG). During SSG, a completely ferritic matrix free of pearlite and carbides is obtained when the cooling rate is 2 to 28 °C/h (3 to 50 °F/h). Figure 2 shows a ferritic malleable iron. This cooling rate, which depends on the silicon content of the iron and the temper carbon nodule count, may be increased to 85 °C/min (150 °F/min) by air quenching from 900 °C (1650 °F) to form a pearlitic matrix. Oil quenching from 900 °C (1650 °F) will produce a martensitic matrix. However, unless the temperature in the furnace is lowered to 845 °C (1550 °F) for at least 4 h (plus 1 h for each 1 in. of section casting thickness), then raised to 900 °C (1650 °F) for 4 h (plus 1 h for each 1 in. of casting section thickness) prior to uniform quenching in oil, the matrix microstructure will not be uniform in combined carbon. This nonuniformity reduces machinability. If the hardness is reduced by extended tempering, the resulting structure may not have a good response to selective hardening.

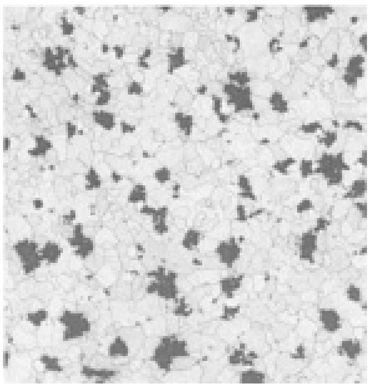


Fig. 2 Ferritic malleable iron etched in 2% nital. 750×

Hardening and Tempering of Malleable Iron

A typical procedure for producing a hardened pearlitic malleable iron consists of, first, air quenching castings after first-stage annealing, which results in retention of about 0.75% combined carbon in the matrix; second, reheating and holding for 1 h at 885 °C (1625 °F) to reaustenitize the matrix and homogenize the combined carbon; and then quenching in heated (50 to 55 °C, or 120 to 130 °F) and agitated oil, thereby developing a matrix consisting of martensite without bainite and having a hardness of 555 to 627 HB. Figure 3 shows the effects of austenitizing temperature and quenching medium on the hardness of ferritic and pearlitic malleable iron. The appropriate austenitizing temperature for pearlitic malleable iron is 885 °C (1625 °F), and for ferritic malleable iron it is 900 °C (1650 °F). If direct oil quenching is used, caution must be exercised to prevent cracking due to high combined carbon.

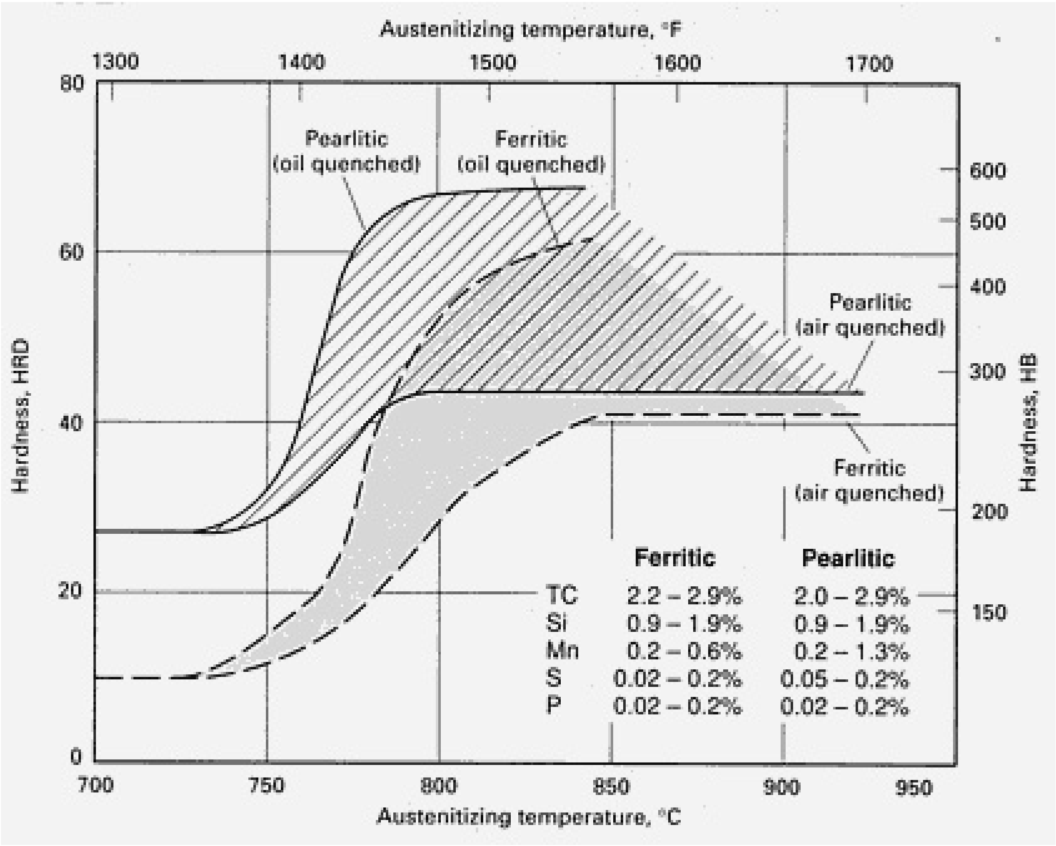


Fig. 3 Effects of austenitizing temperature and quenching medium on hardness of as-quenched malleable iron. The listed composition limits for ferritic and pearlitic malleable iron are general limits given in the *Iron Castings Handbook* (1981). In practice, manganese content is 0.2 to 0.45% Mn for the ferritic class and less than 0.6%

Mn for the pearlitic class.

Figure 4 shows the microstructures of pearlitic malleable iron with various heat treatments. Air-quenched and tempered pearlitic malleable iron has a matrix consisting of a ferrite ring around the tempered carbon (which produces a lower yield strength) and partially broken lamellar pearlite. The remaining lamellar pearlite reduces machinability to a limit of 241 HB. Oil-quenched and tempered pearlitic malleable iron has a matrix of tempered martensite that is totally spheroidizing combined carbon with no ferritic ring around the temper carbon. This produces a higher yield strength and can be machined up to a hardness of 321 HB.

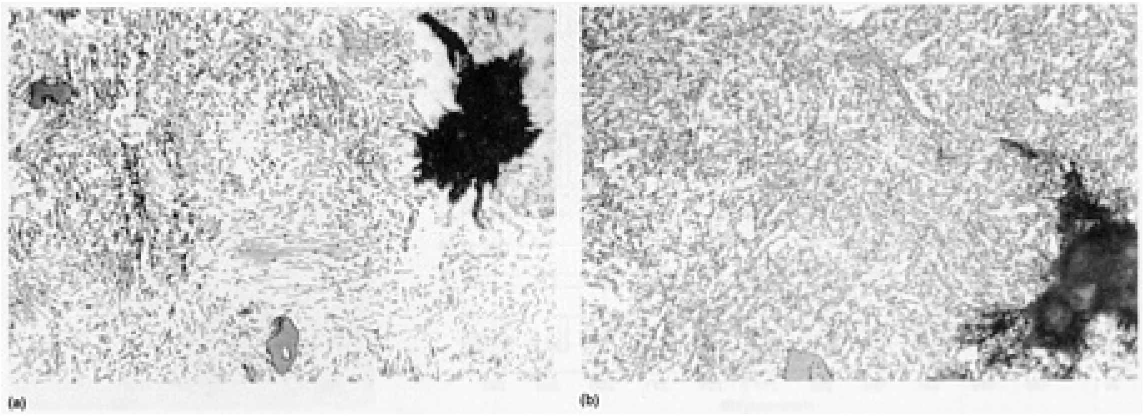


Fig. 4 Pearlitic malleable iron microstructures etched in 2% nital. (a) Arrested anneal (first-stage graphitization), air quenched, and tempered, 212 HB. 750×. (b) Arrested anneal (first-stage graphitization), air quenched, reheated, oil quenched, and tempered, 255 HB. 750×

Increasing the austenitizing time and temperature increases the amount of dissolved carbon, which is measured as combined carbon in the matrix after quenching to room temperature. Austenitizing temperatures in the range of 900 to 930 °C (1650 to 1700 °F) result in a more homogeneous austenite, which is desirable for a more uniform martensite. Higher temperatures can result in a greater tendency toward distortion or cracking. Temperature and time of tempering to attain a specified hardness may be selected from curves such as those shown in Fig. 5. Tempering of pearlite is time and temperature dependent. Tempering of martensite is primarily temperature dependent, with time being secondary.

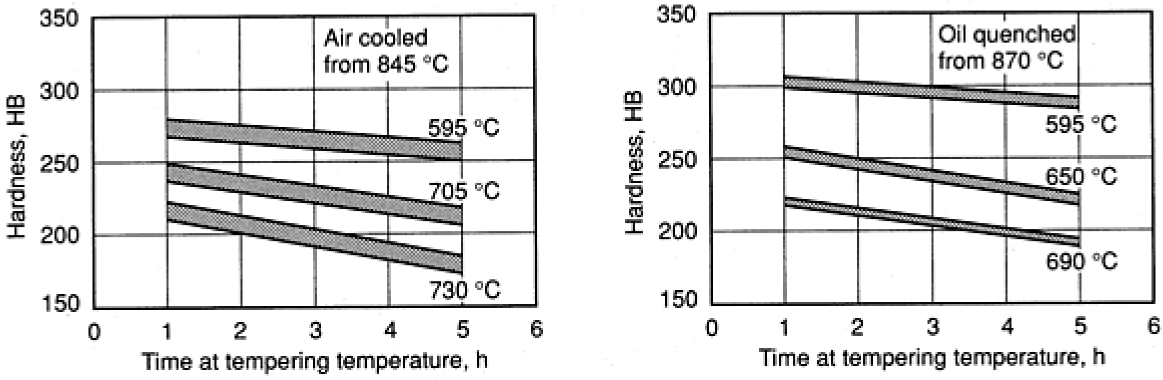


Fig. 5 Influence of time and tempering temperature on room-temperature hardness of pearlitic malleable iron. Composition: 2.35 to 2.45% C, 1.45 to 1.55% Si, 0.03% P, 0.06 to 0.15% S, 0.38 to 0.50% Mn, and less than 0.003% Cr

Hardened and tempered pearlitic malleable iron can also be produced from fully annealed ferritic malleable iron, the matrix of which is essentially carbon-free; graphite can be dissolved in austenite by holding at 900 to 930 °C (1650 to

1700 °F) for a time sufficiently long for the production of an austenite matrix of uniform carbon content. In general, the combined carbon content of the matrix produced by this procedure is slightly lower than that of a pearlitic malleable iron made by air quenching directly from 900 °C (1650 °F), and therefore the final tempering temperatures required for the development of specific hardnesses are lower (Fig. 6).

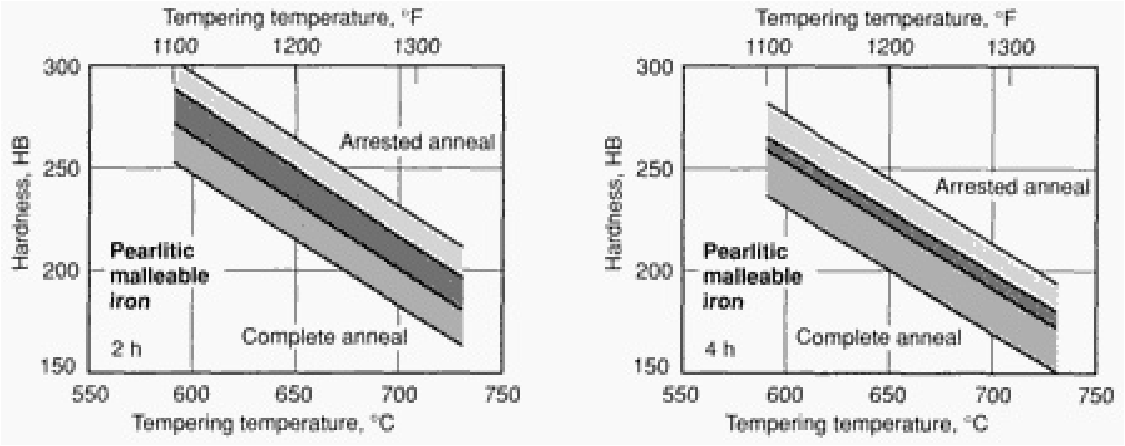


Fig. 6 Room-temperature hardness of tempered pearlitic malleable iron produced by arrested annealing and by complete-ferritize or ferritic annealing and rehardening

Tempering treatments consist of cycles of no less than 2 h at temperature to ensure uniformity of product. Tempering times must also be adjusted for section thickness and quenched microstructures. Fine pearlite and bainite require longer tempering times than that for martensite. In general, final hardness is controlled with process controls approximately the same as those encountered in the heat treatment of medium-carbon and higher-carbon steels. This is particularly true when the specification requires final hardnesses in the range from 241 to 321 HB.

Figure 7 shows the control of hardness attained by one foundry producing quenched and tempered sleeve yokes of grade 80002 pearlitic malleable iron. These yokes were heated at 870 °C (1600 °F) for 30 min, quenched in oil at 65 °C (150 °F), and tempered at 650 °C (1200 °F) for 2 h.

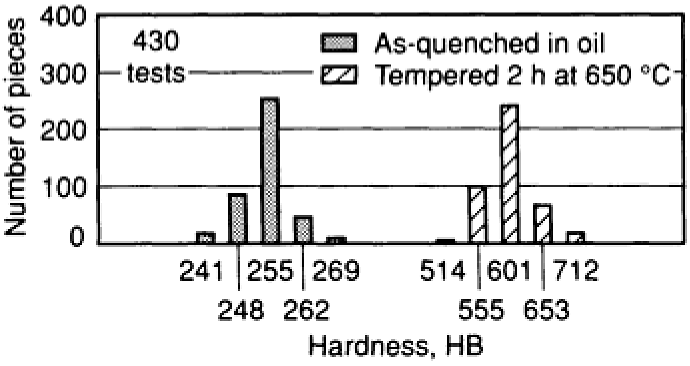
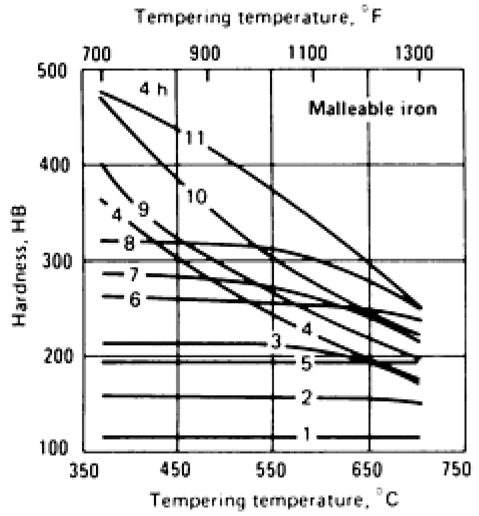
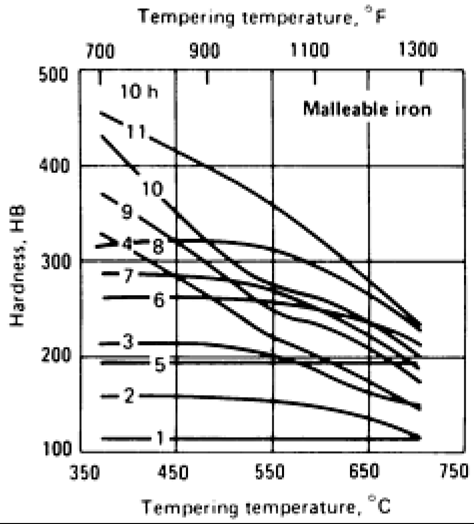


Fig. 7 Room-temperature hardness distribution for quenched and tempered pearlitic malleable iron sleeve yokes. Desired hardness range after tempering was 241 to 269 HB.

The effects of tempering on the hardness of alloyed and unalloyed malleable irons are shown in Table 1; these data illustrate the beneficial effects of alloying on asquenched hardness and stability at elevated temperatures. During all tempering treatments, carbide has a tendency to decompose, with resulting deposition of graphite on existing temper carbon nodules. This tendency is least at the lower tempering temperatures or in suitably alloyed pearlitic malleable irons.

Table 1 Effect of tempering temperature and time on the hardness of ferritic and pearlitic malleable irons in the as-received and reheated-and-quenched conditions





Iron	Material	Composition, %					Alloying and prior heat treatment	Hardness, HB
		TC	Si	S	Mn	Mo		
1	Standard (ferritic) grade 32510	2.40	1.80	0.072	0.30	. . .	Unalloyed; fully malleablized	116
2	Pearlitic malleable iron, grade 45007	2.40	1.80	0.072	0.30	. . .	Unalloyed; air quenched from 925 °C (1700 °F), tempered 8 h at 695 °C (1280 °F)	156
3	Pearlitic malleable iron, grade 60003	2.40	1.80	0.072	0.30	. . .	Unalloyed; oil quenched from 870 °C (1600 °F), tempered 3 h at 650 °C (1200 F)	212
4	Oil-quenched malleable iron	2.40	1.80	0.072	0.30	. . .	Unalloyed; oil quenched from 870 °C (1600 °F), not tempered	444
5	Pearlitic malleable iron, grade 45010	2.40	1.80	0.076	0.90	. . .	Alloyed (Mn); air quenched from 940 °C (1720 °F), tempered 34 h at 715 °C (1320 °F)	192
6	Pearlitic malleable iron, grade 80002	2.40	1.80	0.072	0.90	0.45	Alloyed (Mn and Mo); air quenched from 940 °C (1720 °F), tempered 12 h at 620 °C (1150 °F)	262
7	Air-quenched alloyed malleable iron	2.40	1.80	0.079	0.90	. . .	Alloyed (Mn); air quenched from 925 °C (1700 °F), not tempered	285
8	Air-quenched alloyed malleable iron	2.40	1.80	0.076	1.10	. . .	Alloyed (Mn); air quenched from 925 °C (1700 °F), not tempered	321
9	Oil-quenched alloyed malleable iron	2.40	1.80	0.079	0.90	. . .	Alloyed (Mn); oil quenched from 830 °C (1525 °F), not tempered	514
10	Oil-quenched alloyed	2.40	1.80	0.076	1.10	. . .	Alloyed (Mn); oil quenched from 830 °C (1525 °F),	578

	malleable iron						not tempered	
11	Air-quenched alloyed malleable iron	2.40	1.80	0.072	0.90	0.45	Alloyed (Mn and Mo); air quenched from 940 °C (1720 °F), not tempered	514

Martempering and tempering develops mechanical properties similar to those resulting from conventional oil quenching and tempering: typical tensile strength, 860 MPa (125 ksi); yield strength, 760 MPa (110 ksi); and hardness, 300 HB. Pearlitic malleable iron castings that are susceptible to cracking when quenched in warm oil (40 to 95 °C, or 100 to 200 °F) from the austenitizing temperature may be safely quenched in salt or oil at about 200 °C (400 °F). Elevator camshafts varying in length from 0.3 to 0.45 m (12 to 18 in.) and various sizes of wearchain components are examples of martempered pearlitic malleable iron.

Bainitic Heat Treatment of Pearlitic Malleable Iron

Both upper and lower bainite can be formed in pearlitic malleable iron with a marked increase in tensile strength and hardness but with a decrease in ductility. A pearlitic malleable iron (2.6C-1.4Si-0.5Mn-0.11S), annealed at 930 °C (1700 °F) for 16 h, air quenched, and tempered at 680 °C (1250 °F) for 4 h, developed an ultimate tensile strength of 650 MPa (94.2 ksi), a yield strength of 460 MPa (66.5 ksi), and a 3.4% elongation at 217 HB. This same iron austenitized at 900 °C (1650 °F) in molten salt for 1 h, quenched in molten salt at 295 °C (560 °F) for 3 h, and air cooled gave an ultimate strength of 995 MPa (144.2 ksi), a yield strength of 920 MPa (133.4 ksi), and a 1% elongation at 388 HB.

Surface Hardening of Pearlitic Malleable Iron

Fully pearlitic malleable iron may be surface hardened by either induction heating and quenching or flame heating and quenching. Laser and electron beam techniques also have been used for hardening selected areas on the surface of pearlitic and ferritic malleable iron castings that are free from decarburization. Generally, hardness in the range from 55 to 60 HRC is attainable, with the depth of penetration being controlled by the rate of heating and by the temperature developed at the surface of the part being hardened. In induction hardening, this is accomplished by the close regulation of power output, operating frequency, heating time, and alloy content of the iron.

The maximum hardness obtainable in the matrix of a properly hardened part is 67 HRC; however, conventional hardness measurements show less than the true matrix hardness because of the temper carbon nodules that are averaged into the hardness. Generally, a casting with a matrix micro-hardness of 67 HRC will have about 62 HRC average hardness, as measured with the standard Rockwell tester.

Rocker arms and clutch hubs are examples of automotive production parts that are surface hardened by induction. Flame hardening requires close control for these applications in order to avoid distortion that would interfere with their operation. The two examples that follow describe the successful application of induction and flame hardening to other production parts.

Example 1: Selective Hardening of Crimping Tool Jaws Made of Pearlitic Malleable Iron.

Grade 45010 pearlitic malleable iron was used for tools for crimping electrical connectors. The jaws of these tools as originally designed were inserts made of hardened tool steel. Shell mold casting these jaws and heat treating them to pearlitic malleable iron made it possible for the jaws to be cast integrally to the desired intricate contour and to be hardened by induction heating and water quenching in order to provide required wear resistance. Hardening was thus restricted to the jaws, and the strength and toughness inherent in grade 45010 were maintained in the arms of the handles.

Example 2: Flame Hardening of Malleable Iron Pinion Spacers.

Flame hardening has been used effectively on pearlitic malleable iron pinion spacers that support the cups of roller bearings. The ends of the pinion spacers were flame hardened to file hard (58 HRC or more) to a depth of about 2.4 mm ($\frac{3}{32}$ in.). This treatment eliminated service failures.

Introduction

HIGH-ALLOY CAST IRONS are an important group of materials whose production should be considered separately from that of the ordinary types of cast irons. In these cast iron alloys, alloy content is well above 4% and, consequently, they cannot be produced by ladle additions to irons of otherwise standard compositions. They are usually produced in foundries specially equipped to produce highly alloyed irons. These iron alloys are most often melted in electric furnaces, where precise control of composition and temperature can be achieved. The producing foundries usually have the equipment needed to handle the heat treatment and other thermal processing unique to the production of these alloys.

The cast iron alloys discussed in this article are alloyed for increased abrasion resistance, for strength and oxidation resistance at elevated temperatures, and for improved corrosion resistance. They include the high-alloy graphitic irons and the high-alloy white irons. The heat treatment practices for the following alloys are described:

High-alloy graphitic irons

- Austenitic gray and ductile irons
- High-silicon irons for heat resisting applications
- High-silicon irons for corrosion resisting applications

High-alloy white irons

- Nickel-chromium white irons
- High-chromium white irons

High-Alloy Graphitic Cast Irons

The high-alloy graphitic cast irons have found special use primarily in applications requiring (1) corrosion resistance or (2) strength and oxidation resistance in high-temperature service. They are commonly produced in both flake graphite and nodular graphite versions. Those alloys used in applications requiring corrosion resistance comprise the nickel-alloyed (13 to 36% Ni) gray and ductile irons (also called Ni-Resist irons), and the high-silicon (14.5% Si) gray irons. The alloyed irons produced for high-temperature service comprise the austenitic, nickel-alloyed gray and nodular irons, the high-silicon (4 to 6% Si) gray and nodular irons and the aluminum-alloyed gray and nodular irons. Two groups of aluminum-alloyed irons are recognized: the 1 to 7% Al irons and the 18 to 25% Al irons. Neither the high-silicon (4 to 6% Si) irons or the Al-alloyed irons are covered by ASTM Standards. Although oxidation resistance of the Al-alloyed irons is exceptional, problems in melting and casting the alloys are great; commercial production of the alloys is uncommon, and information on the heat treatment of the alloys is very limited.

The higher alloy contents affect the constitution of the irons, creating conditions for the formation of third phases, and/or secondary eutectics, during solidification; therefore, many of the alloys commonly contain interdendritic carbides or silico-carbides in the as-cast structure. These constituents often remain after heat treatment and are an accepted part of the microstructure.

Austenitic Nickel-Alloyed Graphitic Irons

The nickel-alloyed austenitic irons are produced in both gray and nodular cast iron versions primarily for corrosion resistance and for high-temperature service. Austenitic gray irons date back to the 1930s, at which time they were specialized materials of minor importance. After the invention of ductile iron, austenitic grades with nodular graphite were also developed. These nickel-alloyed austenitic irons have found usefulness in applications requiring corrosion resistance, wear resistance, and high-temperature stability and strength. Additional properties of benefit are low thermal expansion coefficients, nonmagnetic properties, and cast iron materials having good toughness at low temperatures. The procedures and temperatures of the heat treatments for these ductile irons with nodular graphite are similar to those for gray (flake-graphite), corrosion-resistant austenitic cast irons. Heat treatment is discussed in the next section "Heat Treatment of Austenitic Ductile Irons."

Austenitic Gray Irons. These cast irons exhibit properties that include:

- Resistance to corrosion by alkalis, acids, salts, oils, and foods
- High-temperature oxidation resistance
- High electrical resistivity
- Nonmagnetic characteristics
- Abrasive wear resistance
- Uniform thermal expansion
- Moderate strength and toughness

Many of the irons combine several of these properties, which result from the high-temperature austenite phase; this phase is stabilized at room temperature by the high alloy content and contains a uniform dispersion of carbides. The compositions of flake-graphite corrosion-resistant austenitic cast irons are given in Table 1; typical mechanical properties of these irons are presented in Table 2.

Table 1 Compositions of flake-graphite austenitic cast irons per ASTM A 436-84

Type	UNS number	Composition, %					
		TC[(a)]	Si	Mn	Ni	Cu	Cr
1[(b)]	F41000	3.00 max	1.00-2.80	0.50-1.50	13.50-17.50	5.50-7.50	1.50-2.50
1b	F41001	3.00 max	1.00-2.80	0.50-1.50	13.50-17.50	5.50-7.50	2.50-3.50
2[(c)]	F41002	3.00 max	1.00-2.80	0.50-1.50	18.00-22.00	0.50 max	1.50-2.50
2b	F41003	3.00 max	1.00-2.80	0.50-1.50	18.00-22.00	0.50 max	3.00-6.00[(d)]
3	F41004	2.60 max	1.00-2.00	0.50-1.50	28.00-32.00	0.50 max	2.50-3.50
4	F41005	2.60 max	5.00-6.00	0.50-1.50	29.00-32.00	0.50 max	4.50-5.50
5	F41006	2.40 max	1.00-2.00	0.50-1.50	34.00-36.00	0.50 max	0.10 max[(e)]

(a) Total carbon.

(b) Type 1 is recommended for applications in which the presence of copper offers corrosion-resistance advantages.

(c) Type 2 is recommended for applications in which copper contamination cannot be tolerated, such as handling of foods or caustics.

(d) Where some machining is required, 3.0 to 4.0 Cr is recommended.

(e) Where increased hardness, strength; and heat resistance are desired, and where increased expansivity can be tolerated, Cr may be increased to 2.5 to 3.0%.

(f) Type 6 also contains 1.0% Mo.

Table 2 Typical mechanical properties of flake-graphite austenitic cast irons per ASTM 436-84

Type	Tensile strength[(a)]		Hardness, HB[(b)]
	MPa	ksi	
1	170	25	131-183
1b	205	30	149-212
2	170	25	118-174
2b	205	30	171-248
3	170	25	118-159
4	170	25	149-212
5	140	20	99-124

(a) Minimum.

(b) 3000-kg load

These alloys are susceptible to work hardening during machining and require careful cooling from the casting operation and/or subsequent heat-treating operations to minimize the initial stresses and the rate of work hardening during metal-removal operations. Castings that have not been heat treated may cause "chattering" during machining.

ASTM Specification A 436 defines eight grades of austenitic gray iron alloys, four of which are designed to be used in elevated-temperature applications (2, 2b, 3, and 5 in Table 1) and four types are used in applications requiring corrosion resistance (1, lb, 4, and 6 in Table 1). The nickel produces a stable austenitic microstructure with good corrosion resistance and strength at elevated temperatures. The nickel-alloyed irons are additionally alloyed with chromium and silicon for wear resistance and oxidation resistance at elevated temperatures. Types 1 and 1b, which are designed exclusively for corrosion-resistant applications, are alloyed with 13.5 to 17.5% Ni and 6.5% Cu. Types 2b, 3, and 5, which are principally used for high-temperature service, contain from 18 to 36% Ni and varying levels of silicon from 1 to 2.8% and chromium from 0 to 6%. Type 4 is alloyed with 29 to 32% Ni, 5 to 6% Si, and 4.5 to 5.5% Cr and is recommended for stain resistance.

Austenitic Ductile Irons. The ASTM Specification A 439 defines the group of austenitic ductile irons (see Table 3). There are nine alloys listed in the specification. The austenitic ductile iron alloys have similar compositions to the austenitic gray iron alloys but have been treated with magnesium to produce nodular graphite. The ductile family of alloys is available in every type but Type 1, due to its high copper content which is not compatible with production of spheroidal graphite. The ductile iron alloys have high strength and ductility combined with the same desirable properties of the gray iron alloys. They provide resistance to frictional wear, corrosion resistance, strength and oxidation resistance at high temperatures, non-magnetic characteristics and, in some alloys, low thermal expansivity at ambient temperatures. The mechanical properties of several of these ductile austenitic irons are listed in Table 4. Figure 1 illustrates the microstructure typical of austenitic ductile iron.

Table 3 Compositions of nodular-graphite austenitic cast irons per ASTM A 439-83

Type	UNS number	Composition, %					
		TC[(a)]	Si	Mn	P	Ni	Cr
D-2	F43000	3.00 max	1.50-3.00	0.70-1.25	0.08 max	18.0-22.0	1.75-2.75
D-2b	F43001	3.00 max	1.50-3.00	0.70-1.25	0.08 max	18.0-22.0	2.75-4.00
D-2c	F43002	2.90 max	1.00-3.00	1.80-2.40	0.08 max	21.0-24.0	0.50 max
D-3	F43003	2.60 max	1.00-2.80	1.00 max	0.08 max	28.0-32.0	2.50-3.50
D-3a	F43004	2.60 max	1.00-2.80	1.00 max	0.08 max	28.0-32.0	1.00-1.50
D-4	F43005	2.60 max	5.00-6.00	1.00 max	0.08 max	28.0-32.0	4.50-5.50
D-5	F43006	2.60 max	1.00-2.80	1.00 max	0.08 max	34.0-36.0	0.10 max
D-5b	F43007	2.40 max	1.00-2.80	1.00 max	0.08 max	34.0-36.0	2.00-3.00

(a) Total carbon

Table 4 Typical mechanical properties of nodular-graphite austenitic cast irons per ASTM A 439-83

Type	Minimum tensile strength		Minimum yield strength		Minimum elongation[(a)], %	Hardness, HB
	MPa	ksi	MPa	ksi		
D-2	400	58	205	30	8	139-202

D-2b	400	58	205	30	7	148-211
D-3	380	55	205	30	6	139-202
D-4	415	60	. . .	. . .	. . .	202-273
D-5	380	55	205	30	20	131-185

(a) In 50 mm (2 in.)

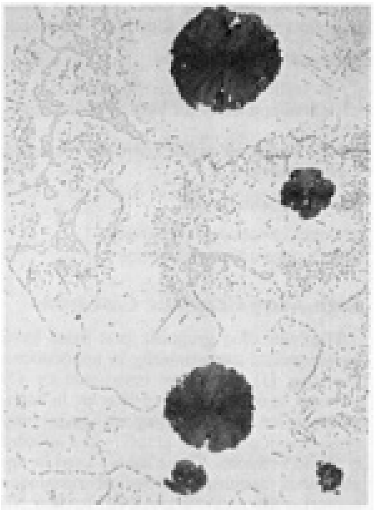


Fig. 1 Photomicrograph of a D5S Ni-Resist ductile iron casting showing nodular graphite structure. 400×

Applications. The nickel-alloyed irons, or Ni-Resist irons, have found wide application in chemical process-related equipment such as compressors and blowers, condenser parts, phosphate furnace parts, pipe, valves and fittings, pots and retorts, and pump casings and impellers. Likewise in food handling equipment the various alloy components include bottling and brewing equipment, canning machinery, distillery equipment, feed screws, meat grinders, and salt filters. In high-temperature applications they are used as cylinder liners, exhaust manifolds, valve guides, gas turbine housings, turbocharger housings, nozzle rings, and piston ring carriers in aluminum pistons.

Heat Treatment of Austenitic Ductile Irons

Heat treatment of the nickel-alloyed austenitic irons serves to reduce residual stresses and to stabilize the microstructure for increased durability. Heat treatments are similar with the graphite in nodular form (ductile iron) or flake form (gray iron).

Stress Relieving. For most applications, it is recommended that austenitic cast irons be stress relieved at 620 to 675 °C (1150 to 1250 °F), for 1 h per 25 mm (1 in.) of section, to remove residual stresses resulting from casting or machining, or both. Stress relieving should follow rough machining, particularly for castings that must conform to close dimensional tolerances, that have been extensively welded, or that are to be exposed to high stresses in service.

Holding of castings at 480 °C (900 °F) for 1 h per 25 mm (1 in.) of thickness will remove about 60% of the stress; stress relieving at 675 °C (1250 °F) will remove almost 95%. It is usually acceptable to cool castings in air at a rate of 1 to 2 h per inch (25 mm) of section thickness, although furnace cooling produces maximum stress relief. Stress relieving does not affect tensile strength, hardness, or ductility.

For large, relatively thin-section castings, mold-cooling to below 315 °C (600 °F) is recommended rather than stress relief heat treatment.

Spheroidize Annealing. Castings with hardnesses above 190 HB may be softened by heating to 980 to 1040 °C (1800 to 1900 °F) for $\frac{1}{2}$ to 5 h except those alloys containing 4% or more chromium. Excessive carbides cause this high hardness and may occur in rapidly cooled castings and thin sections. Annealing dissolves or spheroidizes carbides. Although it lowers hardness, spheroidize annealing does not adversely affect strength.

High-Temperature Stabilization. Except for castings of alloy type 1 (Table 1), which are not recommended for service above 430 °C (800 °F), castings used for either static or cyclic service at 480 °C (900 °F) or above should be given a stabilization heat treatment. This treatment consists of holding at 760 °C (1400 °F) for 4 h minimum or at 870 °C (1600 °F) for 2 h minimum, furnace cooling to 540 °C (1000 °F), and then cooling in air. This treatment stabilizes the microstructure and minimizes growth and warpage in service. The treatment is designed to reduce carbon levels in the matrix and some growth and distortion often accompanies heat treatment. Thus, it is usually advisable to stabilize castings prior to final machining.

Dimensional Stabilization. This treatment normally is limited to castings that require true dimensional stability, such as those used in precision machinery or scientific instruments. The treatment is not applicable to castings of type 1 alloys. Other alloys may be dimensionally stabilized by the following treatment:

- Heat to 870 °C (1600 °F), and hold for 2 h minimum plus 1 h per 25 mm (1 in.) of section
- Furnace cool, at a maximum rate of 50 °C/h (100 °F/h), to 540 °C (1000 °F)
- Hold at 540 °C (1000 °F) for 1 h per 25 mm (1 in.) of section, and then cool uniformly in air
- After rough machining, reheat to 455 to 480 °C (850 to 900 °F) and hold for 1 h per 25 mm (1 in.) of section, and cool uniformly in air
- Finish machine and reheat to 260 to 315 °C (500 to 600 °F), and cool uniformly in air

Solution Treating. Although this treatment is seldom used, quenching from high temperatures is capable of producing higher-than-normal strength levels and slightly higher hardnesses by dissolving some carbon in austenite at elevated temperatures and by preventing precipitation of the carbon by rapid cooling. This treatment consists of heating to 925 to 1010 °C (1700 to 1850 °F) and quenching in oil or water. Because no metallurgical phase change occurs, the possibility of cracking is lessened.

Refrigeration and reaustenitization heat treatments are applied to Type D2 (Table 3) to increase yield strength. Solution heat treatment at 925 °C (1700 °F), followed by refrigeration at -195 °C (-320 °F), followed by reheating between 650 and 760 °C (1200 and 1400 °F) will increase yield strength considerably without materially affecting magnetic properties or corrosion resistance in sea water or dilute sulfuric acid.

High-Silicon Irons for High-Temperature Service

Graphitic irons alloyed with from 4 to 6% Si have provided good service, and low cost, in many elevated-temperature applications. These irons, whether gray or nodular, provide good oxidation resistance and stable ferritic matrix structures that will not go through a phase change at temperatures up to 815 °C (1500 °F). The elevated silicon content of these otherwise normal cast iron alloys reduces the rate of oxidation at elevated temperatures, because it promotes the formation of a dense, adherent film at the surface, which consists of iron silicate rather than iron oxide. This layer is much more resistant to oxygen penetration and its effectiveness improves with increasing silicon content.

The high-silicon gray irons were developed in the 1930s at the British Cast Iron Research Institute and are commonly called "Silal". In Silal, the advantages of a high critical (A_1) temperature, a stable ferritic matrix, and a fine undercooled, type D graphite structure are combined to provide good resistance to growth and oxidation. Oxidation resistance is further improved with additions of chromium, which in these grades can approach levels of 2% Cr. An austenitic grade called "Nicrosilal" was also developed, but the Ni-Resist irons have replaced this alloy. Structural and dimensional stability improve with subcritical annealing heat treatments.

High-Silicon Nodular Irons. The advent of ductile iron led to the development of high-silicon nodular irons, which currently represent the greatest tonnage of these types of irons being produced. Converting the eutectic flake graphite network to isolated graphite nodules further improved resistance to oxidation and growth. The higher strength and ductility of the nodular iron versions of these alloys qualifies them for more rigorous service.

The high-silicon nodular iron alloys are designed to extend the upper end of the range of service temperatures viable for ferritic nodular irons. These irons are used to temperatures of 900 °C (1650 °F). Raising the silicon content to 4% raises the A_1 temperature to 815 °C (1500 °F), and at 5% Si the A_1 temperature is above 871 °C (1600 °F). The mechanical properties of these alloyed irons at the lower end of the range (4 to 4.5% Si) are similar to those of standard ferritic nodular irons. At 5 to 6% Si, oxidation resistance is improved and critical temperature is increased, but the iron can be very brittle at room temperature. At higher silicon levels impact transition temperature rises well above room temperature and upper shelf energy is reduced. Ductility improves when temperatures exceed 430 °C (800 °F).

For most applications alloying with 0.5 to 1% Mo provides adequate elevated-temperature strength and creep resistance. Higher molybdenum additions are used when maximum elevated-temperature strength is needed. High molybdenum additions (>1%) tend to generate interdendritic carbides of the M_2C type, which persist even through annealing, and tend to reduce toughness and ductility at room temperature.

Silicon lowers the eutectic carbon content and the latter must be controlled to avoid graphite flotation. For 4% Si irons, carbon content should range from 3.2 to 3.5% C, depending on section size; and at 5% Si, it should be around 2.9% C.

Applications. While quite brittle at room temperature, the high-silicon gray irons are reasonably tough at temperatures above 260 °C (500 °F) and have been used successfully for furnace and stoker parts, burner nozzles, and for heat treatment trays.

The high-silicon and Si-Mo nodular irons are currently produced as manifolds and turbocharger housings for trucks and some automotive applications. They are also used in heat treating racks.

Heat Treatment of High-Silicon Irons for High-Temperature Service. The high-silicon gray and nodular irons are predominantly ferritic as-cast, but the presence of carbide-stabilizing elements will result in a certain amount of pearlite and often intercellular carbides. These alloys are inherently more brittle than standard grades of iron and usually have higher levels of internal stress due to lower thermal conductivity and higher elevated-temperature strength. These factors should be taken into account when deciding on heat treatment requirements.

For the high-silicon nodular irons, high-temperature heat treatment is advised in all cases to anneal any pearlite and stabilize the casting against growth in service. A normal graphitizing (full) anneal in the austenitic temperature range is recommended when undesirable amounts of carbide are present. For the 4 to 5% Si irons this will require heating to at least 900 °C (1650 °F) for several hours, followed by slow cooling to below 700 °C (1300 °F). At higher silicon contents (>5%), in which carbides readily break down, and in castings relatively carbide-free, subcritical annealing in the temperature range 720 to 790 °C (1325 to 1450 °F) for 4 h is effective in ferritizing the matrix. Compared to full annealing, the subcritically annealed material will have somewhat higher strength, but ductility and toughness will be reduced. Figure 2 illustrates the full-annealed microstructure in a 4Si-Mo ductile iron casting.

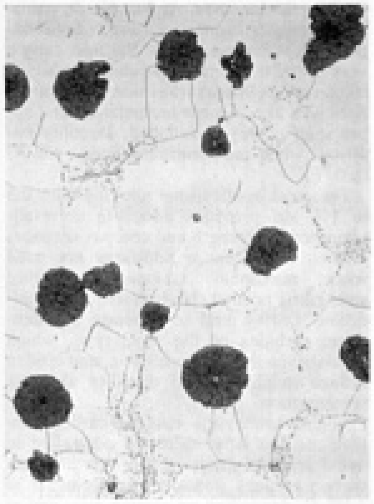


Fig. 2 Photomicrograph of subcritically annealed 4% Si-Mo ductile iron casting showing nodular graphite structure. 400×

High-Silicon Irons for Corrosion Resistance

Irons with high silicon content (14.5% Si) comprise a unique corrosion-resistant ferritic cast iron group. These alloys are widely used in the chemical industry for processing and for transporting highly corrosive liquids. They are particularly good for handling sulfuric and nitric acids. The most common of the high-silicon iron alloys are covered in ASTM Specification A 518M (see Table 5). Three alloys are defined in the specification, all containing 14.2 to 14.75% Si and from 0.7 to 1.15% C. Grades 2 and 3 are additionally alloyed with 3.25 to 5% Cr, and grade 2 also calls for 0.4 to 0.6% Mo. Other compositions are also commercially produced with up to 17% Si. The high-silicon iron castings usually require stress relief heat treatments prior to going into service.

Table 5 Compositions of corrosion-resistant high-silicon cast iron alloys

Alloy	Composition, %					
	C	Mn	Si	Cr	Mo	Cu
Grade 1	0.70-1.10	1.50 max	14.20-14.75	0.50 max	0.50 max	0.50 max
Grade 2	0.75-1.15	1.50 max	14.20-14.75	3.25-5.00	0.40-0.60	0.50 max
Grade 3	0.70-1.10	1.50 max	14.20-14.75	3.25-5.00	0.20 max	0.50 max

Applications. High-silicon irons are extensively used in equipment for the production of sulfuric and nitric acids, for sewage disposal and water treatment, for handling mineral acids in petroleum refining, and in the manufacture of fertilizer, textiles, and explosives. Specific components include pump rotors, agitators, crucibles, and pipe fittings in chemical laboratories.

Heat Treatment of High-Silicon Irons for Corrosion Resistance. Because of the very brittle nature of high-silicon cast iron, castings are usually shaken out only after mold cooling to ambient temperature. However, some casting geometries demand hot shake-out so that the castings can be immediately stress-relieved and furnace cooled to prevent cracking.

Castings are stress relieved by heating in the range of 870 to 900 °C (1600 to 1650 °F) followed by slow cooling to ambient temperatures to minimize the likelihood of cracking. Heat treatments have no significant effect on corrosion resistance.

High-Alloy White Cast Irons

The high-alloy white irons are primarily used for abrasion-resistant applications and are readily cast in the shapes needed in machinery used for crushing, grinding, and general handling of abrasive materials. The large volume of eutectic carbides in their microstructures provide the high hardness needed for crushing and grinding other materials. The metallic matrix supporting the carbide phase in these irons can be adjusted by alloy content and heat treatment to develop the proper balance between resistance to abrasion and the toughness needed to withstand repeated impact.

All high-alloy white irons contain chromium to prevent formation of graphite on solidification and to ensure the stability of the carbide phase. Most also contain nickel, molybdenum, copper, or combinations of these alloying elements to prevent the formation of pearlite in the microstructure. While low-alloyed pearlitic white iron castings develop hardness in the range 350 to 550 HB, the high-alloyed white irons range from 450 to 800 HB. In addition, several grades contain alloy eutectic carbides (M_7C_3 chromium carbides) which are substantially harder than the iron carbide in low-alloy irons. For many applications, the increased abrasion resistance of the more expensive high-alloy white irons adds significantly to wear life, causing them to provide the most cost-effective performance.

ASTM Specification A 532 covers the composition and hardness of white iron grades used for abrasion-resistant applications (see Table 6). Many castings are ordered according to these specifications; however, a large number of castings are produced with modifications to composition for specific applications. It is most desirable that the designer, metallurgist, and foundryman work together to specify the composition, heat treatment, and foundry practice to develop the most suitable alloy and casting design for a specific application.

Table 6 Composition and mechanical requirements of abrasion-resistant cast irons per ASTM A 532-82

Class	Type	UNS number	Designation	Composition, wt%					
				C	Mn	Si	Ni	Cr	Mo
I	A	F45000	Ni-Cr-HC	3.0-3.6	1.3 max	0.8 max	3.3-5.0	1.4-4.0	1.0 max[(a)]
I	B	F45001	Ni-Cr-LC	2.5-3.0	1.3 max	0.8 max	3.3-5.0	1.4-4.0	1.0 max[(a)]
I	C	F45002	Ni-Cr-GB	2.9-3.7	1.3 max	0.8 max	2.7-4.0	1.1-1.5	1.0 max[(a)]
I	D	F45003	Ni-Hi Cr	2.5-3.6	1.3 max	1.0-2.2	5.0-7.0	7.0-11.0	1.0 max[(b)]
II	A	F45004	12% Cr	2.4-2.8	0.5-1.5	1.0 max	0.5 max	11.0-14.0	0.5-1.0[(c)]
II	B	F45005	15% Cr-Mo-LC	2.4-2.8	0.5-1.5	1.0 max	0.5 max	14.0-18.0	1.0-3.0[(c)]
II	C	F45006	15% Cr-Mo-HC	2.8-3.6	0.5-1.5	1.0 max	0.5 max	14.0-18.0	2.3-3.5[(c)]
II	D	F45007	20% Cr-Mo-LC	2.0-2.6	0.5-1.5	1.0 max	1.5 max	18.0-23.0	1.5 max[(c)]
II	E	F45008	20% Cr-Mo-HC	2.6-3.2	0.5-1.5	1.0 max	1.5 max	18.0-23.0	1.0-2.0[(c)]

III	A	F45009	25% Cr	2.3-3.0	0.5-1.5	1.0 max	1.5 max	23.0-28.0	1.5 max[c]

Class	Type	Designation	Mechanical requirements					
			Hardness, HB				Typical section thickness, max	
			Sand cast, min	Chill cast, min	Hardened, min	Softened, max	mm	in.
I	A	Ni-Cr-HC	550	600	. . .	. . .	200	8
I	B	Ni-Cr-LC	550	600	. . .	. . .	200	8
I	C	Ni-Cr-GB	550	600	. . .	. . .	75 diam ball	3 diam ball
I	D	Ni-Hi Cr	550	500	600	400	300	12
II	A	12% Cr	550	. . .	600	400	25 diam ball	1 diam ball
II	B	15% Cr-Mo-LC	450	. . .	600	400	100	4
II	C	15% Cr-Mo-HC	550	. . .	600	400	75	3
II	D	20% Cr-Mo-LC	450	. . .	600	400	200	8
II	E	20% Cr-Mo-HC	450	. . .	600	400	300	12
III	A	25% Cr	450	. . .	600	400	200	8

ASTM A 532-87 data have slight variations.

(a) Maximum: 0.30% P, 0.15% S.

(b) Maximum: 0.10% P, 0.15% S.

(c) Maximum: 0.10% P, 0.06% S, 1.2% Cu

The high-alloy white cast irons fall into three major groups:

- The Ni-Cr white irons, which are low-chromium alloys containing 3 to 5% Ni and 1 to 4% Cr, with one alloy modification which contains 7 to 11% Cr. The Ni-Cr irons are also commonly identified by the tradename Ni-Hard types 1 to 4

- The chromium-molybdenum irons containing 11 to 23% Cr, up to 3% Mo, and often additionally alloyed with nickel or copper
- The 25% Cr or 28% Cr white irons, which may contain other alloying additions of molybdenum and/or nickel up to 1.5%

Mechanical properties for three white irons representing each of these three general groups are shown as bar graphs in Fig. 3. The properties for the austenitic matrix were obtained with as-cast irons; the martensitic properties were obtained by heat treatment. In all irons, heat treating to achieve a martensitic matrix resulted in improved properties.

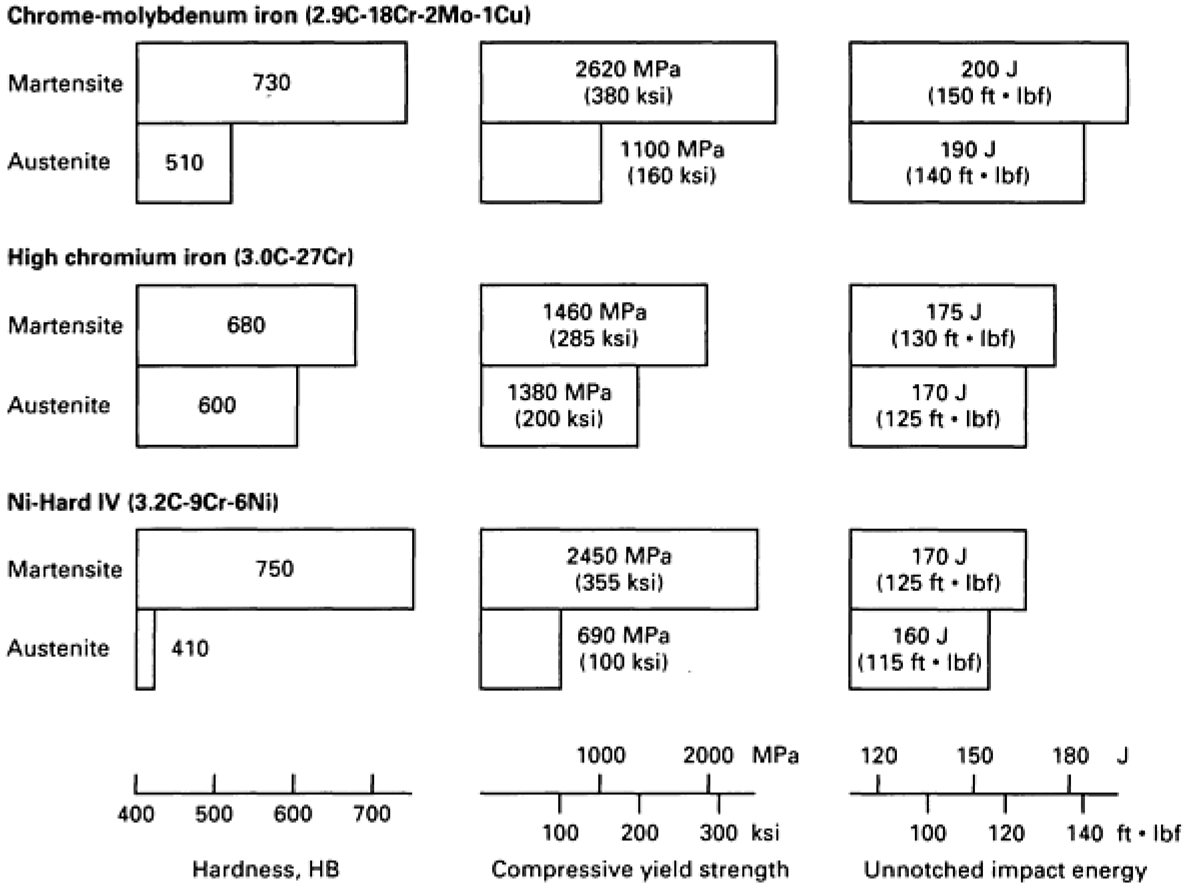


Fig. 3 Typical mechanical properties of white cast irons

In alkali environments, the corrosion-resistant properties of the high-alloyed white irons used in abrasion-resistant applications increase as the pH exceeds 7. In acidic environments, the nickel-chromium white irons are recommended for use in very dilute acid sulfate conditions while high-chromium white irons are recommended for use in very dilute acid chloride conditions.

Nickel-Chromium White Irons

One of the oldest groups of high-alloy irons of industrial importance, the Ni-Cr white irons, or Ni-Hard irons, have been produced for more than 50 years and are very cost-effective materials for crushing and grinding. In these martensitic white irons, nickel is the primary alloying element because at levels of 3 to 5% it is effective in suppressing the transformation of the austenite matrix to pearlite, and thus ensuring that a hard, martensitic structure (usually containing significant amounts of retained austenite) will develop on cooling in the mold. Chromium is included in these alloys, at levels from 1.4 to 4%, to ensure that the irons will solidify with carbides to counteract the graphitizing effect of nickel. A typical microstructure is shown in Fig. 4.

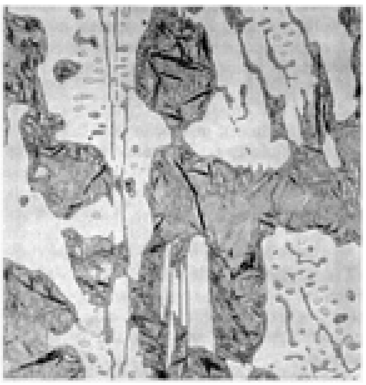


Fig. 4 Typical microstructure of class I type A nickel-chromium white cast iron. 340×

Composition Selection and Control. The optimum composition of the Ni-Cr white iron alloy depends on the properties required for the service conditions and the dimensions and weight of the casting. Abrasion resistance is generally a function of the bulk hardness and the volume of carbide in the microstructure. When abrasion resistance is the principal requirement and resistance to impact loading is secondary, alloys having high carbon contents, ASTM A 532 class I type A (Ni-Hard 1), are recommended. Where conditions of repeated impact are anticipated, the lower carbon alloys, class I type B (Ni-Hard 2), are recommended because they have less carbide and, therefore, greater toughness. A special grade, class I type C, has been developed for producing grinding balls and slugs. Here, the Ni-Cr alloy composition has been adapted for chill casting and specialized sand casting processes.

The class I type D (Ni-Hard 4) alloy is a modified Ni-Cr iron which contains higher levels of chromium ranging from 7 to 11%, and increased levels of nickel ranging from 5 to 7%. Whereas the eutectic carbide phase in the lower-alloyed Ni-Cr irons is M_3C (iron carbide) which forms as a continuous network in these irons, the higher chromium in the type D alloy promotes M_7C_3 chromium carbides which form a relatively discontinuous eutectic carbide distribution (Fig. 5). This modification in eutectic carbide pattern provides an appreciable improvement in resistance to fracture by impact. The higher alloy content of this iron grade also results in improved corrosion resistance, which has proved useful in the handling of corrosive slurries.

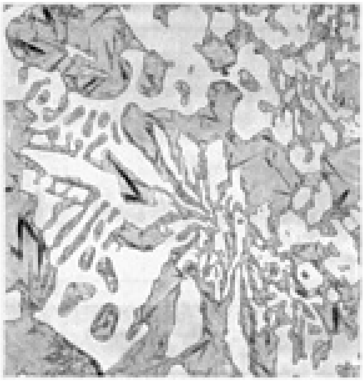


Fig. 5 Typical microstructure of class I type D nickel-chromium white cast iron. 340×

Carbon is varied according to properties needed for the intended service. Carbon contents in the range of 3.2 to 3.6% are prescribed when maximum abrasion resistance is desired. Where impact loading is present, carbon content should be held in the range of 2.7 to 3.2%.

Nickel content is increased with section size or cooling time of the casting to inhibit pearlitic transformation. For castings of 1.5 to 2 in. thick, nickel contents of 3.4 to 4.2% are sufficient to suppress pearlite formation on mold cooling. Heavier

sections may require nickel levels up to 5.5% to avoid the formation of pearlite. It is important to limit nickel content to the level needed for control of pearlite; excess nickel increases the amount of retained austenite and lowers hardness.

Silicon is needed for two reasons. A minimum amount of silicon is necessary to improve fluidity and produce a fluid slag. But of equal importance is its effect on as-cast hardness. Increased levels of silicon, in the range of 1 to 1.5%, have been found to increase the amount of martensite and the resulting hardness. Late additions of ferrosilicon (0.2% as 75% Si FeSi) have been reported to increase toughness. Note that higher silicon contents can promote pearlite and may increase the nickel requirement.

Chromium is primarily added to offset the graphitizing effects of nickel and silicon in the class I types A, B, and C alloys (see Table 6) and ranges from 1.1 to 4.0%. Chromium content must increase with increasing section size. In the type D alloy, chromium levels range from 7 to 11% (typically 9%) for the purpose of producing eutectic carbides of the M_7C_3 chromium carbide type, which are harder and less deleterious to toughness.

Manganese is usually held to 0.8% max. While it provides increased hardenability to avoid pearlite formation, it is also a potent austenite stabilizer, more so than nickel, and will promote increased amounts of retained austenite and lower as-cast hardness. For this reason higher manganese levels are undesirable. In considering the nickel content required to avoid pearlite in a given casting, the level of manganese present should be a factor.

Copper increases hardenability and the retention of austenite and, therefore, must be controlled for the same reason manganese is limited. Copper should be treated as a nickel substitute and, when properly included in the calculation of the amount of nickel required to inhibit pearlite in a given casting, it reduces the nickel requirement.

Molybdenum is a potent hardenability agent in these alloys and is used in heavy section castings to augment hardenability and inhibit pearlite.

Heat Treatment of Nickel-Chromium White Irons. All nickel-chromium white iron castings are given a stress-relief heat treatment because, properly made, they have a martensitic matrix structure, as-cast. Tempering is performed between 205 to 260 °C (400 to 450 °F) for at least 4 h. This tempers the martensite, relieves some of the transformation stresses, and increases the strength and impact toughness by 50 to 80%. Some additional martensite may form on cooling from the tempering temperature. This heat treatment does not reduce hardness or abrasion resistance.

In the heat treatment of any white cast iron, care must be taken to avoid cracking by thermal shock; never place the castings in a hot furnace or otherwise subject them to rapid heating or cooling. The risk of cracking increases with the complexity of the casting shape and section thickness.

High-Temperature Heat Treatment. In the past, hardening of the class I type D, Ni-Hard 4, was performed by supercritical heat treatment when as-cast hardness was insufficient. An austenitizing heat treatment usually comprised heating at temperatures between 750 and 790 °C (1380 and 1450 °F) with a soak time of 8 h. Air or furnace cooling, not over 30 °C/h (50 °F/h), was conducted followed by a tempering/stress-relief heat treatment. Refrigeration heat treatment is the more commonly practiced remedy for low hardness today.

Refrigeration Treatments. To achieve a hardness of 550 HB, it is necessary that the as-cast austenite-martensite microstructure have at least 60% martensite present. When martensite content is increased to 80 to 90%, however, hardness values exceed 650 HB. To reduce the amount of retained austenite (form more martensite), deep freeze treatments are commonly applied. Refrigeration to temperatures between -70 and -180 °C (-100 and -300 °F) for $\frac{1}{2}$ to 1 h will usually raise the hardness level 100 HB units. A subsequent tempering/stress-relief heat treatment usually follows. The typical refrigerated Ni-Cr iron microstructure is shown in Fig. 6.

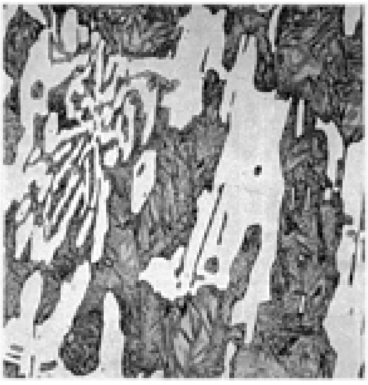


Fig. 6 Microstructure of class I type D nickel-chromium white cast iron after refrigeration. 340×

Special Ni-Cr White Iron Alloys. Certain proprietary grades of the type A alloy have been developed by the rolling mill roll industry. The compositions of these alloys have been modified to produce mottled structures, containing some graphite. The graphite inclusions are reported to improve resistance to thermal cracking. These "indefinite chill" rolls are cast in thick-walled gray iron chiller molds in roll diameters up to 1000 mm (40 in.) or more. The silicon-to-chromium ratios and inoculation with ferrosilicon are carefully regulated to control the amount and distribution of the graphite particles. The rolls can be double-poured with a gray iron core. With molybdenum modification, the matrix of the chill cast shell will be martensitic. Some roll alloys are designed to be heat treated, a modified normalizing heat treatment, to obtain a bainitic microstructure.

High-Chromium White Irons

The oldest high-alloy white irons produced commercially were the high-chromium (28% Cr) white irons. The high-chromium white irons have excellent abrasion resistance and are used effectively in slurry pumps, brick molds, coal-grinding mills, rolling mill rolls, shot blasting equipment, and components for quarrying, hard-rock mining and milling. In some applications they must also be able to withstand heavy impact loading. These alloyed white irons are recognized as providing the best combination of toughness and abrasion resistance attainable among the white cast irons.

In the high-chromium irons, as with most abrasion-resistant materials, there is a trade-off between wear resistance and toughness. Through variations in composition and heat treatment these properties can be adjusted to meet the needs of most abrasive applications.

As a class of alloyed irons, the high-chromium irons are distinguished by the hard, relatively discontinuous, M_7C_3 eutectic carbides present in the microstructure, as opposed to the softer, more continuous M_3C eutectic carbides present in the alloyed irons containing less chromium. With few exceptions, these alloys are usually produced as hypoeutectic compositions.

Classes of High-Chromium Irons. Specification ASTM A 532 covers the compositions and hardnesses of two general classes of the high-chromium irons (see Table 6). The chromium-molybdenum irons (class II of ASTM A 532) contain 11 to 23% Cr and up to 3% Mo and can be supplied either as-cast with an austenitic or austenitic-martensitic matrix, or heat treated with a martensitic matrix microstructure for maximum abrasion resistance and toughness. They are usually considered the hardest of all grades of white cast irons. Compared to the lower alloy Ni-Cr white irons, the eutectic carbides are harder and these alloys can be heat treated to achieve castings of higher hardness. Molybdenum (and nickel and copper when needed) is added to prevent pearlite and assure maximum hardness is obtained.

The high-chromium irons (class III of ASTM A 532) represent the oldest grade of high-chromium irons, with the earliest patents dating back to 1917. These general purpose irons, also called 25% Cr and 28% Cr irons, contain 23 to 28% Cr with up to 1.5% Mo. To prevent pearlite and attain maximum hardness, molybdenum is added in all but the lightest cast sections. Other alloying with nickel and copper up to 1% is also practiced. Although the maximum attainable hardness is not as high as in the class II Cr-Mo white irons, these alloys are selected when resistance to corrosion is also desired.

Special High-Chromium Iron Alloys for Corrosion Resistance. Alloys with improved resistance to corrosion, for applications such as pumps handling fly ash, are produced with high chromium contents (26 to 28% Cr) and low carbon contents (1.6 to 2.0% C). These high-chromium, low-carbon irons will provide the maximum chromium content in the matrix. Addition of 2% Mo is recommended for improving resistance to chloride-containing environments. For this application, fully austenitic matrix structures provide the best resistance to corrosion, but some reduction in abrasion resistance must be expected. Castings are normally supplied in the as-cast condition.

Special High-Chromium Irons for High-Temperature Service. Because of castability and cost, high-chromium white iron castings can often be used for complex and intricate parts in high-temperature applications at considerable savings compared to stainless steel. These cast iron grades are alloyed with 12 to 39% Cr. Chromium causes the formation of an adherent, complex, chromium-rich oxide film providing resistance to scaling at temperatures up to 1040 °C (1900 °F). The high-chromium irons designated for use at elevated temperatures fall into one of three categories, depending upon the matrix structure:

- The martensitic irons alloyed with 12 to 28% Cr
- The ferritic irons alloyed with 30 to 34% Cr
- The austenitic irons which in addition to containing 15 to 30% Cr, also contain 10 to 15% Ni to stabilize the austenite phase

Carbon contents of these alloys range from 1 to 2%. The choice of the exact composition is critical to prevent sigma (σ) phase formation at intermediate temperatures, while at the same time avoiding ferrite-to-austenite transformation during thermal cycling, which leads to distortion and cracking. Typical applications include recuperator tubes, breaker bars and trays in sinter furnaces, grates, burner nozzles and other furnace parts, glass bottle molds and valve seats for combustion engines.

Hardness in High-Chromium Iron Castings. The hardness ranges which can be expected in high-chromium irons with different matrix microstructures are shown in Table 7. The hardness values of microconstituents in abrasion-resistant irons, as well as the hardness of minerals being crushed, are shown in Table 8. It is evident that carbides and martensite are needed to resist abrasion by the common minerals associated with mining and oil drilling.

Table 7 Typical hardness range for castings

Matrix structure	Hardness, HB
Pearlite	320-500
Austenite	420-500
Martensite (as-cast)	550-650
Martensite (heat treated)	650-850

Table 8 Hardness of minerals and microconstituents

Mineral	Hardness		Material or microconstituents	Hardness	
	Knoop	HV		Knoop[(a)]	HV
Talc	20		Ferrite	235	70-200

Carbon	35		Pearlite, unalloyed		250-320
Gypsum	40	36	Pearlite, alloyed		300-460
Calcite	130	140	Austenite, 12% Mn	305	170-230
Fluorite	175	190	Austenite, low alloy		250-350
Apatite	335	540	Austenite, high Cr iron		300-600
Glass	455	500	Martensite	500-800	500-1010
Feldspar	550	600-750	Cementite (Fe_3C)	1025	840-1100
Magnetite	575		Chromium carbide $(Fe,Cr)_7C_3$	1735	1200-1600
Orthoclase	620		Molybdenum carbide (Mo_2C)	1800	1500
Flint	820	950	Tungsten carbide (WC)	1800	2400
Quartz	840	900-1280	Vanadium carbide (VC)	2660	2800
Topaz	1330	1430	Titanium carbide (TiC)	2470	3200
Garnet	1360		Boron carbide (B_4C)	2800	3700
Emery	1400				
Corundum (alumina)	2020	1800			
Silicon carbide	2585	2600			
Diamond	7575	10000			

Source: Ref 1

(a) Typical values.

Figure 7 shows the relation between hardness and abrasive wear loss (in a laboratory pin test which has been shown to correlate with abrasion in mining service), for one composition of high-chromium iron subjected to a wide range of heat treatments to provide matrix structures which are either predominantly austenitic or martensitic (Ref 2). Best resistance to abrasion (low-volume losses in the test) was achieved with martensitic structures using heat treatments with an air-quench

from high austenitizing temperatures (such as data points 9, 11, 15, and 43 in Fig. 7). Subsequent treatments, such as refrigerating or low-temperature tempering, did not improve the abrasion resistance significantly.

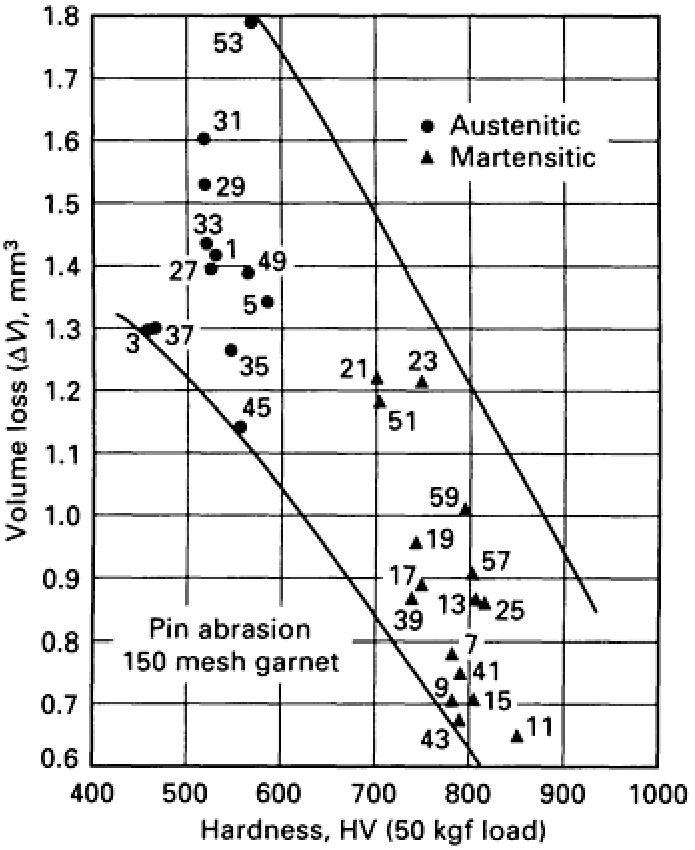


Fig. 7 Volume loss in pin abrasion test as a function of hardness for 2.9% C-19% Cr-2.4% Mo-0.9% Cu iron subjected to various heat treatments. Source: Ref 2

Typical mechanical properties for three white irons of widely varying compositions are shown as bar graphs in Fig. 3. The properties for the austenitic matrix were obtained with as-cast irons; the martensitic properties were obtained by heat treatment. In all irons, heat treating to achieve a martensitic matrix resulted in improved properties.

Optimizing Fracture Toughness and Abrasion Resistance. Abrasion resistance and fracture toughness were determined for a series of high-alloy white irons with varying carbide content and matrix microstructures (Ref 2). Results were correlated for one such iron in Fig. 8 to show the effect of structure and heat treatment. Austenitic matrix structures could provide higher fracture toughness, and martensitic matrix structures could provide better resistance to abrasion. But careful selection of heat treatments (for example data points 17 and 51) provided good wear resistance and reasonable fracture toughness. These heat treatments involved air quenching from high temperatures, followed by tempering at 200 °C (390 °F).

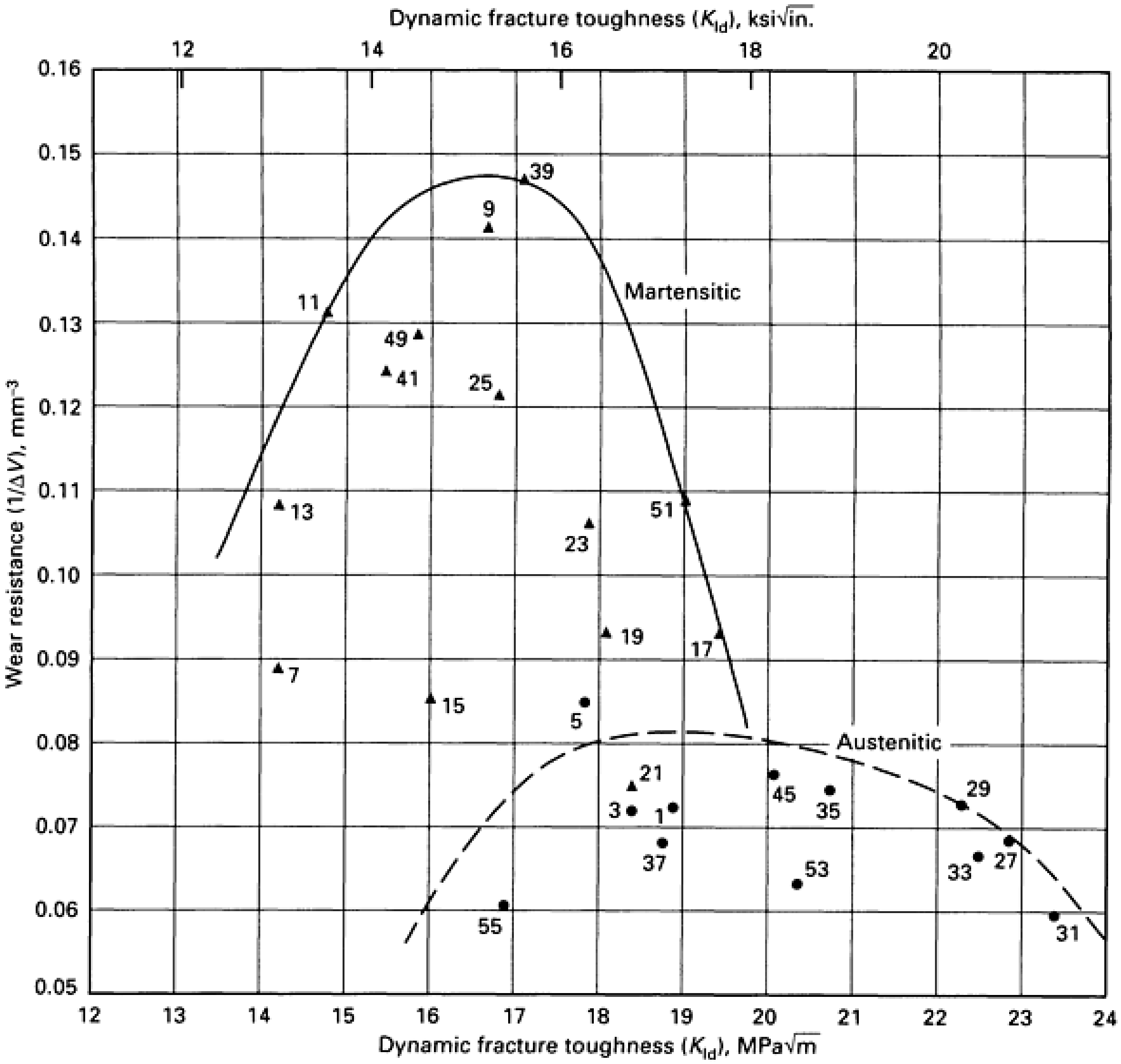


Fig. 8 Abrasive wear resistance versus fracture toughness for a 2.9% C-19% Cr-2.4% Mo-0.9% Cu iron subjected to various heat treatments. Wear resistance expressed as the reciprocal of volume loss (Δ*V*). Source: Ref 2

A study of spalling of high-chromium white cast irons provided data showing the advantage of careful control of heat treatment (Ref 3). Spalling resistance could be maximized by either high-temperature tempering or austenitizing and tempering.

Microstructure of High-Chromium White Irons

Optimum Metallic Matrix. To a large extent the metal matrix in high-chromium irons has characteristics of tool steel. It can be made tough to increase the tolerance to impact loading, or hardened to reduce wear, though generally at the expense of toughness. Matrix structures can be pearlite, austenite, or martensite, or some combination of these.

Detailed studies of microstructures are described in work by Maratray and Poulalion (Ref 4). A summary of this work and of other studies of structures in high-chromium irons was made by Dodd and Parks (Ref 5). As with steels, maximum abrasion resistance is achieved with a fully martensitic matrix structure. As-cast austenitic irons, though relatively soft, can give satisfactory performance in many abrasive wear applications due to pronounced work hardening in service. Resistance to crack propagation is greatest in irons having a fully austenitic matrix. Under conditions of repeated impact, however, martensitic irons, which have been tempered to minimize retained austenite, have the maximum resistance to spalling.

Pearlitic matrix structures have modest abrasion resistance and low toughness and, therefore, are not generally desirable. Pearlite will always occur when alloying is insufficient to inhibit its formation. Most of the chromium is tied up in the chromium carbides and, therefore, other alloying elements are needed to provide adequate hardenability.

The carbides in high-chromium irons are very hard and wear resistant but are also brittle. In general wear resistance is improved by increasing the amount of carbide (increasing the carbon content), while toughness is improved by increasing the proportion of metallic matrix (reducing the carbon content). The influence of carbon content on the shape and distribution of the carbide phase in these alloys is shown in Fig. 9.

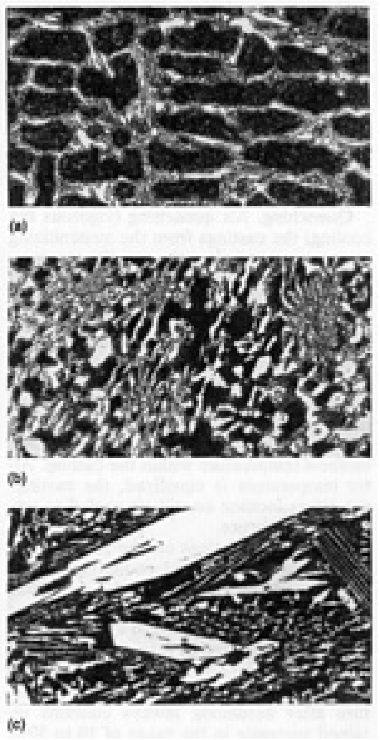


Fig. 9 Microstructures of high-chromium white iron compositions. (a) Low-carbon (hypoeutectic). (b) Eutectic. (c) High-carbon (hypereutectic). All 75×. Courtesy of Climax Molybdenum Company

Large hexagonal carbide rods occur when carbon contents exceed the eutectic carbon content (Fig. 9c). These primary chromium carbides, which precipitate from the melt ahead of eutectic solidification, are quite deleterious to impact toughness and should be avoided in castings subjected to any impact in service. The eutectic carbon content varies inversely with chromium content in these alloys. The relationship between eutectic carbon content and chromium content is shown in Fig. 10.

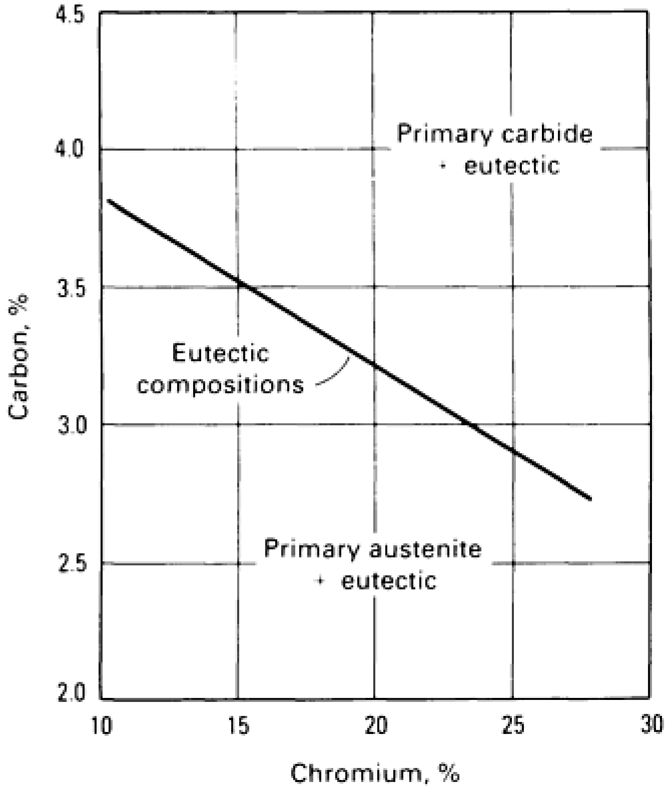


Fig. 10 Relationship between the chromium and carbon contents and the eutectic composition in high-chromium white irons

As-Cast Austenitic Microstructures. Solidification in the hypoeutectic alloys occurs by the formation of austenite dendrites followed by the eutectic formation of austenite and M_7C_3 chromium carbides. Under equilibrium conditions, additional chromium carbide will precipitate from the austenite matrix on cooling from the eutectic to the critical temperature, about 760 °C (1400 °F), and transformation to ferrite and carbide occurs on subsequent cooling. However, when cooling under nonequilibrium conditions such as encountered in most commercial castings, the austenite becomes super-saturated in carbon and chromium. Due to elevated carbon and chromium contents, a metastable austenitic cast iron normally develops, provided pearlitic and bainitic transformations have been inhibited (Fig. 11). With sufficient alloying with molybdenum, manganese, nickel, and copper, pearlitic transformation can be avoided in virtually any cast section.

Fig. 11 High-chromium iron with an as-cast austenitic matrix microstructure. 500×. Courtesy of Climax Molybdenum Company

As-Cast Martensitic Microstructures. Martensitic structures can be obtained as-cast in heavy section castings which cool slowly in the mold. With slow cooling rates, austenite stabilization is incomplete and partial transformation to martensite occurs. But in these castings, martensite is mixed with large amounts of retained austenite (Fig. 12a), and therefore hardness levels are lower than can be achieved in heat treated martensitic castings. These castings must contain sufficient alloy to suppress pearlite on cooling. Some compositions (higher silicon) have been developed to assist martensite formation in refrigeration treatments. Subcritical annealing has been employed to reduce austenite content and, at the same time, increase hardness and toughness.

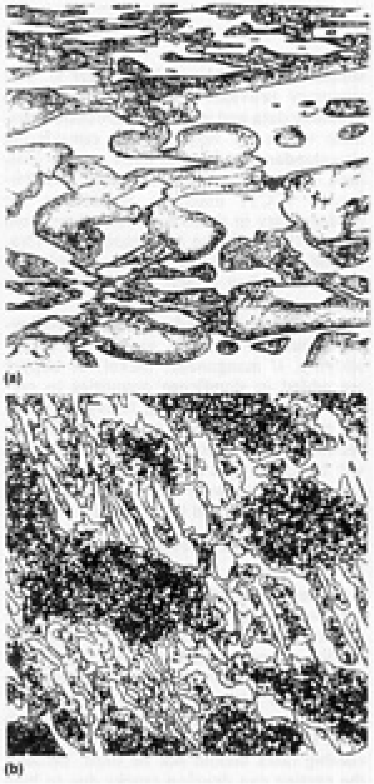


Fig. 12 High-chromium iron microstructures. (a) As-cast austenitic-martensitic matrix microstructure. (b) Heat-treated martensitic microstructure. Both at 500×. Courtesy of Climax Molybdenum Company

Heat Treated Martensitic Microstructures. To obtain maximum hardness and abrasion resistance, martensitic matrix structures must be produced by full heat treatment (Fig. 12b). The casting must contain sufficient alloy to avoid pearlite formation on cooling from the heat treatment temperature.

As-Cast Pearlitic Microstructures. For castings which will be heat treated, the desired mold-cooled structure is often pearlite. This softer structure will facilitate removal of gates and risers and minimize the transformational and thermal stresses that cause cracking. The pearlitic structure will also shorten the response to heat treatment. Careful design of alloy composition will assure that a substantially pearlitic structure develops in the casting after mold-cooling, but will provide enough hardenability to prevent pearlite formation during subsequent heat treatment. Heavy section castings made pearlitic by such an alloy content, can oftentimes be removed from the mold once the castings have reached black heat.

Selecting Compositions to Obtain Desired Structures. Many complex sections, such as slurry pump components, are often used in the as-cast austenitic/martensitic condition to avoid the possibility of cracking and distortion on heat treatment. To avoid forming pearlite during mold cooling, alloying additions are usually required. As the carbon content is increased, more chromium is consumed to form additional carbide, and therefore, larger alloying additions are required.

Table 9 presents a guide to appropriate alloying to prevent pearlite in the various classes of as-cast irons. Table 10 is offered as a guide to alloying for air quenching heat-treated castings of various sections.

Table 9 Minimum alloy content to avoid pearlite in mold-cooled castings for indicated effective section size (plate thickness or radius of rounds)

ASTM A 532 class	Cr[(a)], %	C[(a)], %	Plate thickness or radius of rounds		
			25 mm (1 in.)	**50 mm (2 in.)**	**100 mm (4 in.)**
IIB, C	14-18	2.0	1.0 Mo	1.5 Mo	1.5 Mo + 1.0 (Ni + Cu)
		3.5	2.0 Mo	2.5 Mo	2.5 Mo + 1.0 (Ni + Cu)
IID, E	18-23	2.0	0.5 Mo	1.0 Mo	1.0 Mo + 1.0 (Ni + Cu)
		3.2	1.5 Mo	2.0 Mo	2.0 Mo + 1.0 (Ni + Cu)
IIIA	23-28	2.0	. . .	0.5 Mo	1.0 Mo

(a) In base irons containing 0.6% Si and 0.8% Mn

Table 10 Minimum alloy content to avoid pearlite in heat treatment for indicated effective section size (plate thickness or radius of rounds)

ASTM A 532 class	Cr[(a)], %	C[(a)], %	Plate thickness or radius of rounds		
			50 mm (2 in.)	**125 mm (5 in.)**	**150-255 mm (6-10 in.)**
IIB, C	14-18	2.0	1.5 Mo	1.5 Mo + 0.5 (Ni + Cu)	2.0 Mo + 1.0 (Ni + Cu)
		3.5	3.0 Mo	2.0 Mo + 1.0 (Ni + Cu)	2.5 Mo + 1.2 (Ni + Cu)[(b)]
IID, E	18-23	2.0	1.0 Mo	2.0 Mo	2.0 Mo + 0.5 (Ni + Cu)
		3.2	1.5 Mo	2.0 Mo + 0.7 (Ni + Cu)	2.0 Mo + 1.2 (Ni + Cu)[(b)]
IIIA	23-28	2.0	0.5 Mo	1.5 Mo	1.5 Mo + 0.5 (Ni + Cu)
		3.0	1.5 Mo	1.5 Mo + 0.6 (Ni + Cu)	1.5 Mo + 1.2 (Ni + Cu)[(b)]

(a) In base irons containing 0.6% Si and 0.8% Mn.

(b) Nickel and copper promote retained austenite and should be restricted to combined levels of 1.2% maximum; manganese behaves similarly and should be restricted to 1.0% maximum.

These recommendations for alloying specific ASTM grades are based on studies of continuous-cooling transformation of high-chromium irons, and are cited in a useful summary by Dodd and Parks (Ref 5). The summary provides specific references to available data and includes regression equations which are helpful when considering non-standard grades and thick section castings. Typical continuous-cooling transformation (CCT) diagrams illustrating the hardenability in three common alloys from classes II and III are presented in Fig. 13(a, b, and c). More information on such diagrams and alloy effects in high-chromium irons are given by Cias (Ref 6).

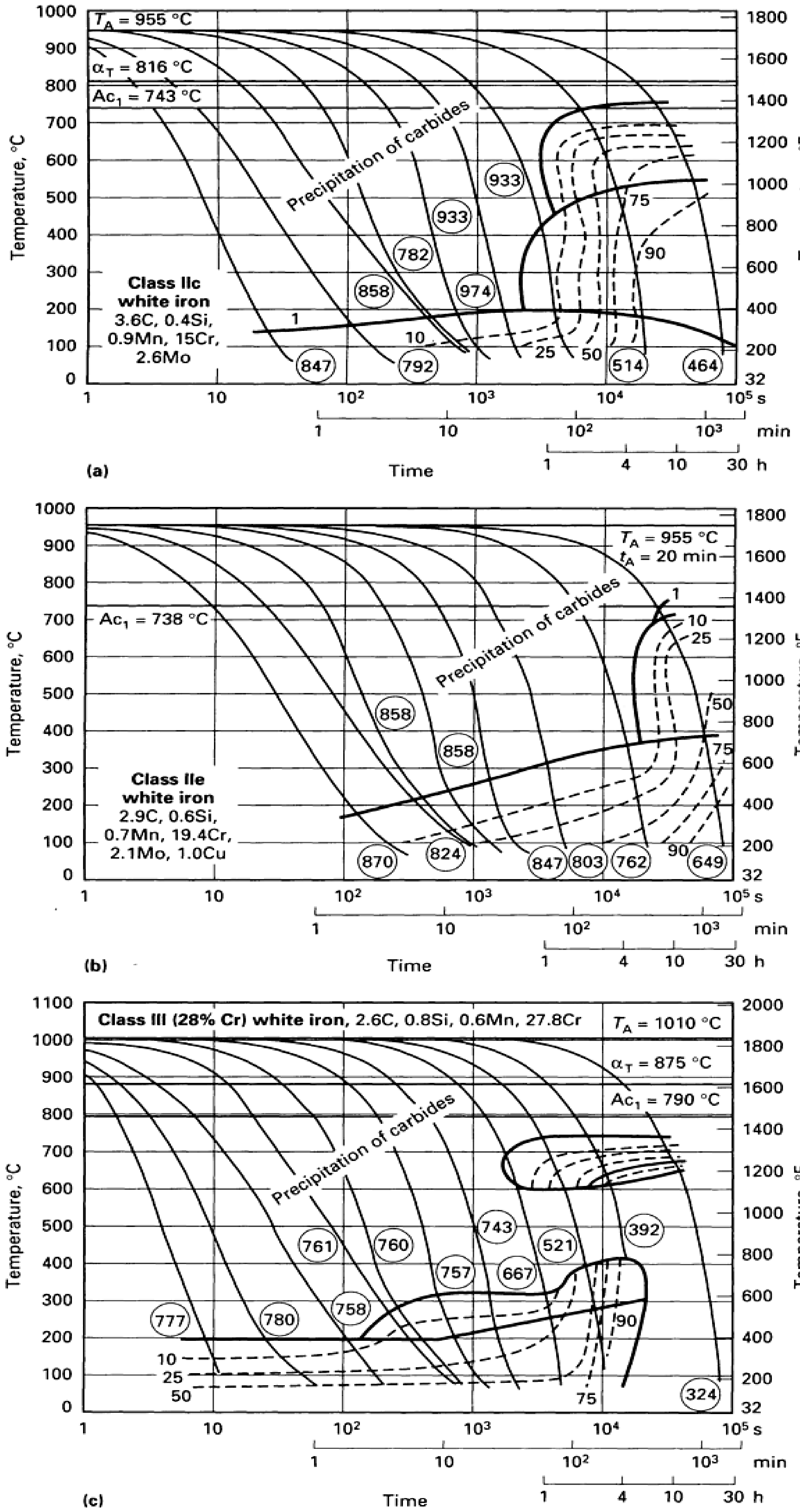

(a)
Class IIc white iron
3.6C, 0.4Si, 0.9Mn, 15Cr, 2.6Mo
T_A = 955 °C
α_T = 816 °C
Ac_1 = 743 °C
Precipitation of carbides
Temperature, °C
Temperature, °F
Time
s
min
h
(b)
Class IIe white iron
2.9C, 0.6Si, 0.7Mn, 19.4Cr, 2.1Mo, 1.0Cu
T_A = 955 °C
t_A = 20 min
Ac_1 = 738 °C
Precipitation of carbides
Temperature, °C
Temperature, °F
Time
s
min
h
(c)
Class III (28% Cr) white iron, 2.6C, 0.8Si, 0.6Mn, 27.8Cr
T_A = 1010 °C
α_T = 875 °C
Ac_1 = 790 °C
Precipitation of carbides
Temperature, °C
Temperature, °F
Time
s
min
h

Fig. 13 Continuous-cooling transformation diagrams. (a) Class IIc white iron containing 3.6% C-0.4% Si-0,9% Mn-15% Cr-2.6% Mo. (b) Class IIe white iron containing 2.9% C-0.6% Si-0.7% Mn-19.4% Cr-2.1% Mo-1.0% Cu. (c) Class III (28% Cr) white iron containing 2.6% C-0.8% Si-0.6% Mn-27.8% Cr

It should be pointed out that over-alloying should be avoided, as well as under-alloying. If manganese, nickel, or copper are added in significant quantities to prevent pearlite formation in heavy sections, too much austenite will be retained in light sections. As a result, air-cooled hardness will be lower than desired in the light sections, and both wear resistance and resistance to spalling will be reduced.

Heat Treatment of High-Chromium White Irons

Optimum performance is usually achieved with heat treated martensitic structures. As described in the previous section, alloying must be sufficient to ensure that a pearlite-free microstructure is obtained in heat treatment. Of necessity, the heat treatment requires an air quench from the austenitizing temperature. Faster cooling rates should not be used, because the casting can develop cracks due to high thermal and/or transformation stresses. Thus the alloy must have sufficient hardenability to allow air hardening. Over-alloying with manganese, nickel, and copper will promote retained austenite, which detracts from resistance to abrasion and spalling.

Toughness and abrasion resistance are improved by heat treatment to a martensitic microstructure. Figure 14, which illustrates the process, emphasizes the importance of slow heating *in a cold furnace* to 650 °C (1200 °F) to avoid cracking. For complex shapes a maximum rate of 30 °C/h (50 °F/h) is recommended. Simple shapes and fully pearlitic castings can be heated at faster rates. The heating rate can be accelerated above red heat.

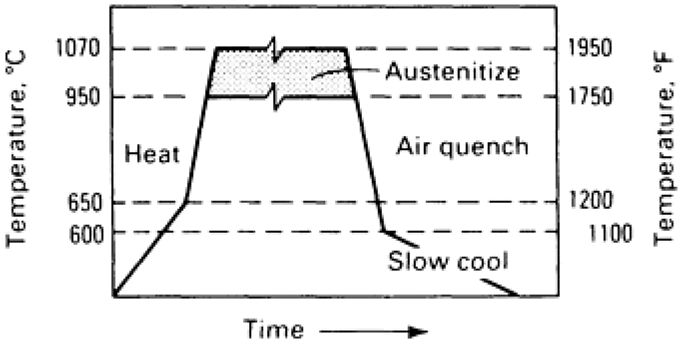


Fig. 14 Heat treatment schedule for hardening high-chromium irons

Austenitization. There is an optimum austenitizing temperature to achieve maximum hardness (Fig. 15), which varies for each composition. The austenitizing temperature determines the amount of carbon that remains in solution in the austenite matrix. Too high a temperature increases the stability of the austenite, and the higher retained austenite content reduces hardness. Low temperatures result in low-carbon martensite reducing both hardness and abrasion resistance. Because of this sensitivity to temperature, furnaces which can produce accurate and uniform temperatures are most desirable. The successful heat treatment produces austenite destabilization by precipitation of fine secondary M_7C_3 carbides within the austenite matrix, as illustrated in Fig. 16.

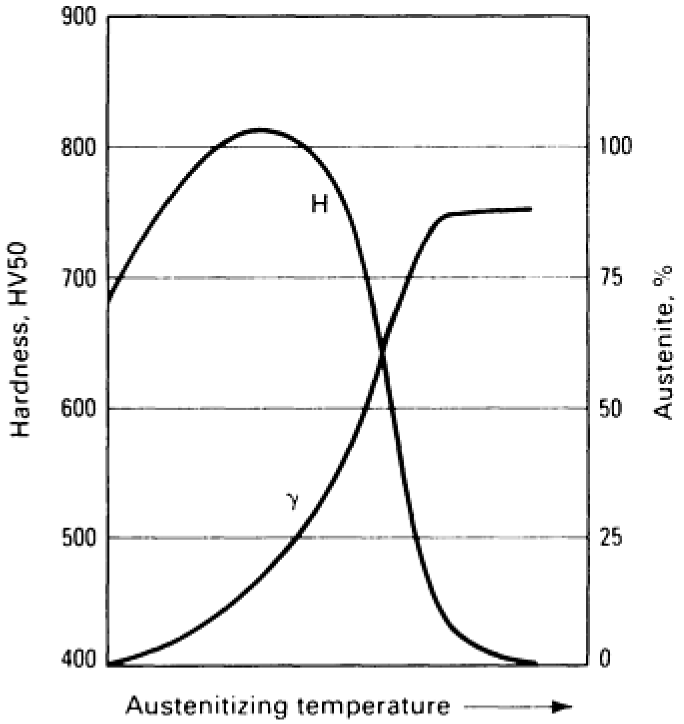


Fig. 15 Influence of austenitizing temperature on hardness (H) and retained austenite (γ) in high-chromium irons

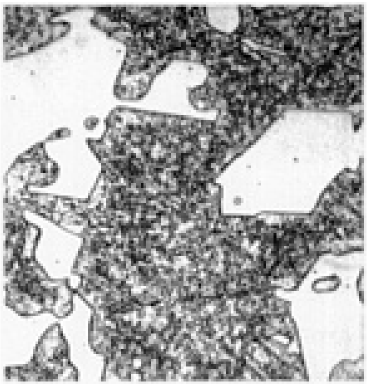


Fig. 16 Microstructure of heat-treated martensitic high-chromium iron illustrating fine secondary M_7C_3 carbides. 680×

Class II irons containing 12 to 20% Cr are austenitized in the temperature range 950 to 1010 °C (1750 to 1850 °F). Class III irons containing 23 to 28% Cr are austenitized in the temperature range 1010 to 1090 °C (1850 to 2000 °F). Heavy sections usually require higher temperatures within the range.

Castings should be held at temperature long enough to accomplish equilibrium dissolution of chromium carbides to ensure proper hardening response. A minimum of 4 h at temperature is necessary. For heavy sections the rule of 1 hour per 25 mm (1 in.) of section thickness is usually adequate. For castings which are fully pearlitic prior to heat treatment, the holding time at temperature can be reduced.

Quenching. Air quenching (vigorous fan cooling) the castings from the austenitizing temperature to below the pearlite temperature range (that is, between 550 and 600 °C, or 1020 and 1110 °F) is highly recommended. The subsequent cooling rate should be substantially reduced to minimize stresses; still-air or even furnace cooling to ambient is common.

Complex and heavy section castings are often placed back into the furnace, which is at 550 to 600 °C (1020 to 1110 °F), and allowed sufficient time to reach uniform temperature within the casting. After temperature is equalized, the castings are either furnace or still-air cooled to ambient temperature.

Tempering. Castings can be put into service in the hardened (as cooled) condition without further tempering or subcritical heat treatments; however, tempering in the range of 200 to 230 °C (400 to 450 °F) for 2 to 4 h is recommended to restore some toughness in the martensitic matrix and to further relieve residual stresses. The microstructure after hardening always contains retained austenite in the range of 10 to 30%. Some retained austenite will be transformed following tempering at low temperatures; but if spalling is a problem, higher subcritical temperature tempering can be used to further reduce austenite contents.

Subcritical Heat Treatment. Subcritical heat treatment (tempering) is sometimes performed, particularly in large heat-treated martensitic castings, to reduce retained austenite contents and increase resistance to spalling. The tempering parameters necessary to eliminate retained austenite are very sensitive to time and temperature and vary depending on the casting's composition and prior thermal history. Typical tempering temperatures range from 480 to 540 °C (900 to 1000 °F) and times range from 8 to 12 h. Excess time or temperature results in softening and a drastic reduction in abrasion resistance. Insufficient tempering results in incomplete elimination of austenite. The amount of retained austenite present cannot be determined metallographically; those experienced with this heat treatment practice have developed techniques, using specialized magnetic instruments, to determine the level of retained austenite after tempering.

Annealing. Castings can be annealed to make them more machinable, either by subcritical annealing or a full anneal. Subcritical annealing is accomplished by pearlitizing, via soaking in the narrow range between 690 and 705 °C (1280 and 1300 °F) for from 4 to 12 h, which will produce hardness in the range 400 to 450 HB. Lower hardness can often be achieved with full annealing, whereby castings are heated in the range 955 to 1010 °C (1750 to 1850 °F) followed by slow cooling to 760 °C (1400 °F) and holding at this temperature for 10 to 50 h depending on composition. Annealing does not affect the primary carbides nor the potential for subsequent hardening; guidelines for hardening as-cast castings also apply to annealed castings.

Stress-Relieving. Very little information is available on the amount of stress relief that occurs with tempering. The predominant stresses present in heat-treated castings develop as a result of the volume change accompanying austenite to martensite transformation. Low-temperature tempering, in the range of 200 to 230 °C (400 to 450 °F), is particularly desirable because a substantial improvement (20%) in fracture toughness occurs when tempering the martensite phase. Tempering at temperatures sufficient to significantly relieve stresses (that is, above 540 °C, or 1000 °F), will substantially reduce abrasion resistance. Therefore, it is much more desirable to minimize the development of transformational stresses via controlled cooling through the martensitic transformation temperature range ($\leq$260 °C, or 500 °F). This is accomplished by slow, controlled cooling to minimize temperature gradients and differential transformation in the casting.

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Introduction to Heat Treating of Tool Steels

Revised by Bruce A. Becherer and Thomas J. Witheford, Teledyne Vasco

Introduction

TOOL STEELS are high-quality steels made to close compositional and physical tolerances; they are used to make tools for cutting, forming, or shaping a material into a part or component adapted to a definite use. The earliest tool steels were simple, plain carbon steels, but beginning in 1868, and to a greater extent early in the 20th century, many complex, highly alloyed tool steels were developed. These complex alloy tool steels, which contain, among other elements, relatively large amounts of tungsten, molybdenum, vanadium, and chromium, make it possible to meet increasingly severe service demands and to provide greater dimensional control and freedom from cracking during heat treating. Many alloy tool steels also are widely used for machinery components and structural applications where particularly severe requirements must be met, such as high-temperature springs, ultrahigh-strength fasteners, special-purpose valves, punches and dies, wear-resistant liners, and bearings of various types for elevated-temperature service. This article discusses procedures and process control requirements for heat treating the principal types of tool steels. It also provides a review of heat-treating processes that are applied to tool steels and the specific applicability of these processes to the various types of tool steels.

In service, most tools are subjected to extremely high loads that are applied rapidly. They must withstand these loads a great number of times without breaking and without undergoing excessive wear or deformation. In many applications, tool steels must provide this capability under conditions that develop high temperatures in the tool. No single tool material combines maximum wear resistance, toughness, and resistance to softening at elevated temperatures. Consequently, selection of the proper tool material for a given application often requires a trade-off to achieve the optimum combination of properties. Table 1 gives the classifications and nominal compositions of various tool steels.

Table 1 Classification and nominal compositions of selected tool steels

Steel	Composition, %							
	C	Mn	Si	W	Mo	Cr	V	Other
Water-hardening tool steels								
W1	0.60-1.40[(b)]	. . .	. . .	. . .	. . .	. . .	. . .	. . .
W2	0.60-1.40[(b)]	. . .	. . .	. . .	. . .	. . .	0.25	. . .
W3 [(a)]	1.00	. . .	. . .	. . .	. . .	. . .	0.50	. . .
W4	0.60-1.40[(b)]	. . .	. . .	. . .	. . .	0.25	. . .	. . .
W5	1.10	. . .	. . .	. . .	. . .	0.50	. . .	. . .
W6 [(a)]	1.00	. . .	. . .	. . .	. . .	0.25	0.25	. . .
W7 [(a)]	1.00	. . .	. . .	. . .	. . .	0.50	0.20	. . .

Steel	Composition, %							
	C	Mn	Si	W	Mo	Cr	V	Other
Shock-resisting tool steels								
S1	0.50	. . .	. . .	2.50	. . .	1.50	. . .	. . .
S2	0.50	. . .	1.00	. . .	0.50	. . .	. . .	. . .
S3 [(a)]	0.50	. . .	. . .	1.00	. . .	0.75	. . .	. . .
S4	0.55	0.80	2.00	. . .	. . .	. . .	. . .	. . .
S5	0.55	0.80	2.00	. . .	0.40	. . .	. . .	. . .
S6	0.45	1.40	2.25	. . .	0.40	1.50	. . .	. . .
S7	0.50	. . .	. . .	. . .	1.40	3.25	. . .	. . .
Oil-hardening cold work tool steels								
O1	0.90	1.00	. . .	0.50	. . .	0.50	. . .	. . .
O2	0.90	1.60	. . .	. . .	. . .	. . .	. . .	. . .
O6	1.45	. . .	1.00	. . .	0.25	. . .	. . .	. . .
O7	1.20	. . .	. . .	1.75	. . .	0.75	. . .	. . .
Medium-alloy air-hardening cold work tool steels								
A2	1.00	. . .	. . .	. . .	1.00	5.00	. . .	
A3	1.25	. . .	. . .	. . .	1.00	5.00	1.00	. . .
A4	1.00	2.00	. . .	. . .	1.00	1.00	. . .	. . .
A5	1.00	3.00	. . .	. . .	1.00	1.00	. . .	. . .
A6	0.70	2.00	. . .	. . .	1.00	1.00	. . .	. . .

Steel	Composition, %							
	C	Mn	Si	W	Mo	Cr	V	Other
A7	2.25	. . .	. . .	1.00[c]	1.00	5.25	4.75	. . .
A8	0.55	. . .	. . .	1.25	1.25	5.00	. . .	. . .
A9	0.50	. . .	. . .	. . .	1.40	5.00	1.00	1.50 Ni
A10	1.35	1.80	1.25	. . .	1.50	. . .	. . .	1.80 Ni
High-carbon high-chromium cold work tool steels								
D1	1.00	. . .	. . .	. . .	1.00	12.00	. . .	. . .
D2	1.50	. . .	. . .	. . .	1.00	12.00	. . .	. . .
D3	2.25	. . .	. . .	. . .	. . .	12.00	. . .	. . .
D4	2.25	. . .	. . .	. . .	1.00	12.00	. . .	. . .
D5	1.50	. . .	. . .	. . .	1.00	12.00	. . .	3.00 Co
D6 [a]		Now included with D3 by AISI						
D7	2.35	. . .	. . .	. . .	1.00	12.00	4.00	. . .
Chromium hot work tool steels								
H10	0.40	. . .	. . .	. . .	2.50	3.25	0.40	. . .
H11	0.35	. . .	. . .	. . .	1.50	5.00	0.40	. . .
H12	0.35	. . .	. . .	1.50	1.50	5.00	0.40	. . .
H13	0.35	. . .	. . .	. . .	1.50	5.00	1.00	. . .
H14	0.40	. . .	. . .	5.00	. . .	5.00	. . .	. . .
H15 [a]	0.40	. . .	. . .	. . .	5.00	5.00	. . .	. . .

Steel	Composition, %							
	C	Mn	Si	W	Mo	Cr	V	Other
H16	0.55	. . .	. . .	7.00	. . .	7.00	. . .	. . .
H19	0.40	. . .	. . .	4.25	. . .	4.25	2.00	4.25 Co
Tungsten hot work tool steels								
H20	0.35	. . .	. . .	9.00	. . .	2.00	. . .	. . .
H21	0.35	. . .	. . .	9.00	. . .	3.50	. . .	. . .
H22	0.35	. . .	. . .	11.00	. . .	2.00	. . .	. . .
H23	0.30	. . .	. . .	12.00	. . .	12.00	. . .	. . .
H24	0.45	. . .	. . .	15.00	. . .	3.00	. . .	. . .
H25	0.25	. . .	. . .	15.00	. . .	4.00	. . .	. . .
H26	0.50	. . .	. . .	18.00	. . .	4.00	1.00	. . .
Molybdenum hot work tool steels								
H41	0.65	. . .	. . .	1.50	8.00	4.00	1.00	. . .
H42	0.60	. . .	. . .	6.00	5.00	4.00	2.00	. . .
H43	0.55	. . .	. . .	. . .	8.00	4.00	2.00	. . .
Tungsten high-speed tool steels, standard group								
T1	0.75	. . .	. . .	18.00	. . .	4.00	1.00	. . .
T2	0.80	. . .	. . .	18.00	. . .	4.00	2.00	. . .
T3 [(a)]	1.05	. . .	. . .	18.00	. . .	4.00	3.00	. . .
T4	0.75	. . .	. . .	18.00	. . .	4.00	1.00	5.00 Co

Steel	Composition, %							
	C	Mn	Si	W	Mo	Cr	V	Other
T5	0.80	. . .	. . .	18.00	. . .	4.00	2.00	8.00 Co
T6	0.80	. . .	. . .	20.00	. . .	4.50	1.50	12.00 Co
T7 [(a)]	0.75	. . .	. . .	14.00	. . .	4.00	2.00	. . .
T8	0.75	. . .	. . .	14.00	. . .	4.00	2.00	5.00 Co
T9 [(a)]	1.20	. . .	. . .	18.00	. . .	4.00	4.00	. . .
T15	1.50	. . .	. . .	12.00	. . .	4.00	5.00	5.00 Co
Molybdenum high-speed tool steels, standard group								
M1	0.85	. . .	. . .	1.50	8.50	4.00	1.00	. . .
M2	0.85 or 1.00	. . .	. . .	6.00	5.00	4.00	2.00	. . .
M3 Cl 1	1.05	. . .	. . .	6.00	5.00	4.00	2.40	. . .
M3 Cl 2	1.20	. . .	. . .	6.00	5.00	4.00	3.00	. . .
M4	1.30	. . .	. . .	5.50	4.50	4.00	4.00	. . .
M6	0.80	. . .	. . .	4.00	5.00	4.00	1.50	12.00 Co
M7	1.00	. . .	. . .	1.75	8.75	4.00	2.00	. . .
M8 [(a)]	0.80	. . .	. . .	5.00	5.00	4.00	1.50	1.25 Nb
M10	0.85 or 1.00	. . .	. . .	. . .	8.00	4.00	2.00	. . .
M15 [(a)]	1.50	. . .	. . .	6.50	3.50	4.00	5.00	5.00 Co
M30	0.80	. . .	. . .	2.00	8.00	4.00	1.25	5.00 Co
M33	0.90	. . .	. . .	1.50	9.50	4.00	1.15	8.00 Co

Steel	Composition, %							
	C	Mn	Si	W	Mo	Cr	V	Other
M34	0.90	. . .	. . .	2.00	8.00	4.00	2.00	8.00 Co
M35 [(a)]	0.80	. . .	. . .	6.00	5.00	4.00	2.00	5.00 Co
M36	0.80	. . .	. . .	6.00	5.00	4.00	2.00	8.00 Co
M41	1.10	. . .	. . .	6.75	3.75	4.25	2.00	5.00 Co
M42	1.10	. . .	. . .	1.50	9.50	3.75	1.15	8.00 Co
M43	1.20	. . .	. . .	2.75	8.00	3.75	2.60	8.25 Co
M44	1.15	. . .	. . .	5.25	6.25	4.25	2.20	12.00 Co
M46	1.25	. . .	. . .	2.00	8.25	4.00	3.20	8.25 Co
M47	1.10	. . .	. . .	1.50	9.50	3.75	1.25	5.00 Co
High-speed tool steels, intermediate group[(d)]								
M50	0.85	. . .	. . .	. . .	4.00	4.00	1.00	. . .
M52	0.90	. . .	. . .	1.25	4.00	4.00	2.00	. . .
Low-alloy special-purpose tool steels								
L1	1.00	. . .	. . .	. . .	. . .	1.25	. . .	. . .
L2	0.50-1.10[(b)]	. . .	. . .	. . .	. . .	1.00	0.20	. . .
L3	1.00	. . .	. . .	. . .	. . .	1.50	0.20	. . .
L4 [(a)]	1.00	0.60	. . .	. . .	. . .	1.50	0.25	. . .
L5 [(a)]	1.00	1.00	. . .	. . .	0.25	1.00	. . .	. . .
L6	0.70	. . .	. . .	. . .	0.25[(c)]	0.75	. . .	1.50 Ni

Steel	Composition, %							
	C	Mn	Si	W	Mo	Cr	V	Other
L7	1.00	0.35	. . .	. . .	0.40	1.40	. . .	. . .
Carbon-tungsten special-purpose tool steels								
F1	1.00	. . .	. . .	1.25	. . .	. . .	. . .	. . .
F2	1.25	. . .	. . .	3.50	. . .	. . .	. . .	. . .
F3	1.25	. . .	. . .	3.50	. . .	0.75	. . .	. . .
Mold steels								
P1	0.10	. . .	. . .	. . .	. . .	. . .	. . .	. . .
P2	0.07	. . .	. . .	. . .	0.20	2.00	. . .	0.50 Ni
P3	0.10	. . .	. . .	. . .	. . .	0.60	. . .	1.25 Ni
P4	0.07	. . .	. . .	. . .	0.75	5.00	. . .	. . .
P5	0.10	. . .	. . .	. . .	. . .	2.25	. . .	. . .
P6	0.10	. . .	. . .	. . .	. . .	1.50	. . .	3.50 Ni
P20	0.35	. . .	. . .	. . .	0.40	1.25	. . .	. . .
P21	0.20	. . .	. . .	. . .	. . .	. . .	. . .	4.00 Ni,1.20 Al
Other alloy tool steels								
6G	0.55	0.80	0.25	. . .	0.45	1.00	0.10	. . .
6F2	0.55	0.75	0.25	. . .	0.30	1.00	0.10[c]	1.00 Ni
6F3	0.55	0.60	0.85	. . .	0.75	1.00	0.10[c]	1.80 Ni
6F4	0.20	0.70	0.25	. . .	3.35	. . .	. . .	3.00 Ni

Steel	Composition, %							
	C	Mn	Si	W	Mo	Cr	V	Other
6F5	0.55	1.00	1.00	. . .	0.50	0.50	0.10	2.70 Ni
6F6	0.50	. . .	1.50	. . .	0.20	1.50	. . .	. . .
6F7	0.40	0.35	. . .	. . .	0.75	1.50	. . .	4.25 Ni
6H1	0.55	. . .	. . .	. . .	0.45	4.00	0.85	. . .
6H2	0.55	0.40	1.10	. . .	1.50	5.00	1.00	. . .

(a) These steels were not included in the March 1978 AISI Steel Products Manual, *Tool Steels*, in the main table of compositions nor in tables of heat-treating practice, because of their less common use.

(b) Available with various carbon contents, in increments of 0.10% within this range.

(c) Optional.

(d) Intermediate high-speed steels M50 and M52, which are lower in alloy content than standard high-speed steels, have been employed successfully in applications requiring greater abrasion resistance than plain carbon steels, but less red hardness than high-speed steels. Typical uses include woodworking tools and hack saw blades. M50 and M52 steels meet the criteria promulgated by the American Society for Testing and Materials for intermediate high-speed steels but do not meet the more stringent criteria for standard high-speed steels.

Most tool steels are wrought products, but precision castings can be used to advantage in some applications (additional information is available in the article "Wrought Tool Steels" in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook*). The powder metallurgy (P/M) process also is used in making tool steels; this process provides more uniform carbide size and distribution in large sections and special compositions that are difficult or impossible to produce by melting and casting and then mechanically working the cast product (additional information is available in the article "P/M Tool Steels" in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook*).

For typical wrought tool steels, raw materials (including scrap) are carefully selected, not only for alloy content but also for qualities that ensure cleanliness and homogeneity in the finished product. Tool steels are generally melted in small-tonnage electric-arc furnaces to achieve composition tolerances economically, cleanliness and precise control of melting conditions. Special refining and secondary remelting processes such as argon oxygen decarburization (AOD), electroslag remelting (ESR), and vacuum arc remelting (VAR) (see the articles "Vacuum Melting and Remelting Processes" and "Degassing Processes (Converter Metallurgy)" in Volume 15 of *ASM Handbook*, formerly 9th Edition *Metals Handbook*), have been introduced to satisfy particularly difficult demands on tool steel quality and performance. The medium-to-high alloy contents of many tool steels require careful control of forging and rolling, which often results in a large amount of process scrap. Semifinished and finished bars are given rigorous in-process and final inspection. This inspection can be so extensive that both ends of each bar may be inspected for macrostructure (etch quality), cleanliness, hardness, grain size, annealed structure, and hardenability. The inspection may require that the entire bar be subjected to magnetic, particle, eddy current, and ultrasonic inspections for surface and internal discontinuities. It is important that finished tool steel bars have limited decarburization, which requires that annealing be done by special procedures under closely controlled

conditions. Controlled atmosphere continuous annealing furnaces, vacuum furnaces, and protective coatings are often used to minimize decarburization during annealing.

Such precise production practices and stringent quality controls contribute to the high cost of tool steels, as do the expensive alloying elements they contain. Insistence on quality in the manufacture of these specialty steels is justified, however, because tool steel bars generally are made into complicated cutting and forming tools worth many times the cost of the steel itself. Although some standard constructional alloy steels resemble tool steels in composition, they are seldom used for expensive tooling because, in general, they are not manufactured to the same rigorous quality standards as are tool steels.

The performance of a tool in service depends on:

- Proper tool design
- Accuracy with which the tool is made
- Selection of the proper tool steel
- Application of the proper heat treatment

A tool can perform successfully in service only when all four of these requirements have been fulfilled.

With few exceptions, all tool steels must be heat treated to develop specific combinations of wear resistance, resistance to deformation or breaking under high loads, and resistance to softening at elevated temperatures. A few simple shapes may be obtained directly from tool steel producers in correctly heat-treated condition. However, most tool steels first are formed or machined to produce the required shape and then heat treated as required. Figure 1 shows typical processing and heat-treatment sequences for tool steels as a function of time, temperature, and phase transformation. Improper finishing after heat treatment--principally grinding--can damage tool steels through the development of surface residual stresses and cracks. Some tools are heat treated (hardened) in a blank or semifinished state and subsequently ground, turned, or electrical discharge machined to create the final tool. Although these manufacturing techniques have progressed in recent years, metallurgical damage and surface stresses are still a major concern.

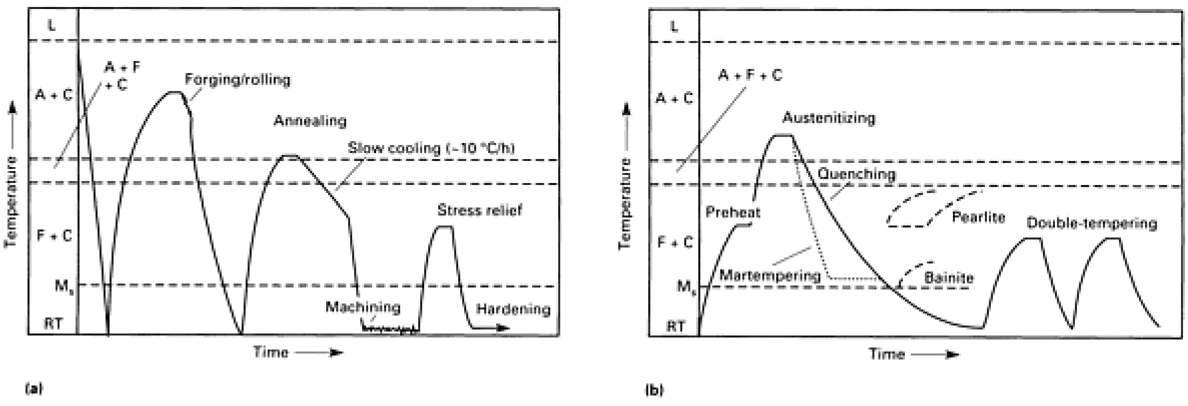

Fig. 1 Plots of temperature versus time showing sequence of operations required to produce tool steels. (a) Thermomechanical processing. (b) Hardening heat treatment. L, liquid; A, austenite; C, cementite; F, ferrite; M_s, temperature at which martensite starts to form on cooling; RT, room temperature. Source: Ref 1

Processing information and service characteristics of tool steels are presented in Tables 2, 3, 4. This information is essential in understanding the problems involved in selection, processing, and application of tool steels. Tool steel suppliers provide more specific information on the properties developed by specific heat treatments in the steels produced by their companies. They should be consulted as to the type of steel and heat treatment best suited to meet all service requirements at the least over-all cost.

Table 2 Normalizing and annealing temperatures of tool steels

Type	Normalizing treatment temperature[(a)]		Annealing[(b)]				
			Temperature		**Rate of cooling, max**		Hardness, HB
	°C	**°F**	**°C**	**°F**	**°C/h**	**°F/h**	
Molybdenum high-speed steels							
M1, M10	Do not normalize		815-870	1500-1600	22	40	**207-235**
M2	Do not normalize		870-900	1600-1650	22	40	**212-241**
M3, M4	Do not normalize		870-900	1600-1650	22	40	**223-255**
M6	Do not normalize		870	1600	22	40	**248-277**
M7	Do not normalize		815-870	1500-1600	22	40	**217-255**
M30, M33, M34, M36, M41, M42, M46, M47	Do not normalize		870-900	1600-1650	22	40	**235-269**
M43	Do not normalize		870-900	1600-1650	22	40	**248-269**
M44	Do not normalize		870-900	1600-1650	22	40	**248-293**
Tungsten high-speed steels							
T1	Do not normalize		870-900	1600-1650	22	40	**217-255**
T2	Do not normalize		870-900	1600-1650	22	40	**223-255**
T4	Do not normalize		870-900	1600-1650	22	40	**229-269**
T5	Do not normalize		870-900	1600-1650	22	40	**235-277**
T6	Do not normalize		870-900	1600-1650	22	40	**248-293**
T8	Do not normalize		870-900	1600-1650	22	40	**229-255**
T15	Do not normalize		870-900	1600-1650	22	40	**241-277**

Type	Normalizing treatment temperature[(a)]		Annealing[(b)]				
			Temperature		**Rate of cooling, max**		Hardness, HB
	°C	**°F**	**°C**	**°F**	**°C/h**	**°F/h**	
Chromium hot work steels							
H10, H11, H12, H13	Do not normalize		845-900	1550-1650	22	40	**192-229**
H14	Do not normalize		870-900	1600-1650	22	40	**207-235**
H19	Do not normalize		870-900	1600-1650	22	40	**207-241**
Tungsten hot work steels							
H21, H22, H25	Do not normalize		870-900	1600-1650	22	40	**207-235**
H23	Do not normalize		870-900	1600-1650	22	40	**212-255**
H24, H26	Do not normalize		870-900	1600-1650	22	40	**217-241**
Molybdenum hot work steels							
H41, H43	Do not normalize		815-870	1500-1600	22	40	**207-235**
H42	Do not normalize		845-900	1550-1650	22	40	**207-235**
High-carbon high-chromium cold work steels							
D2, D3, D4	Do not normalize		870-900	1600-1650	22	40	**217-255**
D5	Do not normalize		870-900	1600-1650	22	40	**223-255**
D7	Do not normalize		870-900	1600-1650	22	40	**235-262**
Medium-alloy air-hardening cold work steels							
A2	Do not normalize		845-870	1550-1600	22	40	**201-229**

Type	**Normalizing treatment temperature**[(a)]		Annealing[(b)]				
			Temperature		**Rate of cooling, max**		Hardness, HB
	°C	**°F**	**°C**	**°F**	**°C/h**	**°F/h**	
A3	Do not normalize		845-870	1550-1600	22	40	**207-229**
A4	Do not normalize		740-760	1360-1400	14	25	**200-241**
A6	Do not normalize		730-745	1350-1375	14	25	**217-248**
A7	Do not normalize		870-900	1600-1650	14	25	**235-262**
A8	Do not normalize		845-870	1550-1600	22	40	**192-223**
A9	Do not normalize		845-870	1550-1600	14	25	**212-248**
A10	790	1450	765-795	1410-1460	8	15	**235-269**
Oil-hardening cold work steels							
O1	870	1600	760-790	1400-1450	22	40	**183-212**
O2	845	1550	745-775	1375-1425	22	40	**183-212**
O6	870	1600	765-790	1410-1450	11	20	**183-217**
O7	900	1650	790-815	1450-1500	22	40	**192-217**
Shock-resisting steels							
S1	Do not normalize		790-815	1450-1500	22	40	**183-229**[(c)]
S2	Do not normalize		760-790	1400-1450	22	40	**192-217**
S5	Do not normalize		775-800	1425-1475	14	25	**192-229**
S7	Do not normalize		815-845	1500-1550	14	25	**187-223**

Type	Normalizing treatment temperature[(a)]		Annealing[(b)]				
			Temperature		**Rate of cooling, max**		Hardness, HB
	°C	**°F**	**°C**	**°F**	**°C/h**	**°F/h**	
Mold steels							
P2	Not required		730-815	1350-1500	22	40	**103-123**
P3	Not required		730-815	1350-1500	22	40	**109-137**
P4	Do not normalize		870-900	1600-1650	14	25	**116-128**
P5	Not required		845-870	1550-1600	22	40	**105-116**
P6	Not required		845	1550	8	15	**183-217**
P20	900	1650	760-790	1400-1450	22	40	**149-179**
P21	900	1650	**Do not anneal**				
Low-alloy special-purpose steels							
L2	870-900	1600-1650	760-790	1400-1450	22	40	**163-197**
L3	900	1650	790-815	1450-1500	22	40	**174-201**
L6	870	1600	760-790	1400-1450	22	40	**183-212**
Carbon-tungsten special-purpose steels							
F1	900	1650	760-800	1400-1475	22	40	**183-207**
F2	900	1650	790-815	1450-1500	22	40	**207-235**
Water-hardening steels							
W1, W2	790-925[(d)]	1450-1700[(d)]	740-790[(e)]	1360-1450[(e)]	22	40	**156-201**

Type	Normalizing treatment temperature[(a)]		Annealing[(b)]				
			Temperature		Rate of cooling, max		Hardness, HB
	°C	°F	°C	°F	°C/h	°F/h	
W5	**870-925**	**1600-1700**	**760-790**	**1400-1450**	**22**	**40**	**163-201**

(a) Time held at temperature varies from 15 min for small sections to 1 h for large sizes. Cooling is done in still air. Normalizing should not be confused with low-temperature annealing.

(b) The upper limit of ranges should be used for large sections and the lower limit for smaller sections. Time held at temperature varies from 1 h for light sections to 4 h for heavy sections and large furnace charges of high-alloy steel.

(c) For 0.25 Si type, 183 to 207 HB; for 1.00 Si type, 207 to 229 HB.

(d) Temperature varies with carbon content: 0.60 to 0.75 C, 815 °C (1500 °F); 0.75 to 0.90 C, 790 °C (1450 °F); 0.90 to 1.10 C, 870 °C (1600 °F); 1.10 to 1.40 C, 870 to 925 °C (1600 to 1700 °F).

(e) Temperature varies with carbon content: 0.60 to 0.90 C, 740 to 790 °C (1360 to 1450 °F); 0.90 to 1.40 C, 760 to 790 °C (1400 to 1450 °F).

Table 3 Hardening and tempering of tool steels

Type	Rate of heating	Hardening				Time at temperature, min	Quenching medium[(a)]	Tempering temperature	
		Preheat temperature		Hardening temperature					
		°C	°F	°C	°F			°C	°F
Molybdenum high-speed steels									
M1, M7, M10	Rapidly from preheat	730-845	1350-1550	1175-1220	2150-2225[(b)]	2-5	O, A, or S	540-595[(c)]	**1000-1100[(c)]**
M2	Rapidly from preheat	730-845	1350-1550	1190-1230	2175-2250[(b)]	2-5	O, A, or S	540-595[(c)]	**1000-1100[(c)]**
M3, M4, M30, M33, M34	Rapidly from preheat	730-845	1350-1550	1205-1230[(b)]	2200-2250[(b)]	2-5	O, A, or S	540-595[(c)]	**1000-1100[(c)]**
M6	Rapidly from	790	1450	1175-	2150-	2-5	O, A, or S	540-	**1000-**

Type	**Rate of heating**	**Hardening**				**Time at temperature, min**	**Quenching medium[a]**	Tempering temperature	
		Preheat temperature		**Hardening temperature**					
		°C	**°F**	**°C**	**°F**			**°C**	°F
	preheat			1205[b]	2200[b]			595[c]	**1100[c]**
M36	Rapidly from preheat	730-845	1350-1550	1220-1245[b]	2225-2275[b]	2-5	O, A, or S	540-595[c]	**1000-1100[c]**
M41	Rapidly from preheat	730-845	1350-1550	1190-1215[b]	2175-2220[b]	2-5	O, A, or S	540-595[d]	**1000-1100[d]**
M42	Rapidly from preheat	730-845	1350-1550	1190-1210[b]	2175-2210[b]	2-5	O, A, or S	510-595[d]	**950-1100[d]**
M43	Rapidly from preheat	730-845	1350-1550	1190-1215[b]	2175-2220[b]	2-5	O, A, or S	510-595[d]	**950-1100[d]**
M44	Rapidly from preheat	730-845	1350-1550	1200-1225[b]	2190-2240[b]	2-5	O, A, or S	540-625[d]	**1000-1160[d]**
M46	Rapidly from preheat	730-845	1350-1550	1190-1220[b]	2175-2225[b]	2-5	O, A, or S	525-565[d]	**975-1050[d]**
M47	Rapidly from preheat	730-845	1350-1550	1180-1205[b]	2150-2200[b]	2-5	O, A, or S	525-595[d]	**975-1100[d]**
Tungsten high-speed steels									
T1, T2, T4, T8	Rapidly from preheat	815-870	1500-1600	1260-1300[b]	2300-2375[b]	2-5	O, A, or S	540-595[c]	**1000-1100[c]**
T5, T6	Rapidly from preheat	815-870	1500-1600	1275-1300[b]	2325-2375[b]	2-5	O, A, or S	540-595[c]	**1000-1100[c]**
T15	Rapidly from preheat	815-870	1500-1600	1205-1260[b]	2200-2300[b]	2-5	O, A, or S	540-650[d]	**1000-1200[d]**
Chromium hot-work steels									
H10	Moderately from preheat	815	1500	1010-1040	1850-1900	15-40[e]	A	540-650	**1000-1200**

Type	Rate of heating	Hardening				Time at temperature, min	Quenching medium[a]	Tempering temperature	
		Preheat temperature		Hardening temperature					
		°C	**°F**	**°C**	**°F**			**°C**	°F
H11, H12	Moderately from preheat	815	1500	995-1025	1825-1875	15-40[e]	A	540-650	**1000-1200**
H13	Moderately from preheat	815	1500	995-1040	1825-1900	15-40[e]	A	540-650	**1000-1200**
H14	Moderately from preheat	815	1500	1010-1065	1850-1950	15-40[e]	A	540-650	**1000-1200**
H19	Moderately from preheat	815	1500	1095-1205	2000-2200	2-5	A or O	540-705	**1000-1300**
Molybdenum hot work steels									
H41, H43	Rapidly from preheat	730-845	1350-1550	1095-1190	2000-2175	2-5	O, A, or S	565-650	**1050-1200**
H42	Rapidly from preheat	730-845	1350-1550	1120-1220	2050-2225	2-5	O, A, or S	565-650	**1050-1200**
Tungsten hot work steels									
H21, H22	Rapidly from preheat	815	1500	1095-1205	2000-2200	2-5	A or O	595-675	**1100-1250**
H23	Rapidly from preheat	845	1550	1205-1260	2200-2300	2-5	O	650-815	**1200-1500**
H24	Rapidly from preheat	815	1500	1095-1230	2000-2250	2-5	O	565-650	**1050-1200**
H25	Rapidly from preheat	815	1500	1150-1260	2100-2300	2-5	A or O	565-675	**1050-1250**
H26	Rapidly from preheat	870	1600	1175-1260	2150-2300	2-5	O, A, or S	565-675	**1050-1250**
Medium-alloy air-hardening cold work steels									

Type	**Rate of heating**	**Hardening**				**Time at temperature, min**	**Quenching medium**[(a)]	Tempering temperature	
		Preheat temperature		**Hardening temperature**					
		°C	**°F**	**°C**	**°F**			**°C**	°F
A2	Slowly	790	1450	925-980	1700-1800	20-45	A	175-540	**350-1000**
A3	Slowly	790	1450	955-980	1750-1800	25-60	A	175-540	**350-1000**
A4	Slowly	675	1250	815-870	1500-1600	20-45	A	175-425	**350-800**
A6	Slowly	650	1200	830-870	1525-1600	20-45	A	150-425	**300-800**
A7	Very slowly	815	1500	955-980	1750-1800	30-60	A	150-540	**300-1000**
A8	Slowly	790	1450	980-1010	1800-1850	20-45	A	175-595	**350-1100**
A9	Slowly	790	1450	980-1025	1800-1875	20-45	A	510-620	**950-1150**
A10	Slowly	650	1200	790-815	1450-1500	30-60	A	175-425	**350-800**
Oil-hardening cold work steels									
O1	Slowly	650	1200	790-815	1450-1500	10-30	O	175-260	**350-500**
O2	Slowly	650	1200	760-800	1400-1475	5-20	O	175-260	**350-500**
O6	Slowly	. . .	. . .	790-815	1450-1500	10-30	O	175-315	**350-600**
O7	Slowly	650	1200	790-830	W:1450-1525 O:1550-1625	10-30	O or W	175-290	**350-550**

Type	**Rate of heating**	**Hardening**				**Time at temperature, min**	**Quenching medium**[(a)]	Tempering temperature	
		Preheat temperature		**Hardening temperature**					
		°C	**°F**	**°C**	**°F**			**°C**	°F
Shock-resisting steels									
S1	Slowly	. . .	. . .	900-955	1650-1750	15-45	O	205-650	**400-1200**
S2	Slowly	650[(f)]	1200[(f)]	845-900	1550-1650	5-20	B or W	175-425	**350-800**
S5	Slowly	760	1400	870-925	1600-1700	5-20	O	175-425	**350-800**
S7	Slowly	650-705	1200-1300	925-955	1700-1750	15-45	A or O	205-620	**400-1150**
Mold steels									
P2	. . .	900-925[(g)]	1650-1700[(g)]	830-845[(h)]	1525-1550[(h)]	15	O	175-260	**350-500**
P3	. . .	900-925[(g)]	1650-1700[(g)]	800-830[(h)]	1475-1525[(h)]	15	O	175-260	**350-500**
P4	. . .	970-995[(g)]	1775-1825[(g)]	970-995[(h)]	1775-1825[(h)]	15	A	175-480	**350-900**
P5	. . .	900-925[(g)]	1650-1700[(g)]	845-870[(h)]	1550-1600[(h)]	15	O or W	175-260	**350-500**
P6	. . .	900-925[(g)]	1650-1700[(g)]	790-815[(h)]	1450-1500[(h)]	15	A or O	175-230	**350-450**
P20	. . .	870-900[(h)]	1600-1650[(h)]	815-870	1500-1600	15	O	480-595[(i)]	**900-1100[(i)]**
P21[(j)]	Slowly	Do not preheat		705-730	1300-1350	60-180	A or O	510-550	**950-1025**
Low-alloy special-purpose steels									

Type	**Rate of heating**	**Hardening**				**Time at temperature, min**	**Quenching medium[(a)]**	Tempering temperature	
		Preheat temperature		**Hardening temperature**					
		°C	**°F**	**°C**	**°F**			**°C**	°F
L2	Slowly	. . .	. . .	W: 790-845 O: 845-925	W: 1450-1550 O: 1550-1700	10-30	O or W	175-540	**350-1000**
L3	Slowly	. . .	. . .	W: 775-815 O: 815-870	W: 1425-1500 O: 1500-1600	10-30	O or W	175-315	**350-600**
L6	Slowly	. . .	. . .	790-845	1450-1550	10-30	O	175-540	**350-1000**
Carbon-tungsten special-purpose steels									
F1, F2	Slowly	650	1200	790-870	1450-1600	15	W or B	175-260	**350-500**
Water-hardening steels									
W1, W2, W3	Slowly	565-650[(k)]	1050-1200[(k)]	760-815	1400-1550	10-30	B or W	175-345	**350-650**
High-carbon, high-chromium cold work steels									
D1, D5	Very slowly	815	1500	980-1025	1800-1875	15-45	A	205-540	**400-1000**
D3	Very slowly	815	1500	925-980	1700-1800	15-45	O	205-540	**400-1000**
D4	Very slowly	815	1500	970-1010	1775-1850	15-45	A	205-540	**400-1000**
D7	**Very slowly**	**815**	**1500**	**1010-1065**	**1850-1950**	**30-60**	**A**	**150-540**	**300-1000**

(a) O, oil quench; A, air cool; S, salt bath quench; W, water quench; B, brine quench.

(b) When the high-temperature heating is carried out in a salt bath, the range of temperatures should be about 15 °C (25 °F) lower than given in this line.

(c) Double tempering recommended for not less than 1 h at temperature each time.

(d) Triple tempering recommended for not less than 1 h at temperature each time.

(e) Times apply to open-furnace heat treatment. For pack hardening, a common rule is to heat 1.2 min/mm (30 min/in.) of cross section of the pack.

(f) Preferable for large tools to minimize decarburization.

(g) Carburizing temperature.

(h) After carburizing.

(i) Carburized case hardness.

(j) P21 is a precipitation-hardening steel having a thermal treatment that involves solution treating and aging rather than hardening and tempering.

(k) Recommended for large tools and tools with intricate sections

Table 4 Processing and service characteristics of tool steels

AISI designation	Hardening and tempering					Fabrication and service			
	Resistance to decarburization	**Hardening response**	**Amount of distortion**[(a)]	**Resistance to cracking**	**Approximate hardness**[(b)]**, HRC**	**Machinability**	**Toughness**	**Resistance to softening**	Resistance to wear
Molybdenum high-speed steels									
M1	Low	Deep	A or S, low; O, medium	Medium	60-65	Medium	Low	Very high	**Very high**
M2	Medium	Deep	A or S, low; O, medium	Medium	60-65	Medium	Low	Very high	**Very high**
M3 (class 1 and class 2)	Medium	Deep	A or S, low; O, medium	Medium	61-66	Medium	Low	Very high	**Very high**
M4	Medium	Deep	A or S, low; O, medium	Medium	61-66	Low to medium	Low	Very high	**Highest**
M6	Low	Deep	A or S, low; O, medium	Medium	61-66	Medium	Low	Highest	**Very high**
M7	Low	Deep	A or S, low; O, medium	Medium	61-66	Medium	Low	Very high	**Very high**
M10	Low	Deep	A or S, low; O, medium	Medium	60-65	Medium	Low	Very high	**Very high**
M30	Low	Deep	A or S, low; O, medium	Medium	60-65	Medium	Low	Highest	**Very high**
M33	Low	Deep	A or S, low; O, medium	Medium	60-65	Medium	Low	Highest	**Very high**
M34	Low	Deep	A or S, low; O, medium	Medium	60-65	Medium	Low	Highest	**Very high**
M36	Low	Deep	A or S, low; O, medium	Medium	60-65	Medium	Low	Highest	**Very high**

AISI designation	**Hardening and tempering**					Fabrication and service			
	Resistance to decarburization	**Hardening response**	**Amount of distortion[(a)]**	**Resistance to cracking**	**Approximate hardness[(b)], HRC**	**Machinability**	**Toughness**	**Resistance to softening**	Resistance to wear
M41	Low	Deep	A or S, low; O, medium	Medium	65-70	Medium	Low	Highest	**Very high**
M42	Low	Deep	A or S, low; O, medium	Medium	65-70	Medium	Low	Highest	**Very high**
M43	Low	Deep	A or S, low; O, medium	Medium	65-70	Medium	Low	Highest	**Very high**
M44	Low	Deep	A or S, low; O, medium	Medium	62-70	Medium	Low	Highest	**Very high**
M46	Low	Deep	A or S, low; O, medium	Medium	67-69	Medium	Low	Highest	**Very high**
M47	Low	Deep	A or S, low; O, medium	Medium	65-70	Medium	Low	Highest	**Very high**
Tungsten high-speed steels									
T1	High	Deep	A or S, low; O, medium	High	60-65	Medium	Low	Very high	**Very high**
T2	High	Deep	A or S, low; O, medium	High	61-66	Medium	Low	Very high	**Very high**
T4	Medium	Deep	A or S, low; O, medium	Medium	62-66	Medium	Low	Highest	**Very high**
T5	Low	Deep	A or S, low; O, medium	Medium	60-65	Medium	Low	Highest	**Very high**
T6	Low	Deep	A or S, low; O, medium	Medium	60-65	Low to medium	Low	Highest	**Very high**

AISI designation	**Hardening and tempering**					Fabrication and service			
	Resistance to decarburization	**Hardening response**	**Amount of distortion**[(a)]	**Resistance to cracking**	**Approximate hardness**[(b)]**, HRC**	**Machinability**	**Toughness**	**Resistance to softening**	Resistance to wear
T8	Medium	Deep	A or S, low; O, medium	Medium	60-65	Medium	Low	Highest	**Very high**
T15	Medium	Deep	A or S, low; O, medium	Medium	63-68	Low to medium	Low	Highest	**Highest**
Chromium hot work steels									
H10	Medium	Deep	Very low	Highest	39-56	Medium to high	High	High	**Medium**
H11	Medium	Deep	Very low	Highest	38-54	Medium to high	Very high	High	**Medium**
H12	Medium	Deep	Very low	Highest	38-55	Medium to high	Very high	High	**Medium**
H13	Medium	Deep	Very low	Highest	38-53	Medium to high	Very high	High	**Medium**
H14	Medium	Deep	Low	Highest	40-47	Medium	High	High	**Medium**
H19	Medium	Deep	A, low; O, medium	High	40-57	Medium	High	High	**Medium to high**
Tungsten hot work steels									
H21	Medium	Deep	A, low; O, medium	High	36-54	Medium	High	High	**Medium to high**
H22	Medium	Deep	A, low; O, medium	High	39-52	Medium	High	High	**Medium to high**

AISI designation	**Hardening and tempering**					Fabrication and service			
	Resistance to decarburization	**Hardening response**	**Amount of distortion[(a)]**	**Resistance to cracking**	**Approximate hardness[(b)], HRC**	**Machinability**	**Toughness**	**Resistance to softening**	Resistance to wear
H23	Medium	Deep	Medium	High	34-47	Medium	Medium	Very high	**Medium to high**
H24	Medium	Deep	A, low; O, medium	High	45-55	Medium	Medium	Very high	**High**
H25	Medium	Deep	A, low; O, medium	High	35-44	Medium	High	Very high	**Medium**
H26	Medium	Deep	A or S, low; O, medium	High	43-58	Medium	Medium	Very high	**High**
Molybdenum hot work steels									
H42	Medium	Deep	A or S, low; O, medium	Medium	50-60	Medium	Medium	Very high	**High**
Air-hardening medium-alloy cold work steels									
A2	Medium	Deep	Lowest	Highest	57-62	Medium	Medium	High	**High**
A3	Medium	Deep	Lowest	Highest	57-65	Medium	Medium	High	**Very high**
A4	Medium to high	Deep	Lowest	Highest	54-62	Low to medium	Medium	Medium	**Medium to high**
A6	Medium to high	Deep	Lowest	Highest	54-60	Low to medium	Medium	Medium	**Medium to high**
A7	Medium	Deep	Lowest	Highest	57-67	Low	Low	High	**Highest**

AISI designation	Hardening and tempering					Fabrication and service			
	Resistance to decarburization	**Hardening response**	**Amount of distortion[(a)]**	**Resistance to cracking**	**Approximate hardness[(b)], HRC**	**Machinability**	**Toughness**	**Resistance to softening**	Resistance to wear
A8	Medium	Deep	Lowest	Highest	50-60	Medium	High	High	**Medium to high**
A9	Medium	Deep	Lowest	Highest	35-56	Medium	High	High	**Medium to high**
A10	Medium to high	Deep	Lowest	Highest	55-62	Medium to high	Medium	Medium	**High**
High-carbon, high-chromium cold work steels									
D2	Medium	Deep	Lowest	Highest	54-61	Low	Low	High	**High to very high**
D3	Medium	Deep	Very low	High	54-61	Low	Low	High	**Very high**
D4	Medium	Deep	Lowest	Highest	54-61	Low	Low	High	**Very high**
D5	Medium	Deep	Lowest	Highest	54-61	Low	Low	High	**High to very high**
D7	Medium	Deep	Lowest	Highest	58-65	Low	Low	High	**Highest**
Oil-hardening cold work steels									
O1	High	Medium	Very low	Very high	57-62	High	Medium	Low	**Medium**
O2	High	Medium	Very low	Very high	57-62	High	Medium	Low	**Medium**

AISI designation	**Hardening and tempering**					Fabrication and service			
	Resistance to decarburization	**Hardening response**	**Amount of distortion[(a)]**	**Resistance to cracking**	**Approximate hardness[(b)], HRC**	**Machinability**	**Toughness**	**Resistance to softening**	Resistance to wear
O6	High	Medium	Very low	Very high	58-63	Highest	Medium	Low	**Medium**
O7	High	Medium	W, high; O, very low	W, low; O, very high	58-64	High	Medium	Low	**Medium**
Shock-resisting steels									
S1	Medium	Medium	Medium	High	40-58	Medium	Very high	Medium	**Low to medium**
S2	Low	Medium	High	Low	50-60	Medium to high	Highest	Low	**Low to medium**
S5	Low	Medium	Medium	High	50-60	Medium to high	Highest	Low	**Low to medium**
S6	Low	Medium	Medium	High	54-56	Medium	Very high	Low	**Low to medium**
S7	Medium	Deep	A, lowest; O, low	A, highest; O, high	45-57	Medium	Very high	High	**Low to medium**
Low-alloy special-purpose steels									
L2	High	Medium	W, low; O, medium	W, high; O, medium	45-63	High	Very high[(c)]	Low	**Low to medium**
L6	High	Medium	Low	High	45-62	Medium	Very high	Low	**Medium**
Low-carbon mold steels									

AISI designation	**Hardening and tempering**					Fabrication and service			
	Resistance to decarburization	**Hardening response**	**Amount of distortion**[(a)]	**Resistance to cracking**	**Approximate hardness**[(b)], **HRC**	**Machinability**	**Toughness**	**Resistance to softening**	Resistance to wear
P2	High	Medium	Low	High	58-64[(c)]	Medium to high	High	Low	**Medium**
P3	High	Medium	Low	High	58-64[(c)]	Medium	High	Low	**Medium**
P4	High	High	Very low	High	58-64[(c)]	Low to medium	High	Medium	**High**
P5	High	. . .	W, high; O, low	High	58-64[(c)]	Medium	High	Low	**Medium**
P6	High	. . .	A, very low; O, low	High	58-61[(c)]	Medium	High	Low	**Medium**
P20	High	Medium	Low	High	28-37	Medium to high	High	Low	**Low to medium**
P21	High	Deep	Lowest	Highest	30-40[(d)]	Medium	Medium	Medium	**Medium**
Water-hardening steels									
W1	Highest	Shallow	High	Medium	50-64	Highest	High[(e)]	Low	**Low to medium**
W2	Highest	Shallow	High	Medium	50-64	Highest	High[(e)]	Low	**Low to medium**
W5	Highest	Shallow	High	Medium	50-64	Highest	High[(e)]	Low	Low to medium

(a) A, air cool; B, brine quench; O, oil quench; S, salt bath quench; W, water quench.

(b) After tempering in temperature range normally recommended for this steel.

(c) Carburized case hardness.

(d) After aging at 510 to 550 °C (950 to 1025 °F).

(e) Toughness decreases with increasing carbon content and depth of hardening.

Physical properties--density, thermal expansion, and thermal conductivity--of selected tool steels are given in Tables 5 and 6.

Table 5 Density and thermal expansion of selected tool steels

Type	**Density**		Thermal expansion									
			μm/m · K from 20 °C to					μin./in. · °F from 70 °F to				
	g/cm³	**lb/in.³**	**100 °C**	**200 °C**	**425 °C**	**540 °C**	**650 °C**	**200 °F**	**400 °F**	**800 °F**	**1000 °F**	1200 °F
W1	7.84	0.282	10.4	11.0	13.1	13.8[(a)]	14.2[(b)]	5.76	6.13	7.28	7.64[(a)]	**7.90[(b)]**
W2	7.85	0.283	. . .	. . .	14.4	14.8	14.9	. . .	. . .	8.0	8.2	**8.3**
S1	7.88	0.255	12.4	12.6	13.5	13.9	14.2	6.9	7.0	7.5	7.7	**7.9**
S2	7.79	0.281	10.9	11.9	13.5	14.0	14.2	6.0	6.6	7.5	7.8	**7.9**
S5	7.76	0.280	. . .	. . .	12.6	13.3	13.7	. . .	. . .	7.0	7.4	**7.6**
S6	7.75	0.279	. . .	. . .	12.6	13.3	. . .	. . .	. . .	7.0	7.4	**. . .**
S7	7.76	0.280	. . .	12.6	13.3	13.7[(a)]	13.3	. . .	7.0	7.4	7.6[(a)]	**7.4**
O1	7.85	0.283	. . .	10.6[(c)]	12.8	14.0[(d)]	14.4[(d)]	. . .	5.9[(c)]	7.1	7.8[(d)]	**8.0[(d)]**
O2	7.66	0.277	11.2	12.6	13.9	14.6	15.1	6.2	7.0	7.7	8.1	**8.4**
O6	7.70	0.277	. . .	11.2	12.6	12.9	13.7	. . .	6.2	7.0	7.2	**7.6**
O7	7.8	0.282	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
A2	7.86	0.284	10.7	10.6[(c)]	12.9	14.0	14.2	5.96	5.91[(c)]	7.2	7.8	**7.9**
A6	7.84	0.283	11.5	12.4	13.5	13.9	14.2	6.4	6.9	7.5	7.7	**7.9**
A7	7.66	0.277	. . .	. . .	12.4	12.9	13.5	. . .	. . .	6.9	7.2	**7.5**
A8	7.87	0.284	. . .	. . .	12.0	12.4	12.6	. . .	. . .	6.7	6.9	**7.0**
A9	7.78	0.281	. . .	. . .	12.0	12.4	12.6	. . .	. . .	6.7	6.9	**7.0**

Type	Density		Thermal expansion									
			µm/m · K from 20 °C to					µin./in. · °F from 70 °F to				
	g/cm³	**lb/in.³**	**100 °C**	**200 °C**	**425 °C**	**540 °C**	**650 °C**	**200 °F**	**400 °F**	**800 °F**	**1000 °F**	1200 °F
A10	7.68	0.278	12.8	13.3	. . .	. . .	. . .	7.1	7.4	. . .	. . .	**. . .**
D2	7.70	0.278	10.4	10.3	11.9	12.2	12.2	5.8	5.7	6.6	6.8	**6.8**
D3	7.70	0.278	12.0	11.7	12.9	13.1	13.5	6.7	6.5	7.2	7.3	**7.5**
D4	7.70	0.278	. . .	. . .	12.4	. . .	. . .	. . .	. . .	6.9	. . .	**. . .**
D5	. . .	. . .	. . .	. . .	. . .	12.0	. . .	. . .	. . .	. . .	6.7	**. . .**
H10	7.81	0.281	. . .	. . .	12.2	13.3	13.7	. . .	. . .	6.8	7.4	**7.6**
H11	7.75	0.280	11.9	12.4	12.8	12.9	13.3	6.6	6.9	7.1	7.2	**7.4**
H13	7.76	0.280	10.4	11.5	12.2	12.4	13.1	5.8	6.4	6.8	6.9	**7.3**
H14	7.89	0.285	11.0	. . .	. . .	. . .	. . .	6.1	. . .	. . .	. . .	**. . .**
H19	7.98	0.288	11.0	11.0	12.0	12.4	12.9	6.1	6.1	6.7	6.9	**7.2**
H21	8.28	0.299	12.4	12.6	12.9	13.5	13.9	6.9	7.0	7.2	7.5	**7.7**
H22	8.36	0.302	11.0	. . .	11.5	12.0	12.4	6.1	. . .	6.4	6.7	**6.9**
H26	8.67	0.313	. . .	. . .	. . .	12.4	. . .	. . .	. . .	. . .	6.9	**. . .**
H42	8.15	0.295	. . .	. . .	. . .	11.9	. . .	. . .	. . .	. . .	6.6	**. . .**
T1	8.67	0.313	. . .	9.7	11.2	11.7	11.9	. . .	5.4	6.2	6.5	**6.6**
T2	8.67	0.313	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
T4	8.68	0.313	. . .	. . .	. . .	11.9	. . .	. . .	. . .	. . .	6.6	**. . .**
T5	8.75	0.316	11.2	. . .	. . .	11.5	. . .	6.2	. . .	. . .	6.4	**. . .**

Type	**Density**		Thermal expansion									
			µm/m · K from 20 °C to					µin./in. · °F from 70 °F to				
	g/cm^3	**lb/in.^{3}**	**100 °C**	**200 °C**	**425 °C**	**540 °C**	**650 °C**	**200 °F**	**400 °F**	**800 °F**	**1000 °F**	1200 °F
T6	8.89	0.321	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
T8	8.43	0.305	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
T15	8.19	0.296	. . .	9.9	11.0	11.5	. . .	. . .	5.5[c]	6.1	6.4	**. . .**
M1	7.89	0.285	. . .	10.6[c]	11.3	12.0	12.4	. . .	5.9[c]	6.3	6.7	**6.9**
M2	8.16	0.295	10.1	9.4[c]	11.2	11.9	12.2	5.6	5.2[c]	6.2	6.6	**6.8**
M3, class 1	8.15	0.295	. . .	. . .	11.5	12.0	12.2	. . .	. . .	6.4	6.7	**6.8**
M3, class 2	8.16	0.295	. . .	. . .	11.5	12.0	12.8	. . .	. . .	6.4	6.7	**7.1**
M4	7.97	0.288	. . .	9.5[c]	11.2	12.0	12.2	. . .	5.3[c]	6.2	6.7	**6.8**
M7	7.95	0.287	. . .	9.5[c]	11.5	12.2	12.4	. . .	5.3[c]	6.4	6.8	**6.9**
M10	7.88	0.255	. . .	. . .	11.0	11.9	12.4	. . .	. . .	6.1	6.6	**6.9**
M30	8.01	0.289	. . .	. . .	11.2	11.7	12.2	. . .	. . .	6.2	6.5	**6.8**
M33	8.03	0.290	. . .	. . .	11.0	11.7	12.0	. . .	. . .	6.1	6.5	**6.7**
M36	8.18	0.296	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
M41	8.17	0.295	. . .	9.7	10.4	11.2	. . .	. . .	5.4	5.8	6.2	**. . .**
M42	7.98	0.288	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
M46	7.83	0.283	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
M47	7.96	0.288	10.6	11.0	11.9	. . .	12.6	5.9	6.1	6.6	. . .	**7.0**
L2	7.86	0.284	. . .	. . .	14.4	14.6	14.8	. . .	. . .	8.0	8.1	**8.2**

Type	**Density**		Thermal expansion									
			µm/m · K from 20 °C to					µin./in. · °F from 70 °F to				
	g/cm³	**lb/in.³**	**100 °C**	**200 °C**	**425 °C**	**540 °C**	**650 °C**	**200 °F**	**400 °F**	**800 °F**	**1000 °F**	1200 °F
L6	7.86	0.284	11.3	12.6	12.6	13.5	13.7	6.3	7.0	7.0	7.5	**7.6**
P2	7.86	0.284	. . .	. . .	13.7	. . .	. . .	. . .	. . .	7.6	. . .	**. . .**
P5	7.80	0.282	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
P6	7.85	0.284	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
P20	**7.85**	**0.284**	**. . .**	**. . .**	**12.8**	**13.7**	**14.2**	**. . .**	**. . .**	**7.1**	**7.6**	**7.9**

(a) From 20 °C to 500 °C (70 °F to 930 °F).

(b) From 20 °C to 600 °C (70 °F to 1110 °F).

(c) From 20 °C to 260 °C (70 °F to 500 °F).

(d) From 40 °C (100 °F)

Table 6 Thermal conductivity of selected tool steels

Temperature		Thermal conductivity	
°C	**°F**	**W/m · K**	Btu/ft · h · °F
Type W1			
95	200	48.3	**27.9**
260	500	41.5	**24.0**
400	750	38.1	**22.0**
540	1000	34.6	**20.0**

Temperature		Thermal conductivity	
°C	**°F**	**W/m · K**	Btu/ft · h · °F
675	1250	29.4	**17.0**
815	1500	24.2	**14.0**
Type H11			
95	200	42.2	**24.4**
260	500	36.3	**21.0**
400	750	33.4	**19.3**
540	1000	31.5	**18.2**
675	1250	30.1	**17.4**
815	1500	28.6	**16.5**
Type H13			
215	420	28.6	**16.5**
350	660	28.4	**16.4**
475	890	28.4	**16.4**
605	1120	28.7	**16.6**
Type H21			
95	200	27.0	**15.6**
260	500	29.8	**17.2**
400	750	29.8	**17.2**
540	1000	29.4	**17.0**

Temperature		Thermal conductivity	
°C	**°F**	**W/m · K**	Btu/ft · h · °F
675	1250	29.1	**16.8**
Type T1			
95	200	19.9	**11.5**
260	500	21.6	**12.5**
400	750	23.2	**13.4**
540	1000	24.7	**14.3**
Type T15			
95	200	20.9	**12.1**
200	500	24.1	**13.9**
400	750	25.4	**14.7**
540	1000	26.3	**15.2**
Type M2			
95	200	21.3	**12.3**
200	500	23.5	**13.6**
400	750	25.6	**14.8**
540	1000	27.0	**15.6**
675	**1250**	**28.9**	16.7

Reference

1. J.R.T. Branco and G. Krauss, Heat Treatment and Microstructure of Tool Steels for Molds and Dies, in *Tool*

Materials for Molds and Dies, G. Krauss and H. Nordberg, Ed., Colorado School of Mines Press, 1987, p 94-117

Normalizing

Normalizing requires slow and uniform heating above the transformation range to dissolve excess constituents, then cooling in still air (see the article "Normalizing of Steel" in this Volume). Normalizing breaks up nonuniform structures, relieves residual stresses, and produces greater uniformity in grain size--thus counteracting undesirable results of unequal reductions for different sections during forging, differences in temperature between varying thicknesses of sections, and the subsequent irregular cooling rates. Normalizing also conditions the steel for subsequent spheroidizing, annealing, or hardening.

Applicability. Many tool steels harden even when cooled in still air; normalizing these steels for the purpose of refining a structure is not recommended. Tool steels that should not be normalized include all high-speed steels, all shock-resisting steels, all hot work steels, cold work steels of types A and D (except A10), and the mold steel P4.

For other types of tool steel, normalizing is most commonly applied after forging and before annealing. Normalizing also may be used before full annealing for parts that are being hardened for a second time.

Standard practice consists of heating to the normalizing temperature, soaking for a suitable time to allow the bar to reach a uniform temperature, and then cooling in still air. No special equipment is required, but the work should be protected against decarburization during heating.

Annealing

Tool steels usually are received from the supplier in the annealed condition. This condition allows the steel to be easily machined and heat treated. However, if they are subjected to hot or cold forming, often they must be fully annealed again before subsequent operations. If a tool is to be rehardened, it should first be thoroughly annealed. This procedure is important with the steels of higher alloy content; otherwise, irregular grain growth occurs and a mixed grain size (sometimes called fish scale or duplex grains) will result.

Full annealing involves heating the steel slowly and uniformly to a temperature above the transformation range, holding it at the temperature for from 1 to 4 h (which is generally long enough for complete heat penetration), and cooling slowly at a controlled rate followed by air cooling.

Atmosphere furnaces, salt baths, vacuum furnaces, or lead pots may be used for annealing. Requirements of the heating equipment include reasonably accurate temperature control and a means of preventing decarburization. In box or roller-hearth furnaces, surface protection often is accomplished through proprietary decarb-resistant coating or by packing the workpieces in pipes, in which they are then surrounded by nondecarburizing material, such as spent charcoal and mica, or cast iron chips. Furnaces with prepared atmospheres frequently are used for the annealing of tool steels.

These packing materials may carburize, decarburize, or be neutral to steel, depending on the heating temperature, the carbon content of the steel, and the density of the packing (also the particle size of the packing material). The principal aim of such materials is to exclude the decarburizing gases from contact with the steel. If oxygen is to be excluded, the packing must be very tight and the sealing of the container perfect, for most gases can diffuse through ordinary seals at a surprisingly rapid rate at elevated temperatures. Materials that contain carbonaceous substances are, therefore, somewhat better where this is the case. In the annealing operation, where scale is present on the bars as charged in the furnace, decarburization may occur unless a carbonaceous material is present. Needless to say, the presence of moisture in the packing material is not tolerable as decarburization will take place very readily.

Figure 2 shows the range of usefulness of each of the packing compounds. This should be used only as a guide, as the presence of scale, the age of the packing compound, the moisture content, and the carbon content of the steel will appreciably alter the range. Furthermore, the temperature at which one material will change from neutral to decarburizing is not necessarily as definite as that indicated. It is to be noted that the effect of carbon content is not included. The chart applies particularly to high-carbon steels.

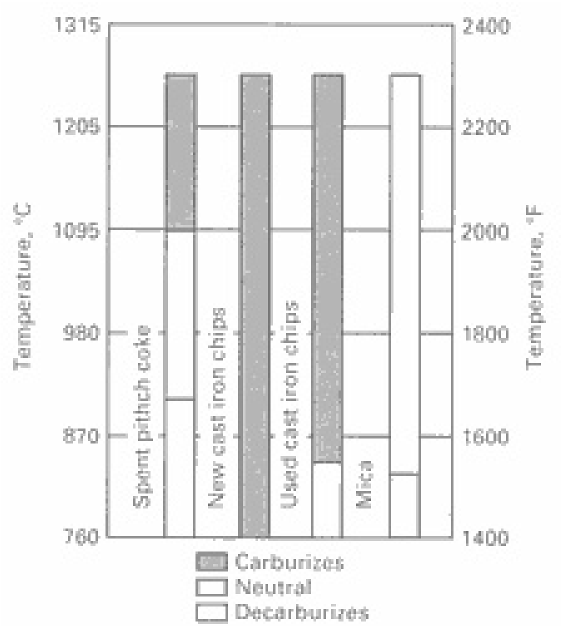

Fig. 2 Approximate range of usefulness of selected packing compounds used in the annealing of tool steels. Temperatures of change from one behavior to another are actually not sharp. For cast iron chips, the temperature below which decarburization will take place depends on the carbon content of the chip. Source: Ref 2

Cracking from thermal shock can be minimized by loading the furnace at a relatively low temperature (room temperature or a few hundred degrees Fahrenheit) to permit the furnace load to heat up slowly with the furnace. Following the soak at annealing temperature, the workpieces (and container, if used) should be cooled in the furnace at 8 to 22 °C/h (15 to 40 °F/h) to 540 °C (1000 °F) or lower. Below about 540 °C (1000 °F), the cooling rate for most tool steels is no longer critical, and the work may then be cooled in air. Typical annealed hardness values for the various tool steels are given in Table 1.

Additional information is available in the articles "Annealing of Steel" and "Continuous Annealing of Steel" in this Volume.

Isothermal annealing is an alternative method of cooling that consists of rapidly cooling the workload in the furnace from the annealing temperature to a temperature just below the transformation range and holding the load and furnace at this temperature for one or more hours. Following this period of soaking at just below the transformation range, the load may be safely air cooled. This process, known as isothermal annealing, is best suited for applications in which full advantage can be taken of the rapid cooling to the transformation temperature, and from this temperature to room temperature. Thus, for small parts that can be handled in salt or lead baths, or for light loads in batch furnaces, isothermal annealing makes possible large savings in time, as compared with the conventional slow furnace cooling. It can also be adapted conveniently to continuous annealing cycles where adequate equipment is available.

Isothermal annealing offers no particular advantage for applications (such as the batch annealing of large furnace loads) in which the rate of cooling at the center of the load may be so slow as to preclude any rapid cooling to the transformation temperature. For such applications, conventional full annealing usually offers a better assurance of obtaining the desired properties.

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Stress Relieving

Stress relieving removes or reduces residual stress induced in tools by heavy machining or forming, and thereby decreases the probability of distortion or cracking during hardening of the tool (see the article "Stress-Relief Heat Treating of Steel" in this Volume).

The ground surface of a hardened tool may be highly stressed after grinding but not cracked. The high stress may, however, cause cracks to develop immediately after grinding, before use, or during use. Ground tools with high residual stress can often be salvaged by stress relieving, immediately after grinding, at or just below the tempering temperature in order to maintain the specified tool hardness.

Tools also develop high residual stress in use. It is sometimes advantageous to relieve this stress at each redressing of the tool by retempering at an appropriate temperature. This temperature should not exceed the tempering temperature; otherwise, undesirable softening will occur.

Procedure. Stress relieving is most commonly performed in air furnaces or salt baths used for tempering. Neither the heating nor the cooling rate is critical, although cooling should be slow enough to prevent the introduction of new stress. Protection against scaling or decarburization is seldom required, unless the stress-relieving temperature is above 650 °C (1200 °F). Under some conditions, vacuum or inert atmosphere furnaces may be required to prevent scaling or discoloration.

After stress relieving, it may be necessary to correct certain dimensions before hardening, because the relief of stress causes some dimensional change. Precision tools usually are stress relieved after machining and before hardening; it is often desirable to stress relieve after rough machining but before finish machining. Stress relieving after electrical discharge machining (EDM) work will reduce some of the residual stress but will not remove all of the effects of this machining method.

Austenitizing

Austenitizing is the most critical of all heating operations performed on tool steels. Excessively high austenitizing temperatures or abnormally long holding times may result in excessive distortion, abnormal grain growth, loss of ductility, and low strength; this is especially true for high-speed steels, which are frequently austenitized at a temperature close to that at which melting begins. Underheating may result in low hardness and low wear resistance. At the time of quenching, if the center of a tool is cooler than the exterior, spalling or fracturing of the corners may result, particularly with water-hardening steels. Prior to heat treatment, all tool surfaces must be free of decarburization. Typically, steel is supplied decarb free of centerless ground bar or precision ground flats. If hot rolled material is purchased, sufficient stock must be removed.

Austenitizing is the heat treatment where the final alloy element partitioning between the austenitic matrix (that will transform to martensite) and the retained carbides occurs. This partitioning fixes the chemistry, volume fraction, and dispersion of the retained carbides. The retained alloy carbides not only contribute to wear resistance, but also control austenitic grain size. The finer the carbides and the larger the volume fraction of carbides, the more effectively austenitic grain growth is controlled. Thus if austenitizing is performed at too high a temperature, undesirable grain growth may occur as the alloy carbides increasingly coarsen or dissolve into the austenite.

The alloying elements not tied up in retained carbides are in solution in the austenite, and thus the carbides provide an important mechanism by which austenite composition is fixed. The austenite composition then sets the hardenability, M_s temperature, retained austenite content, and secondary hardening potential of a tool steel.

Figure 3 shows the effect of increasing austenitizing temperature on the as-quenched, quenched and subzero cooled, and tempered hardness of an A2 tool steel. The highest as-quenched hardness is produced by austenitizing at 950 °C (1740 °F), the recommended austenitizing temperature for A2. In this condition after quenching, the retained austenite content is finely dispersed and at a minimum and therefore subzero cooling has little effect on hardness. With increasing austenitizing temperature, more alloying elements go into solution, the M_s temperature drops, and more austenite is retained at room temperature. As a result, the as-quenched room temperature hardness decreases and subzero cooling has a greater effect as more of the large volume fraction of retained austenite transforms to martensite on subzero cooling. Figure 4 shows that eventually tempering, by a combination of retained austenite transformation and secondary hardening, will also raise the hardness of as-quenched structures with large amounts of retained austenite. Not shown is the deleterious increase in austenite grain size which develops as more and more carbides dissolve at the higher austenitizing temperatures.

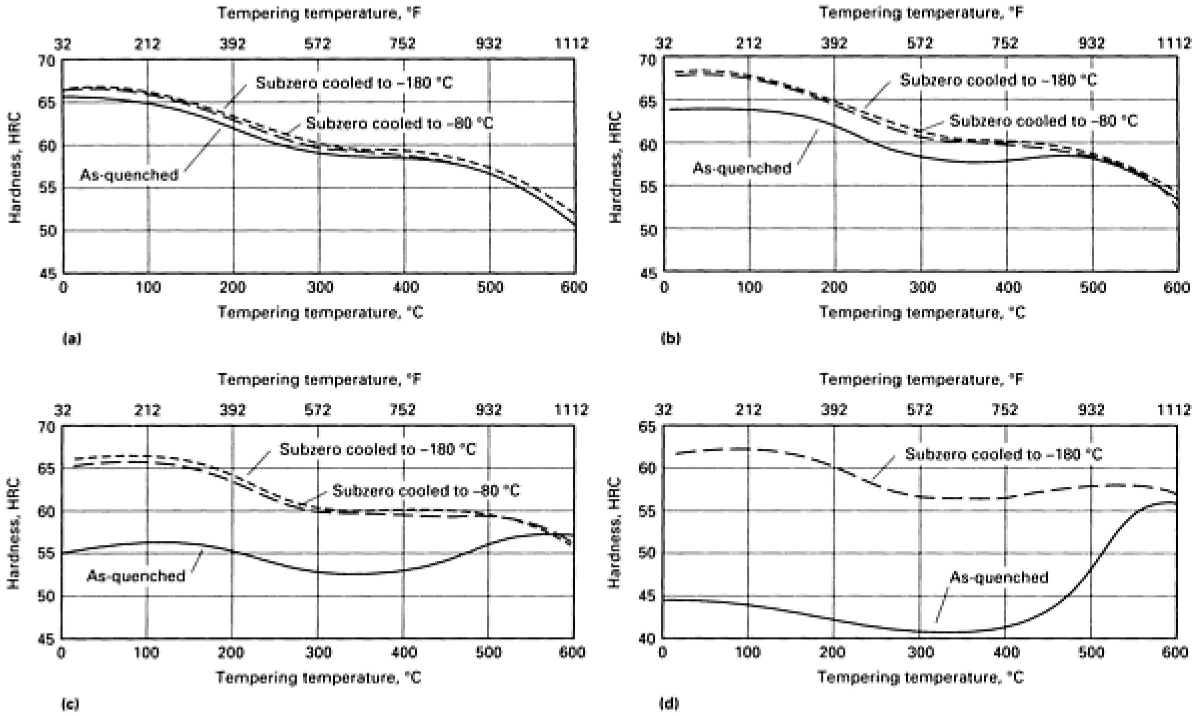

Fig. 3 Plots of hardness versus tempering temperatures of as-quenched, quenched, and subzero cooled to -80 °C (-110 °F), and quenched and subzero cooled to -180 °C (-290 °F) A2 tool steels to show effect of increasing austenitizing temperatures. (a) 950 °C (1740 °F). (b) 1000 °C (1830 °F). (c) 1050 °C (1920 °F). (d) 1100 °C (2010 °F). Source: Ref 3

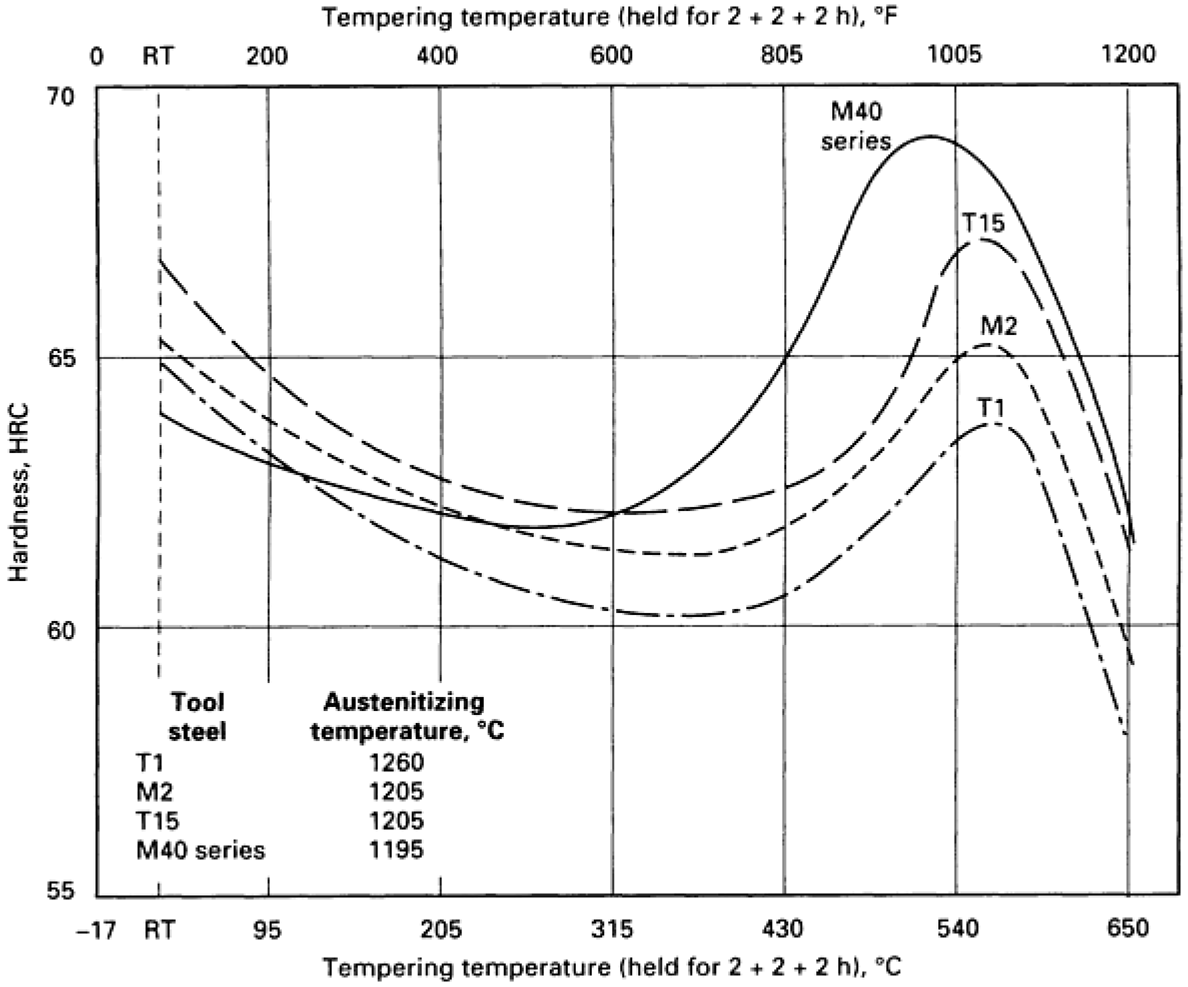

Fig. 4 Plot of hardness versus tempering temperature for selected high-speed tool steels. Source: Ref 4

Equipment for austenitizing tool steels is chosen on the basis of steel composition, size and shape of workpieces, amount of stock removal after hardening, and production requirements. Vacuum furnaces, atmosphere furnaces, and salt baths have proved satisfactory for service over the entire austenitizing temperature range of 760 to 1300 °C (1400 to 2375 °F). Lead pots are suitable for the temperature range of about 760 to 925 °C (1400 to 1700 °F).

Workpieces must be supported during austenitizing. Lead and salt provide some of the support, but in atmosphere furnaces, special attention must be given to prevent workpieces from sagging or making contact with the furnace brickwork.

During austenitizing, continuous control of the furnace internal environment must be maintained to prevent workpieces from becoming carburized or decarburized. Salt baths must be rectified; atmospheres must be controlled for proportion of gases and dew point; lead baths must be kept free of contamination. Vacuum furnaces must be maintained at low leak rates and partial pressure control at austenitizing temperatures, above 1095 °C (2000 °F).

Preheating for Austenitizing. Preheating tool steels before austenitizing is sound practice, but it is not always required. For small pieces of simple shape, preheating may be eliminated. Preheating normally is employed as a safeguard against the cracking and extreme distortion resulting from the thermal shock undergone by a cold workpiece when it is exposed to the high temperature of the austenitizing furnace.

Preheating is especially beneficial for the highly alloyed hot work and high-speed steels, because it gives them a greater length of time to reach thermal equilibrium and eliminates most of the risk of prolonged exposure to austenitizing temperatures such as decarburization and the tendency for surfaces of large sections to experience longer exposure times.

Tools that are to be austenitized in salt are usually preheated in salt, but they may be preheated in an atmosphere furnace if it is more convenient. Tools that are to be austenitized in an atmosphere furnace are preheated in a gaseous atmosphere.

Procedure. Preheating is usually done in a furnace adjacent to the austenitizing furnace, although it is possible to preheat and austenitize in the same furnace. In the latter procedure, once the workpiece is heated through to the preheat temperature, the furnace temperature is raised to the austenitizing temperature and the workpiece is thus brought to the austenitizing temperature without leaving the furnace. The practicality of this one-furnace procedure depends on the difference between preheating and austenitizing temperatures for the type of steel being treated and on production requirements. Some experts do not recommend this procedure for high-speed steels, especially where high-inertia furnaces are used, because the difference between preheating and austenitizing temperatures for these steels may be as much as 485 °C (875 °F). In high-volume operations, where preheating is frequently performed solely to shorten production time, separate furnaces can be used for preheating and austenitizing.

References cited in this section

3. K.-E. Thelning, *Steel and Its Heat Treatment,* 2nd ed., Butterworths, 1984

4. S.G. Fletcher and C.R. Wendell, *ASM Met. Eng. Q.,* Vol 1, Feb 1966, p 146

Quenching

Quenching from the austenitizing temperature may be done in water, brine, oil, salt, inert gas, or air, depending on composition and section thickness. The quenching medium must cool the workpiece rapidly enough to obtain full hardness; it is poor practice, however, to use a quenching medium with a cooling capacity that exceeds requirements, because of the possibility that cracking or excessive distortion may occur.

Tool steels that will harden during air cooling are frequently hot quenched to the range 540 to 650 °C (1000 to 1200 °F) after austenitizing. Quenching time is long enough for decomposition of austenite to begin. After hot quenching, the steels are air cooled or oil quenched to ambient temperature. Hot quenching minimizes distortion without adversely affecting hardness and spaIls away or prevents the hard scale from forming on most air-hardening steels during air cooling. Additional information is available in the article "Quenching of Steel" in this Volume.

Martempering is often utilized to minimize distortion without sacrifice of hardness in oil-hardening tool steels or in extremely thin sections of water-hardening tool steels (see the article "Martempering of Steel" in this Volume). Workpieces are quenched from the austenitizing temperature in an agitated bath of oil or salt. Bath temperature should be near the temperature at which martensite starts to form on cooling (M_s), usually about 31 °C (57 °F) above it. Time in the bath should be just sufficient for temperature to equalize throughout the workpieces, which are then air cooled to room temperature prior to tempering.

Tempering

Tempering modifies the properties of quench-hardened tool steels to produce a more desirable combination of strength, hardness, and toughness than obtained in the quenched steel (see the article "Tempering of Steel" in this Volume). The as-quenched structure of tool steel is a heterogeneous mixture of retained austenite, untempered martensite, and carbides. More than one tempering cycle may be necessary to produce an optimum structure. It is normally desirable to transform all retained austenite to ensure complete hardness, improve toughness, and minimize distortion during service. This can be more nearly accomplished by two or more shorter tempering cycles than by a single and longer cycle (see Fig. 4).

In the higher-alloy tool steels, a small amount of untempered martensite is formed from retained austenite during the cool-down from the first tempering cycle. It is good practice to double temper to ensure more nearly complete transformation of retained austenite and to temper freshly formed martensite. For some highly alloyed grades of tool steel, triple or quadruple tempering is recommended.

The changes that take place in the microstructure during tempering of hardened tool steels are time-temperature dependent. Time at tempering temperature should not be less than 1 h for any given cycle.

Most manufacturers of high-speed steels recommend multiple tempers of 2 h or more each to attain the desired microstructure and properties. Maintaining recommended tempering times, temperatures, and number of tempers (a

minimum of two) ensure attainment of consistent tempered martensitic structures and overcomes uncertainties caused by variations in the amount of retained austenite in the as-quenched condition. These variances are functions of differences in heat chemistry, prior thermal history, hardening temperatures, and quenching conditions. Other factors that influence the tempering requirements of high-speed steels are:

- Increasing the free (matrix) carbon content increases the amount of retained austenite in the as-quenched condition
- The amount of retained austenite significantly affects the rate of transformation, particularly for short tempering cycles. Multiple tempering is more important to attain an acceptable structure if short tempering times are used
- Cobalt in alloys such as M42 reduces the amount of retained austenite in the as-quenched condition and accelerates the transformation of the retained austenite during tempering

Enough time should be allowed during tempering for the temperature to be distributed uniformly throughout the tools before time at temperature is counted. This is especially true for low tempering temperatures and for tools that have large sections. Table 7 indicates the time needed for various section sizes to reach uniform temperature in different kinds of furnaces. If not enough time is allowed for the tool to reach the tempering temperature, the result will be nonuniform tempering and possible damage to the tool. Color of the oxide film should not be used as a guide in tempering, because these temper colors indicate only the surface temperature of the tool, not the internal temperature. Grinding cracks in hardened tools may be caused by inadequate tempering.

Table 7 Approximate heating time to attain tempering temperature

Tempering temperature		Time required to reach furnace temperature[a]:											
		In hot air oven without circulation[b]						In circulating air oven or an oil bath[c]					
		Cubes or spheres		**Squares or cylinders**		**Average flats**		**Cubes or spheres**		**Squares or cylinders**		Average flats	
°C	**°F**	**min/mm**	**min/in.**	**min/mm**	**min/in.**	**min/mm**	**min/in.**	**min/mm**	**min/in.**	**min/mm**	**min/in.**	**min/mm**	min/in.
120	250	1.2	30	2.2	55	3.2	80	0.6	15	0.8	20	1.2	**30**
150	300	1.2	30	2.0	50	3.0	75	0.6	15	0.8	20	1.2	**30**
175	350	1.2	30	2.0	50	2.8	70	0.6	15	0.8	20	1.2	**30**
205	400	1.0	25	1.8	45	2.6	65	0.6	15	0.8	20	1.2	**30**
260	500	1.0	25	1.6	40	2.4	60	0.6	15	0.8	20	1.2	**30**
315	600	1.0	25	1.6	40	2.2	55	0.6	15	0.8	20	1.2	**30**
370	700	0.8	20	1.4	35	2.0	50	0.6	15	0.8	20	1.2	**30**
425	800	0.8	20	1.2	30	1.8	45	0.6	15	0.8	20	1.2	**30**
$\geq$**480**	$\geq$**900**	**0.8**	**20**	**1.2**	**30**	**1.6**	**40**	**0.6**	**15**	**0.8**	**20**	**1.2**	30

(a) Data are given in minutes per millimeter, and in minutes per inch, of diameter or thickness, with furnace maintained at the temperature indicated in column 1. Data may be used as a guide for charges of irregular shapes and quantities by estimating total size of charge and applying the above allowance to the number of inches from outside to center of charge.

(b) Times indicated are for tools with dark or scaled surfaces. If surfaces are finish ground, or otherwise brightened, twice as much time should be allowed in a still hot air oven. No extra allowance need be made for bright surfaces in a circulating oven or in an oil bath.

(c) Oil baths are usually not used above 205 °C (400 °F).

Proper tempering depends on the accurate determination of the temperature of the load and on proper spacing of workpieces in the load to ensure that it is uniformly heated. The most common medium used for tempering tools is recirculating-atmosphere furnaces, where the atmosphere may be flue gas, nitrogen, argon, or even a partial vacuum. Regardless of the medium used for tempering, accurate means of temperature control are mandatory for reproducible results.

Procedure. Before a tool steel part is tempered, it should be cooled in the quenched medium or in air until it can be held in the hand without discomfort (near 50 °C, or 120 °F, for most steels). For particularly large or intricate parts, it is essential to temper as soon as possible after the quench, to prevent cracking.

Heating to the tempering temperature should be slow, to obtain uniform distribution of temperature within the tool and to prevent the nonuniform relief of hardening stress that could cause cracking or warping. Satisfactory results may be obtained by charging the tools into a freely circulating medium at the desired tempering temperature and then permitting them to reach this temperature. If tempered in a liquid medium, the tools should be placed in a basket and not permitted to come in contact with the hot walls or bottom of the pot or tank. Heat transfer is most rapid for molten lead baths, less rapid for salt and oil baths, and slowest in still air.

Cooling after tempering should be relatively slow in order to prevent development of residual stress in the steel. Still air cools at a satisfactory rate.

Equipment. Recirculating-air furnaces have several advantages over most other types of equipment used for tempering. For example, such a furnace can be cooled rapidly between batches of tempering temperatures so that successive work loads may enter the furnace safely at a low temperature. Another advantage of the recirculating-air furnace is its relatively low heat transfer rate, which permits the load to be brought to temperature more slowly. As-quenched tools heated too rapidly may develop cracks. Recirculating-air furnaces also usually afford a wider range of useful tempering temperatures than other tempering mediums, with no hazards of fire or burns from splashing of hot liquids.

Surface Treatments and Cold Treating

Carburizing of tool steels is usually restricted to special applications. Mold steels, however, are commonly carburizing and then case hardened. A marked increase in surface carbon renders most tools too brittle for their intended uses. However, tools made of shock-resisting steel, hot work steel, and especially the lower-carbon types of high-speed steel are sometimes carburized to advantage for use in certain die applications involving severe wear. Carburizing is also useful for applications such as cold work dies that require extreme wear resistance and that are not subjected to impact or highly concentrated loading. All the common methods of carburizing (gas, pack, and liquid) have been employed for these special applications (see the articles "Gas Carburizing," "Pack Carburizing," and "Liquid Carburizing and Cyaniding" in this Volume). Case depths are shallower, about 0.05 to 0.25 mm (0.002 to 0.010 in.), rather than the 0.75 to 1.5 mm (0.030 to 0.060 in.) that is common on conventional carburizing steels.

Carburizing temperatures, typically 1040 to 1065 °C (1900 to 1950 °F) are held for 10- to 60-min durations. The carburizing treatment also serves as an austenitizing treatment for the whole tool. A carburized case on high-speed steels has a hardness of 65 to 70 HRC but does not have the high resistance to softening at elevated temperatures exhibited by normally hardened high-speed steel.

Nitriding successfully increases the life of all types of high-speed steel cutting tools. For nitrided high-speed steel taps, drills, and reamers used in machining annealed steel, five-fold increases in life have been reported, with average increases of 100 to 200%. Obviously, if this nitrided case is removed when the tool is reground, the tool must then be retreated, which reduces the cost advantage of the process.

Gas nitriding, however, produces a case that is too brittle for most applications. Gas nitriding of tool steels is limited to applications such as hot work tool steels (H grades) and tooling for aluminum extrusion dies. Additional information is available in the article "Gas Nitriding" in this Volume.

Liquid nitriding of finished high-speed steel tools in cyanide-base salt baths at 510 to 565 °C (950 to 1050 °F) is a common method of increasing tool life because it provides a light case, increasing both surface hardness and resistance to adhesion. Nitriding time ranges from 15 min to 2 h, resulting in case depths up to about 0.05 mm (0.002 in.). Due to environmental considerations, sources for liquid nitriding are becoming rare. Additional information is available in the article "Liquid Nitriding" in this Volume.

Vacuum Nitriding. Vacuum furnaces, especially vacuum tempering furnaces, can be used for nitriding of tools. The tempering furnace is ideally suited for this purpose because it is designed to operate in the nitriding temperature range. For high-speed steels and other tools tempered at 455 to 595 °C (850 to 1100 °F), the nitriding cycle can be incorporated into the final tempering cycle, by introducing a partial pressure of ammonia during the final temper. In this way, the vacuum furnace operates similar to a normal nitriding furnace, except that nitrogen or the vacuum itself acts as the dilutant for nitriding, replacing dissociated ammonia. Cycle times would be the same as for gas nitriding.

Plasma Nitriding. Another process used for nitriding tool steels is plasma nitriding, also known as ion nitriding. It is used in the nitriding of high-speed (M and T series), cold work (A and D series), and hot work (H series) tool steels (Ref 5). This process is also a vacuum process, but employs the principle of glow discharge to provide energy for heating and nitriding (see Fig. 5). Because it relies on electrical energy to dissociate gases, activate surfaces, and to provide energy for reaction, ordinary nitrogen at pressures in the range 0.1 to 1 kPa (1 to 10 mm Hg) are all that is required for nitriding. In addition, by adjusting the amount of nitrogen, the surface white layer can be closely controlled or eliminated. As in the other methods, the cycles are very short. In addition, the temperature range is greatly expanded, to as low as 350 °C (660 °F), because the glow discharge reaction is not dependent on ammonia breakdown as in gas nitriding. This permits greater flexibility in choice of nitriding temperature so that surface hardness, case depth, and core hardness can be optimized for a given steel.

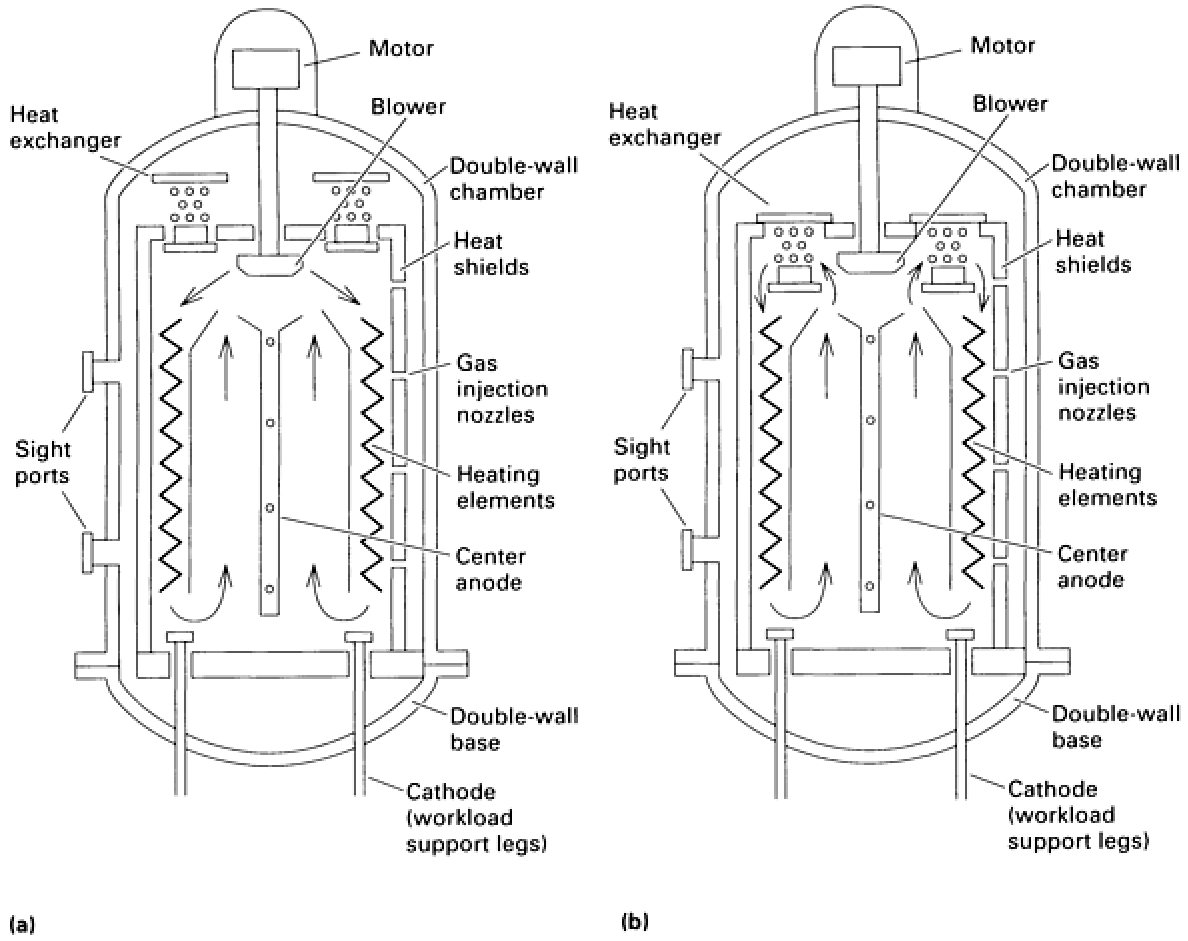

Fig. 5 Schematic of plasma-nitriding furnace showing gas circulation during (a) heating and (b) cooling. Source: Ref 5

Titanium Nitride Coatings. Several techniques are being used for the application of nitride coatings. Most processes are proprietary and carried out on a commercial basis. The most frequently applied material is titanium nitride. Very thin coatings in the 0.025 mm (0.001 in.) thickness range or less produce 69 HRC high hardness, cutting edges on drills, reamers, and other cutting tools. See the article "High-Speed Tool Steels" in Volume 16 of *ASM Handbook*, formerly 9th Edition *Metals Handbook.*

Sulfide Treatment. A low-temperature (190 °C, or 375 °F) electrolytic process using sodium and potassium thiocyanate provides a seizing-resistant iron sulfide layer. This process can be used as a final treatment for all types of hardened tool steels without much danger of overtempering.

Oxide coatings, provided by treatment of the finish-ground tool in an alkali-nitrate bath or by steam oxidation, prevent or reduce adhesion of the tool to the workpiece. Oxide coatings have doubled tool life--particularly in machining of gummy materials such as soft copper and nonfree-cutting low-carbon steels.

Chromium plating of finished high-speed steel tools with 0.0025 to 0.0125 mm (0.1 to 0.5 mil) of chromium also prolongs tool life by reducing adhesion of the tool to the workpiece. Chromium plating is relatively expensive, and precautions must be taken to prevent tool failure in service due to hydrogen embrittlement.

Electroless nickel plating has been used successfully as a replacement for chromium plating, both in routine production and for salvage plating operations on tool steel parts. Because plating by this method is accomplished by means of chemical reduction, it does not depend on any galvanic coupling between dissimilar metals, and there is no electrolysis involved. Therefore, there is no danger of hydrogen embrittlement. Plated hardness is in the high Rockwell 50's range, with good, uniform plated thickness on all surfaces, and the plated surfaces have a low coefficient of friction.

Cold Treating. The main purpose of cold treating tool steels (to -75 °C, or -100 °F, or lower) is to transform retained austenite in the unfinished tool and thus to provide dimensional stability in subsequent finishing operations. The use of cold treatment on properly heat-treated cutting tools does not affect tool performance. When used, cold treatment should be performed between the first and second tempering operations. Although cold treating an as-quenched tool is more effective in transforming retained austenite than after the first temper, it does increase the chance of cracking.

Additional information is available in the article "Cold Treating and Cryogenic Treatment of Steel" in this Volume.

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Processes and Furnace Equipment for Heat Treating of Tool Steels

Bruce A. Becherer, Teledyne Vasco

Introduction

THE HEAT TREATMENT of tool steels is as important to their success as the selection of the grade itself. Machine tools or production dies made from tool steels should never have their rigid metallurgical requirements compromised or out-weighed by cost considerations. Attempting to reduce production costs by bypassing steps in the heat treat processing of tool steels will yield an end product that fails to meet tool life expectations and does not justify its high initial expense. These metallurgical requirements involve the control of the surface condition and chemistry, accurate control of the temperatures often up to 1315 °C (2400 °F), the time at a given temperature, and the control of the heating and cooling rates. Special attention must be paid to these requirements in the design, construction, and operation of the furnaces used to heat treat tool steels, especially those used for hardening, where the metallurgical factors involved become all-important.

Tool steels are typically heat treated in ceramic-lined salt bath furnaces, in vacuum furnaces, in controlled atmosphere furnaces, and in fluidized-bed furnaces.

Salt Bath Furnaces

Molten salts of various compositions are well adapted to all operations in the heat treatment of tool steels. For tools that cannot be ground after hardening or for tools that require an excellent surface condition and the maintenance of sharp edges, salt bath heating provides excellent results. Table 1 lists various salt bath compositions and processing temperatures for the heat treating of tool steels. The salt bath method of hardening is predominant with high-speed steel

tools. With correct operating conditions, tools can be heat treated without carburization, decarburization, and scaling. The surface will be fully hard with a minimum of distortion. Three types of salt baths are generally used:

- Preheating baths
- High-temperature baths
- Quenching baths

Table 1 Typical compositions and recommended working temperature ranges of salt mixtures used in heat treating tool steels

Salt mixture No.	**Composition, %**						**Melting point**		Working range	
	$BaCl_2$	**NaCl**	**KCl**	**$CaCl_2$**	**$NaNO_3$**	**KNO_3**	**°C**	**°F**	**°C**	°F
Austenitizing salts (high heat)										
1	98-100	. . .	. . .	. . .	. . .	. . .	950	1742	1035-1300	**1895-2370**
2	80-90	10-20	. . .	. . .	. . .	. . .	870	1598	930-1300	**1705-2370**
Preheat salts										
3	70	30	. . .	. . .	. . .	. . .	335	635	700-1035	**1290-1895**
4	55	20	25	. . .	. . .	. . .	550	1022	590-925	**1095-1700**
Quench and temper salts										
5	30	20	. . .	50	. . .	. . .	450	842	500-675	**930-1250**
6	**. . .**	**. . .**	**. . .**	**. . .**	**55-80**	**20-45**	**250**	**482**	**285-575**	**545-1065**

Preheating serves to minimize thermal shock, equalize temperature, and minimize the amount of time required at the high-temperature stage. The high-temperature salt bath serves as the austenitizing step. The function of the quenching bath is to equalize the temperature as well as to ensure a clean surface after heat treatment.

Most tools heat treated in salt baths are fully hard from surface to core regardless of the section thickness. Because salt baths provide temperature uniformity in preheating, in high-temperature heating, and in quenching, distortion and residual stress are minimized.

Tools that are heat treated in molten salt baths are heated by conduction with the molten salt providing a ready source of heat as required. Although steels come in contact with heat through the tool surfaces, the core of a tool rises in temperature at approximately the same rate as its surface. Heat is quickly drawn to the core from the surface. Salt baths provide heat at a rate equal to the heat absorption rate of the total tool. Convection or radiation heating methods are unable to maintain the rate of heating necessary to reach equilibrium with the rate of heat absorption. The ability of a molten salt bath to supply heat at a rapid rate enhances the uniformity of properties and resultant high quality of tools heat treated in salt baths. Heat-treating times are also shortened; for example, a 25 mm (1 in.) diam bar can be heated to

temperature equilibrium in 4 min in a salt bath, while 20 to 30 min would be required to obtain the same properties in convection or radiation furnaces.

Salt baths are an efficient method of heat treating tool steels; about 93 to 97% of the electric power consumed in a salt bath operation goes directly into heating. Tool steels that are heat treated in molten salts typically are processed in ceramic-lined furnaces with submerged or immersed electrodes containing chloride-base salts.

Immersed-Electrode Salt Bath Furnaces

Ceramic-lined furnaces with immersed (over-the-side) electrodes have greatly extended the useful range and capacity of molten salt equipment when compared with externally heated pot furnaces (see Fig. 1). Detailed information is available in the article "Salt Bath Equipment" in this Volume.

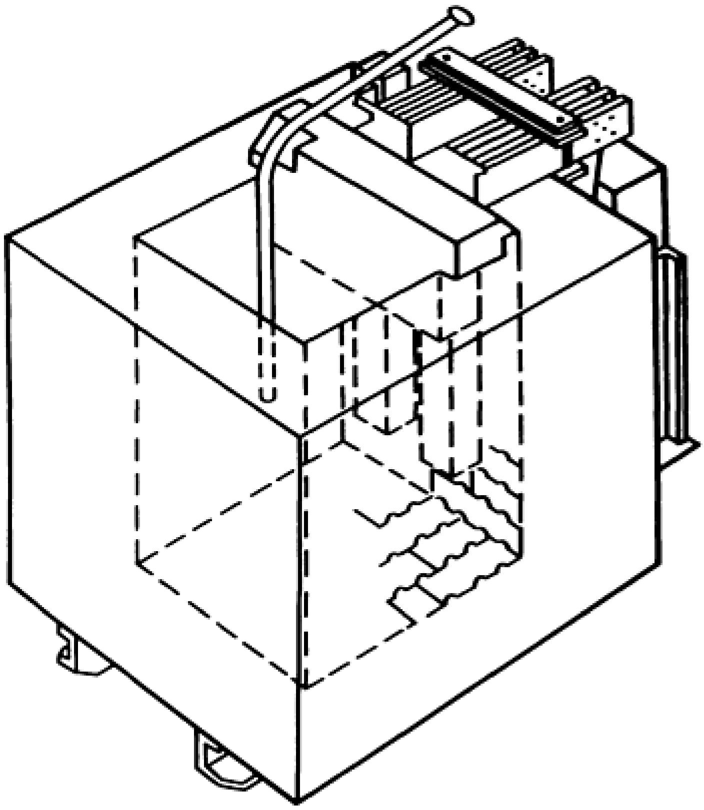

Fig. 1 Salt bath furnace used for neutral heating applications. Furnace features a ceramic pot and over-the-top (immersed) electrodes.

Submerged-Electrode Salt Bath Furnaces

Submerged-electrode furnaces have the electrodes placed beneath the working depth for bottom heating. Figure 2 is a cutaway showing typical construction of a submerged-electrode furnace. Detailed information is available in the article "Salt Bath Equipment" in this Volume.

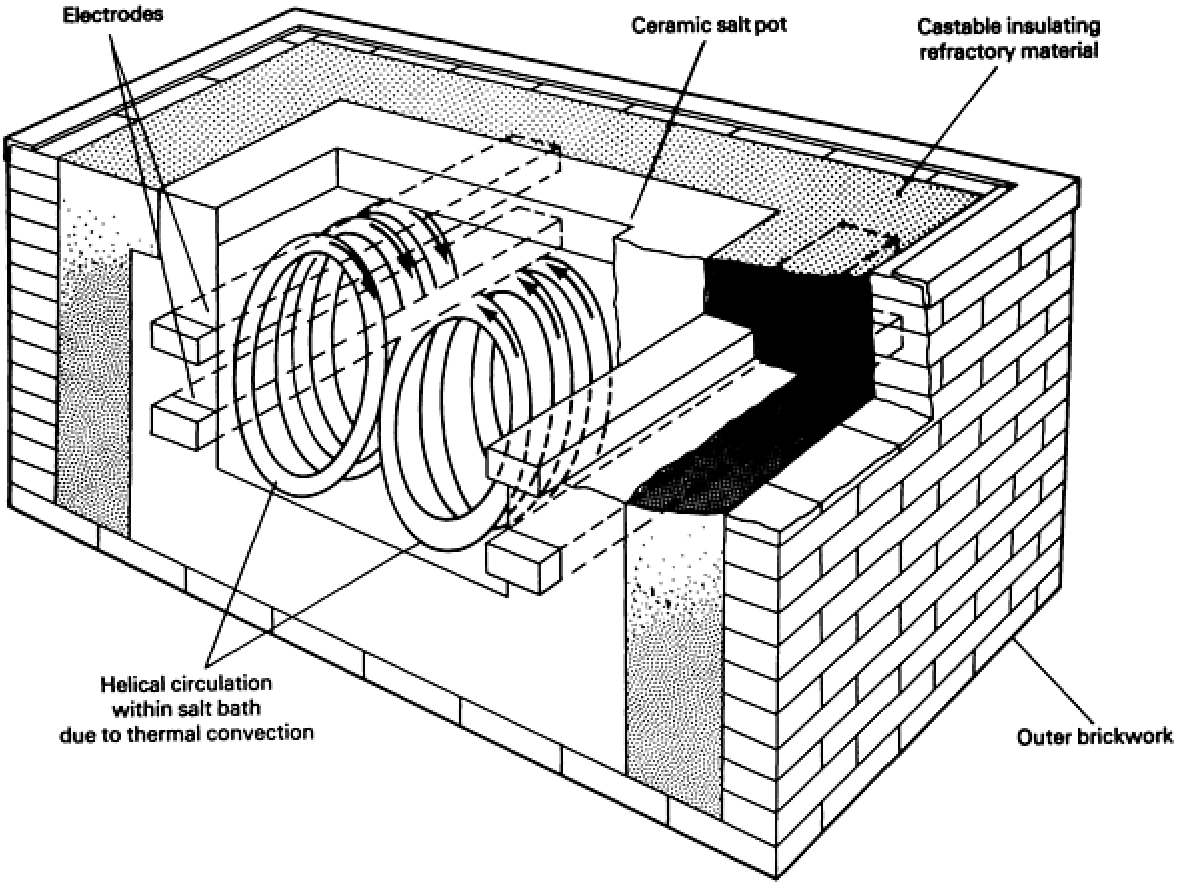

Fig. 2 Typical submerged-electrode salt bath furnace

Automatic Heat Treating of Tool Steels

Figure 3 illustrates three different heat treating arrangements for the production heat treatment of tool steels. Table 2 gives relative process times and temperatures for heat treating, and Table 3 gives process times for twist drills. The systems are equipped for cycles ranging from less than 1 min to 10 min. The parts are suspended on tong-type fixtures and are carried through the process by a chain conveyor on carrier bars. To facilitate rapid transfer of the tool steels, rotary transfer arms are placed between the preheat and the high heat units and between the high heat and the quench units. Transfer-arm placement is chiefly governed by the production rate; however, transfer arms are always required between the high heat and the quench units to satisfy metallurgical conditions. The lines also have areas above the furnaces to accommodate air cooling of the tools. In special cases, lines will be made with a station for an isothermal nitrate quench after the neutral salt quench. This additional stage allows rapid reduction of the temperature of the tools and reduces the air cooling time from 24 times to 6 times the time at the high-heat temperature. *Caution: If as little as 600 ppm of nitrate salts are allowed to enter the high heat furnace, extreme surface damage can be done to the tool being heat treated.*

Table 2 Relative process times and temperatures for automated heat treating of tool steels

Process stage	**Operating temperature**		Total time in furnace[(a)]
	°C	**°F**	
First preheat	650-870	1200-1600	**X**
Second preheat	760-1040	1400-1900	**X**

High heat	1010-1290	1850-2350	**X**
Isothermal quench	540-705	1000-1300	**X**
Air cool	Room temperature	Room temperature	**6X, 12X, 24X**
Wash, hot water	80-95	180-200	**6X**
Rinse, hot water	**80-95**	**180-200**	**X**

(a) See Table 3 for drill sizes and times in the high heat indicated by an "X" in this table.

Table 3 Time cycles for heat treating twist drills

Diameter		Time
mm	**in.**	
2.54-4.78	0.100-0.188	**1 min 30 s**
4.80-8.08	0.189-0.318	**1 min 40 s**
8.10-12.90	0.319-0.508	**1 min 50 s**
12.93-18.24	0.509-0.718	**2 min 0 s**
18.26-23.32	0.719-0.918	**2 min 20 s**
23.34-38.10	0.919-1.500	**2 min 40 s**
102 mm (4 in.) diam cups		**6 min**
64 mm (2 $\frac{1}{2}$ in.) diam end mills		**7 min**
76 mm (3 in.) diam end mills		**10 min**
Pieces in high heat on smaller diameters		
2.54 mm (0.100 in.) = 160 pieces/tong = 480 pieces in bath = 1.2 kg (2.6 lb)		

4.78 mm (0.188 in.) = 85 pieces/tong = 255 pieces in bath = 3.5 kg (7.65 lb)
6.50 mm (0.256 in.) = 63 pieces/tong = 188 pieces in bath = 5.6 kg (12.3 lb)
8.08 mm (0.318 in.) = 25 pieces/tong = 75 pieces in bath = 3.9 kg (8.6 lb)
12.90 mm (0.508 in.) = 16 pieces/tong 48 pieces in bath = 8.3 kg (18.2 lb)

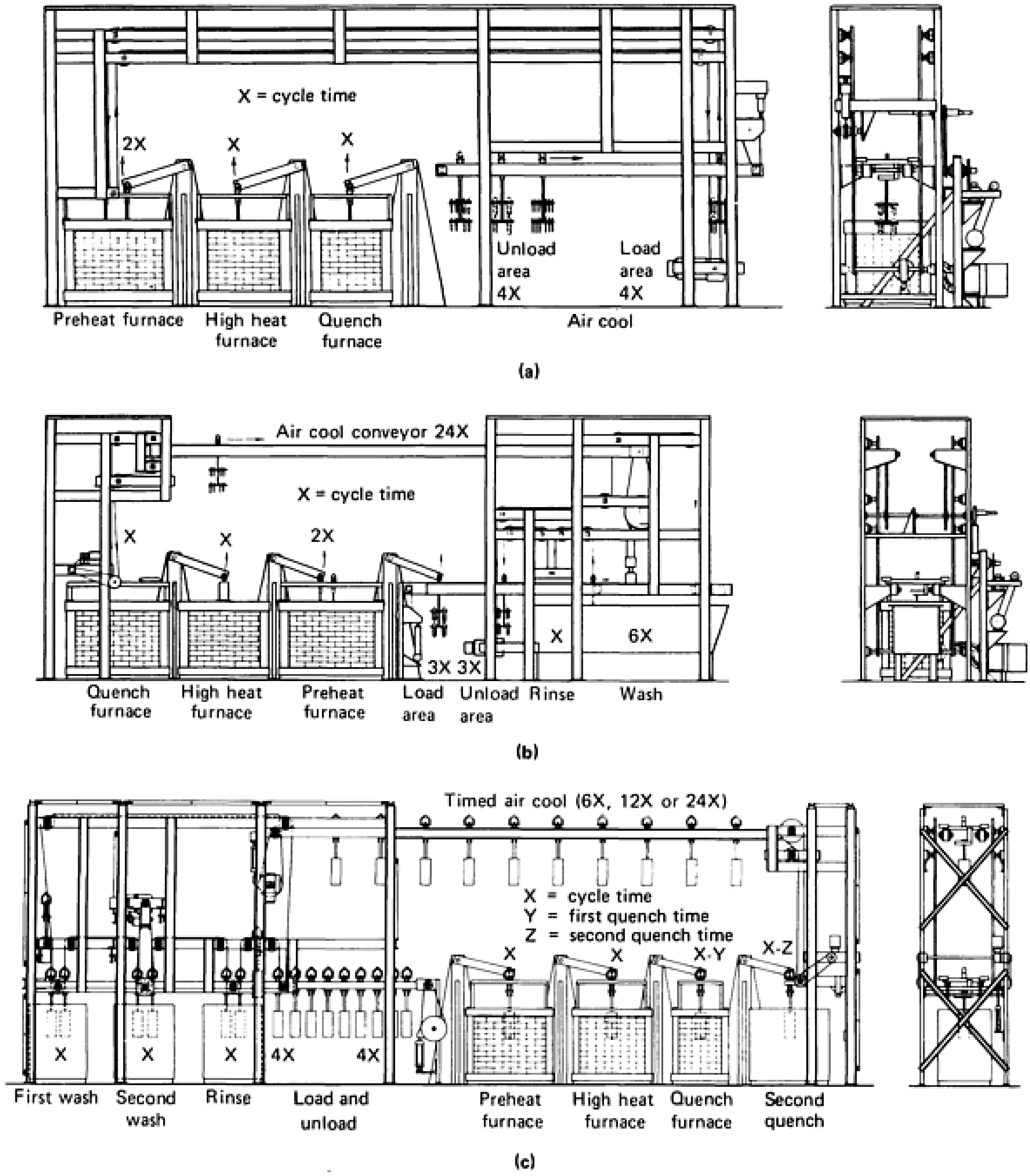

Fig. 3 Process designs for automated salt bath furnaces for heat treating high-speed tool steels. Installations can be custom designed to meet specific customer requests. (a) Does not include wash and rinse. (b) Similar to (a), but includes wash and rinse operation necessitating relocation of load and unload operations. (c) Similar to

(b), but includes second quench and a variation in wash cycles specified by customer

Rectification of Salt Baths

Neutral salts used for austenitizing steel become contaminated with soluble oxides and dissolved metals during use, resulting from a reaction between the oxide layers present on fixtures and workpieces and the chloride salts. Because the buildup of resulting oxides and dissolved metals renders the bath oxidizing and decarburizing toward steel, the bath must be rectified periodically.

Baths of salts such as salt mixtures No. 1 and 2 in Table 1 can be rectified with silica, methyl chloride, or ammonium chloride. The higher the temperature of operation, the more frequent the need for rectification. Baths in which the electrodes protrude above the surface require daily rectification with either ferrosilicon or silicon carbide. Baths operated above 1080 °C (1975 °F) require rectification a minimum of at least once a day, with more frequent rectification certainly recommended. During rectification of a bath, the silica combines with the dissolved metallic oxides to form silicates. Although these silicates settle out as a viscous sludge that can be removed, sufficient soluble silicates can remain to cause the bath to become decarburizing. If the bath is not rectified, it becomes more viscous than water. Any sludge or salts obtained as a by-product of the heat treatment must be disposed of in accordance with federal, state, and local regulations.

Methyl chloride bubbled through the bath or the submerging of ammonium chloride pellets in a perforated cage in the bath are more effective methods of rectifying salt baths. The ammonium chloride pellets react with the oxides to regenerate the original neutral salt without sludge formation or bath thickening. To remove dissolved metals from high-temperature baths, graphite rods are introduced at operating temperature. The graphite reduces any metallic oxides to metals that adhere to the rod. The metal can be scraped off and the rod reused.

To control the decarburizing tendency of high-temperature baths, test specimens frequently should be hardened by quenching in oil or brine. A file-soft surface indicates a need for more rectification. This test may be supplemented by analysis of the bath. High-heat baths containing in excess of 0.5% BaO are likely to be decarburizing to steel.

The following method can be used to rectify austenitizing baths such as salt mixtures No. 2 and 3 of Table 1:

- Add 57 g (2 oz) of boric acid for each 45 kg (100 lb) of salt, after every 4 h of operation
- Insert a 75 mm (3 in.) graphite rod into the bath for 1 h for every 4 h of operation

Controlled Atmosphere Furnaces

In selecting an atmosphere that will protect the surface of tool steel against the addition or the depletion of carbon during heat treatment, it is desirable to choose one that requires no adjustment of composition to suit various steels. An ammonia-based atmosphere (American Gas Association, or AGA, class 601) meets this requirement and has the advantage of being sufficiently reducing to prevent oxidation of high-chromium steels. In the range of dew points generally found in this gas, -40 to -50 °C (-40 to -60 °F), there is no serious depletion of carbon, because the decarburizing action is slow and any loss of carbon at the surface is partially replaced by diffusion from the interior. For applications in which high superficial hardness is important, a carburized surface can be obtained by the addition of about 1% methane (CH_4) to the atmosphere. Although ammonia-based atmosphere costs more than an endothermic gas atmosphere, this seldom becomes important because tool treating furnaces generally are comparatively small and therefore require a correspondingly small quantity of gas.

Endothermic-based atmospheres are often used for the protection of tool steel during heat treatment. Suggested ranges of dew point for an AGA class 302 endothermic atmosphere when used for hardening some common tool steels are listed in Table 4. Relatively short heating times for hardening small tools allow treatment to be carried out with the theoretical carbon balance of the atmosphere varying over a rather wide range. However, for the hardening of large die sections, the particular composition of the die steel being treated requires careful control of the atmosphere if carburization or decarburization is to be avoided during the relatively long heat-treating cycle.

Table 4 Ranges of endothermic-atmosphere dew point for hardening tool steels

Data compiled for short times at temperature; furnace dew point; AGA class 302 atmosphere

Steel	**Furnace temperature**[(a)]		Dew point range	
	°C	**°F**	**°C**	°F
W2, W3	800	1475	7 to 13	**45 to 55**
S1	925	1700	4 to 7	**40 to 45**
S2	870	1600	4 to 16	**40 to 60**
O1	800	1475	7 to 12	**45 to 55**
O2	775	1425	7 to 12	**45 to 55**
07	855	1575	-4 to 2	**25 to 36**
D2, D4	995	1825	-7 to -1	**20 to 30**
D3, D6	955	1750	-7 to -1	**20 to 30**
H11, H12, H13	1010	1850	2 to 7	**35 to 45**
T1	1290	2350	-18 to -12	**0 to 10**
M1	1205	2200	-15 to -12	**5 to 10**
F2, F3	**830**	**1525**	**5 to 1**	**23 to 34**

(a) Approximate midrange of austenitizing temperatures for the specific types of tool steels

Vacuum Furnaces

One of the most important considerations that must be met when heat treating tool steels is that the treatment must be accomplished with minimal change of the surface of the workpiece. Minimizing the exposure to air during heat treatment by minimizing or reducing the quantity of air in a vessel as with creating a partial vacuum is an excellent method for retaining workpiece surface integrity. Vacuum furnaces with pressures of 26 Pa to 1.3 mP (200 to 0.01 μm Hg) are possible with the sophisticated pumping equipment integral to vacuum furnaces.

Vacuum furnaces have historically been popular with heat-treating processes such as brazing, sintering, and outgassing. More recently, vacuum furnaces have become predominant for hardening of selected tool steels. One reason for the widespread use of vacuum furnaces is the freedom from environmental problems they afford the user. In contrast to salt bath heat treating, disposal problems are eliminated with the use of vacuum furnace heat treating. Another reason for the widespread use of vacuum furnaces is their flexibility. Vacuum furnaces can be designed for operating temperatures in excess of 2760 °C (5000 °F) and can be programmed to run an almost limitless variety of stress relieving, preheating, hardening, and quenching cycles. Design of computer hardware and software will allow these steps to be programmed individually or sequentially to enhance productivity.

Hot Wall Furnaces. Until recently, vacuum furnaces were inhibited by technical considerations in their use for hardening of tool steels. Two factors limited their use of vacuum furnaces in early hot wall designs. First, the retort in which the vacuum was developed lost considerable strength when it was heated and would tend to collapse. Secondly, a retort was limited in the type of cooling or quenching techniques which are required by tool steels.

Cold Wall Furnaces. Vacuum furnaces now incorporate a heating unit inside a vacuum chamber that is of double-wall construction. Between the two walls, water or coolant is circulated for effective cooling of the vacuum chamber, therefore enabling high-temperature operation. These cold wall vacuum furnaces have been designed by various manufacturers and offer countless variations in size, pumping capacity, heating capacities, quenching methods, speed, computerization, and so on.

In cold wall furnaces, the electric heating elements are located inside the retort. The heating elements can be made of a refractory metal (molybdenum) or from graphite rods or cloth. The heating elements are surrounded by refractory metal baffles to provide insulation and direct radiant reflection. Centered or positioned within the furnace is a refractory (metal) hearth on which a fixtured or basketed work load can be positioned.

Single-Chamber Vacuum Furnaces. A simple vacuum furnace (Fig. 4) consists of one chamber in which the workpiece is both heated and cooled. Cooling or quenching is accomplished by back filling or blowing inert gas across the workpieces. In order to quench rapidly enough to obtain the desired microstructure of tool steel, it is necessary to increase the pressure of the quench gas (usually nitrogen). This is accomplished by high-velocity, high-pressure blowers which have reported cooling gas pressures of up to 60 kPa (6 bar).

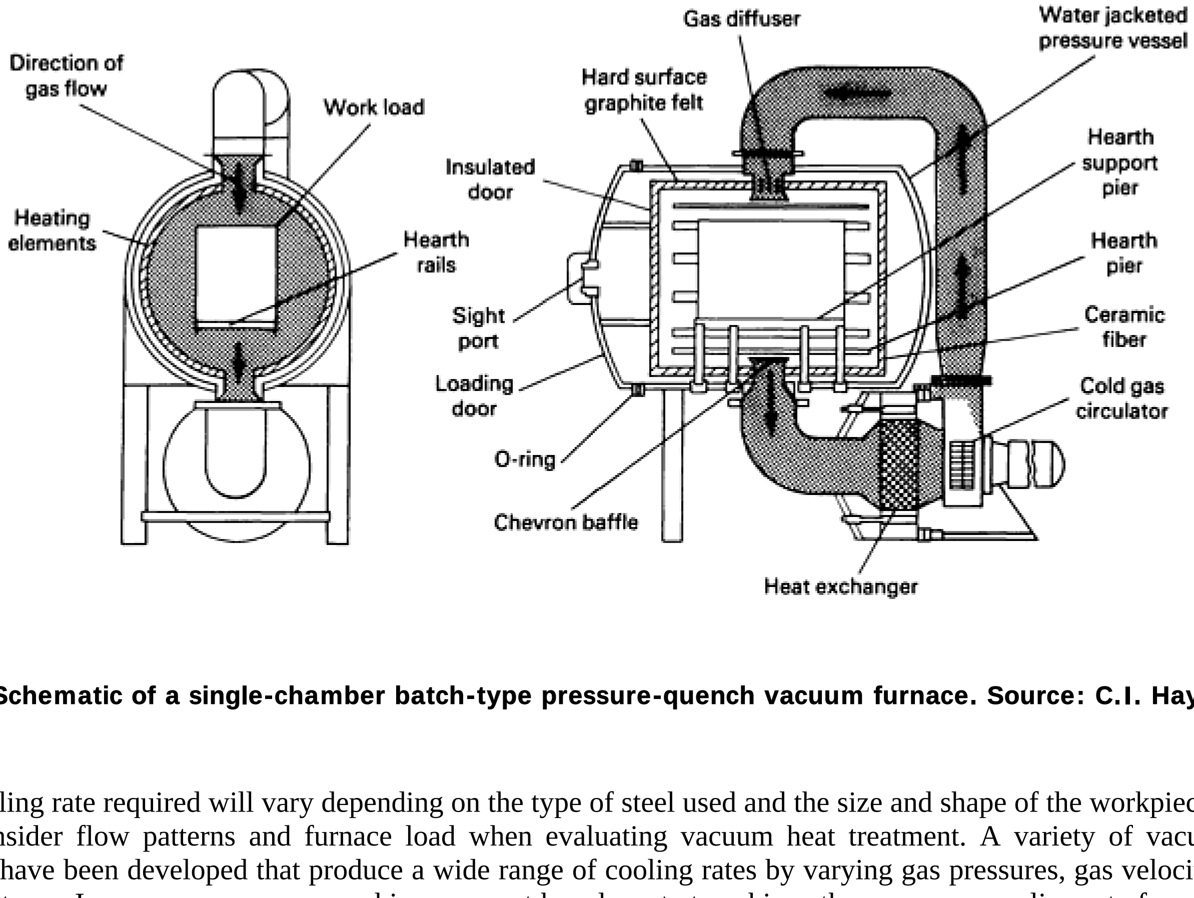

Fig. 4 Schematic of a single-chamber batch-type pressure-quench vacuum furnace. Source: C.I. Hayes, Inc.

The cooling rate required will vary depending on the type of steel used and the size and shape of the workpiece. One must also consider flow patterns and furnace load when evaluating vacuum heat treatment. A variety of vacuum furnace designs have been developed that produce a wide range of cooling rates by varying gas pressures, gas velocities, and gas flow patterns. In some cases, gas quenching may not be adequate to achieve the necessary cooling rate for a component, and other quenching methods may need to be considered (that is, salt bath, fluidized bed, or oil quenching) (see Table 1).

Multiple-chamber vacuum furnaces or integrated quench furnaces have been designed to improve throughput or enhance quench rate. Vacuum furnaces typically have thermocouples available at several locations in the furnace as well as on the surface of the load or within the confines of the load itself.

Multiple-chamber furnaces (see Fig. 5) allow nearly continuous hardening of components. In such systems three chambers of modules exist:

- A purge (loading chamber)
- A multiple-zone heating chamber
- A quench chamber

A loaded tray automatically moves into the purge chamber where decompression begins. Once the vacuum level is similar to the level in the heating chamber, the tray or basket is moved through an insulated door for heating. Heating is accomplished by transfer through multiple preheating zones and one final high-heat zone. Meanwhile, another tray has moved into the purge chamber. Once the preprogrammed time interval has elapsed in the high-heat zone, the basket is transferred to the final quench chamber for immersion. Ultimately, the basket is transported from the quench chamber through a door to an unloading tray.

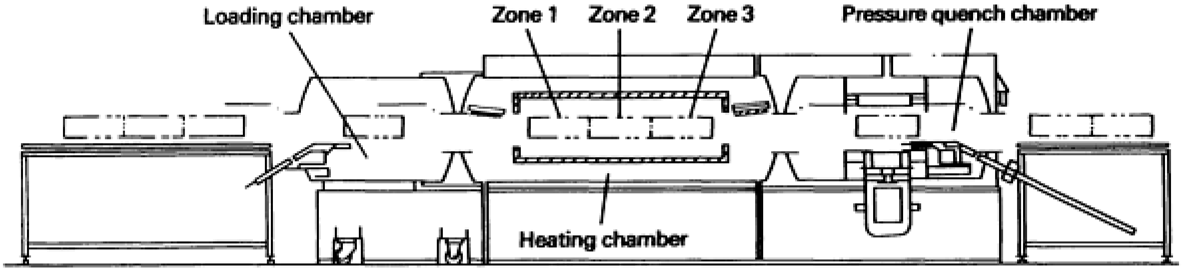

Fig. 5 Schematic of a typical in-line multiple-chamber vacuum furnace. Source: C.I. Hayes, Inc.

Additional information is available in the article "Heat Treating in Vacuum Furnaces and Auxiliary Equipment" in this Volume.

Furnace Kinetics. The suitability of a vacuum furnace to harden a particular component is governed by many factors, not the least of which is the quenching capability. With gas quenching, the effects of gas variables such as pressure, velocity, and flow patterns are significant.

Fundamentally, in the cooling of any steel, the process is limited by:

- Gas parameters which control the rate of heat from the surface of the component (surface thermal resistance)
- Component parameters which control the rate of heat transfer within the component from the center to the surface (component thermal resistance effect) of the workpiece

In general, the gas parameters predominate in determining the cooling rate in large diameter components (greater than 250 mm, or 10 in., diameter). Both types of parameters must be taken into consideration.

Gas Parameters. The gas parameter constituent of heat removal is described by the following equation:

$$Q = h\,A \cdot \Delta T \qquad \textbf{(Eq 1)}$$

where Q is the heat removal rate, h is the heat transfer coefficient, A is the surface area of component, and ΔT is the temperature difference between the component and the gas.

During the initial cooling period, the gas temperature has only a minor effect on the workpiece. However, after this initial cooling period, the component cooling rate becomes increasingly sensitive to changes in gas temperature with the cooling rate decreasing as the gas temperature increases.

Two important features of furnace design that affect gas temperature are:

- Heat exchanger type, location, and size, because these factors control the bulk gas temperature into the furnace
- Flow distribution, which controls the local gas temperature around the workpiece

High gas temperatures usually occur only in the initial cooling period of a workpiece, when the effect of gas temperature, as discussed previously, is minimal.

The effect of heat transfer coefficient on the cooling rate of a 25 mm (1 in.) diameter slug is shown in Fig. 6.

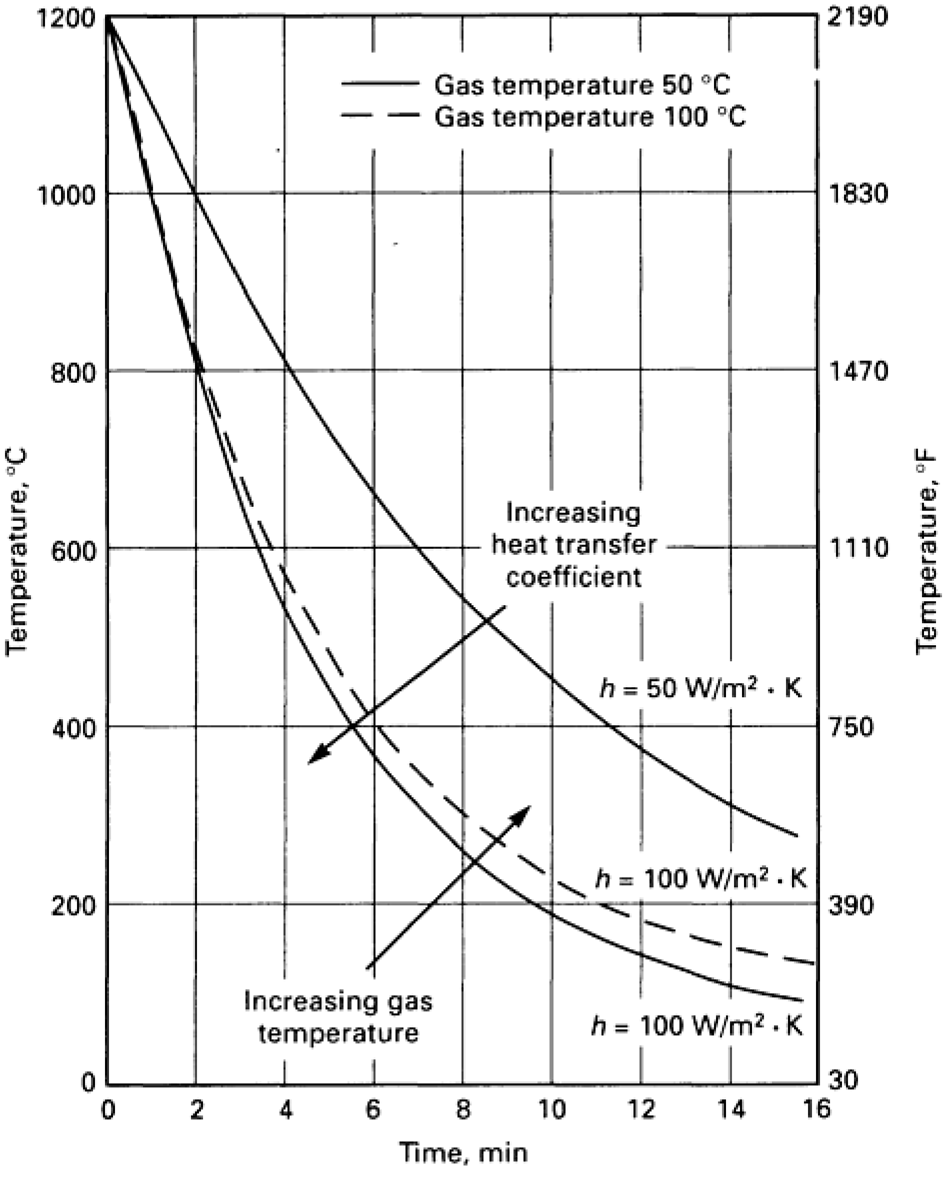

Fig. 6 Plot of temperature versus time showing the effect of gas temperature and heat transfer coefficient, *h*, on the cooling of 25 mm (1 in.) diam steel slugs. Source: Ref 1

The heat transfer coefficient, *h*, for a given gas is related to local gas velocity, *V*, and gas pressure, *P*, as follows:

$$h = C(VP)^m \qquad \textbf{(Eq 2)}$$

where m and C are constants which depend on the furnace type, component size, and workload configuration.

Equal increases in either the local gas velocity or the pressure have the same effect on the heat transfer coefficient and hence on the cooling rate of a component.

The effect of increased gas velocity on cooling is shown in Fig. 7. Local gas velocities were increased around the 25 mm (1 in.) diameter components by increasing the gas flow rate from 2.1 m^3/s (4400 ft^3/min) to 3.5 m^3/s (7500 ft^3/min). The effect of increased gas pressures on the cooling of similar components is shown in Fig. 8.

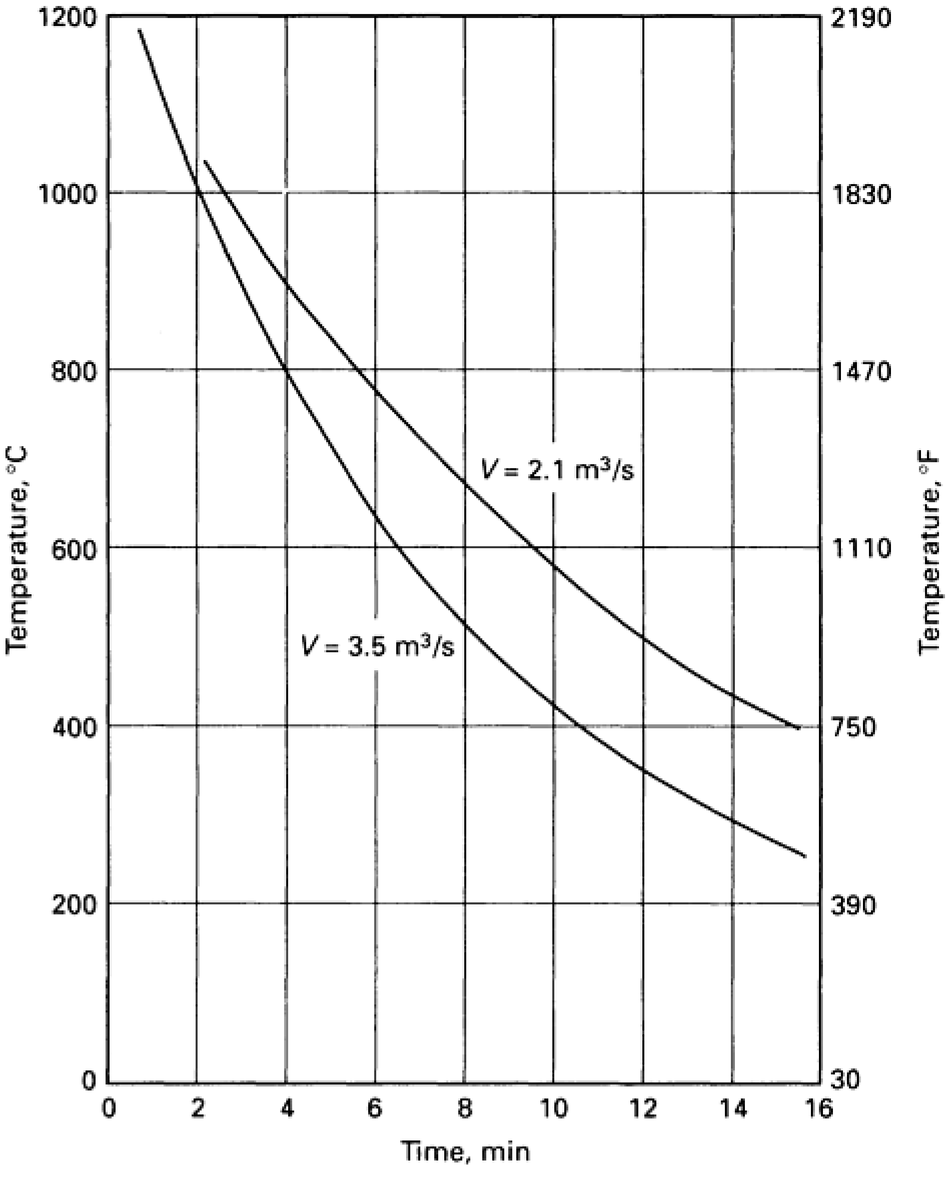

Fig. 7 Plot of temperature versus time showing the effect of local gas velocity, *V*, on the cooling of 25 mm (1 in.) diam steel slugs. Slugs are cooled with 105 kPa (15 psig) N_2 quench gas. Load size is 836.4 kg (1844 lb). Source: Ref 1

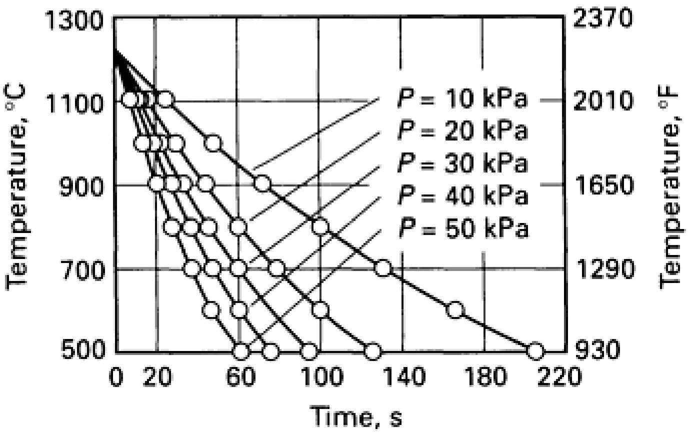

Fig. 8 Plot of temperature versus time showing the effect of nitrogen gas pressure, *P*, on the cooling of 25 mm (1 in.) diam by 48 mm ($1\frac{7}{8}$ in.) long M2 tool steel slugs. Source: Ref 1

Two practical considerations to be taken into account when increasing either gas velocity or pressure are:

- High-pressure vacuum furnaces are required to be designed and built to stringent safety regulations
- Increases in both gas velocity and pressure affect the design of the blower and the power required to recirculate the gases (doubling the gas velocity increases the blower power by a factor of eight, while doubling the gas pressure only increases the blower power by a factor of two)

The heat transfer coefficient, *h*, is also a function of the gas properties. The effect of four gases on the cooling of 25 mm (1 in.) diameter slugs is demonstrated in Fig. 9. Nitrogen is usually the gas of choice because:

- Hydrogen is explosive and must be used with extreme care
- Helium is expensive
- Argon gives poor cooling rates

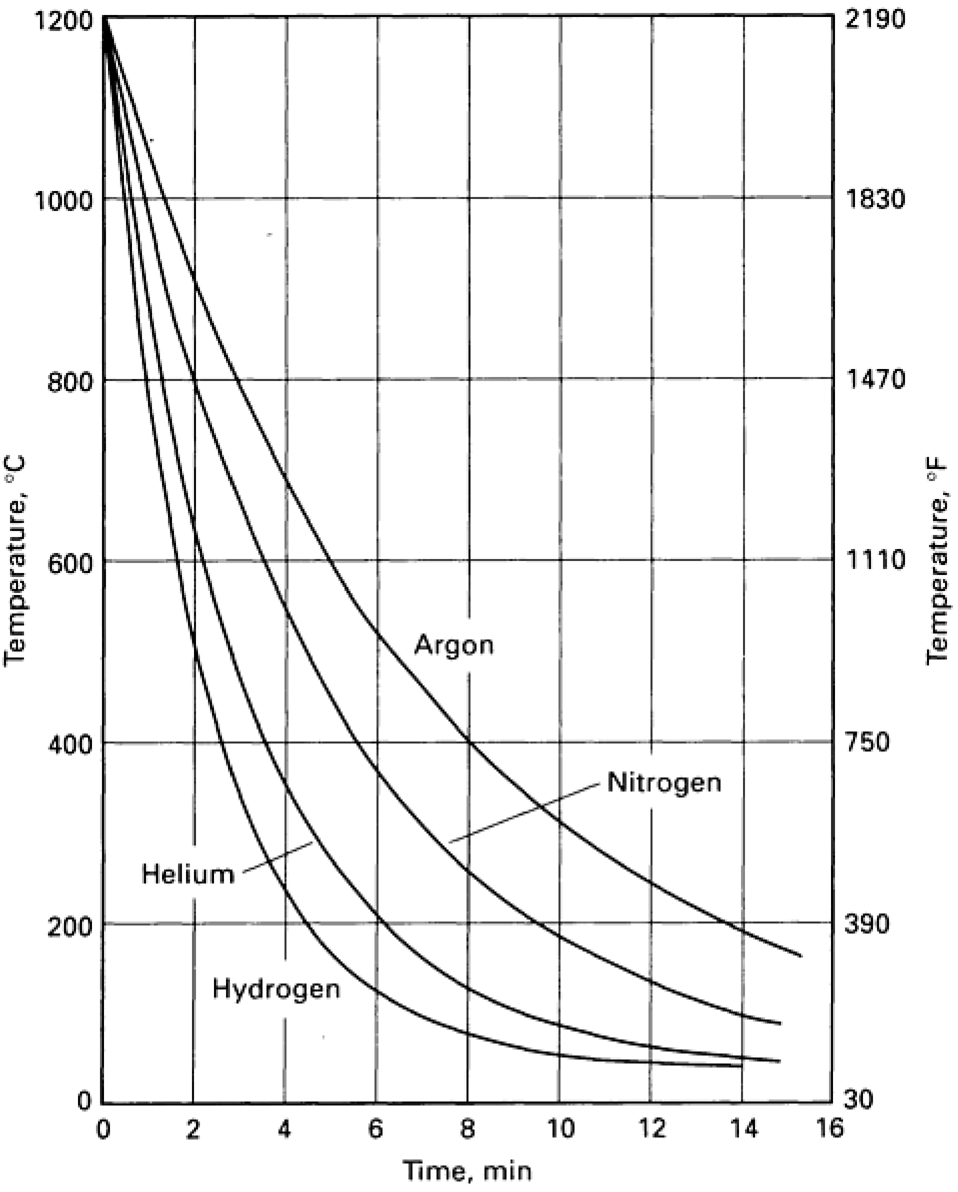

Fig. 9 Plot of temperature versus time showing the effect of selected gases on the cooling of 25 mm (1 in.) diam tool steel slugs. Source: Ref 1

Thus, it is evident that the cooling rates of steel components are not only determined by gas parameters such as gas temperature, gas velocity, and gas pressure but also depend on the physical properties (that is, conductivity, density, and viscosity) of the gas itself.

In practice, it is the gas velocity and the gas pressure that are the most significant factors in controlling component cooling rates.

Component Parameters. Component size, shape, and material properties control the rate of heat transfer within components from the center of the material core to the surface of the material. Material properties (that is, density, specific heat, and thermal conductivity) vary only marginally from one steel to another and hence have been considered constants for the purpose of this discussion. Component size and shape can vary greatly.

The effect of diameter on cooling is shown in Fig. 10. At the surface of the component, the cooling rate is inversely proportional to the component diameter; thus, increasing the diameter by a factor of two decreases the cooling rate by a factor of two. The temperature at the center of the component lags behind the temperature at the surface of the

component. This effect is more clearly shown in Fig. 11, where the ratio of surface temperature to center temperature of the component is plotted over a wide range of diameters and heat transfer coefficients.

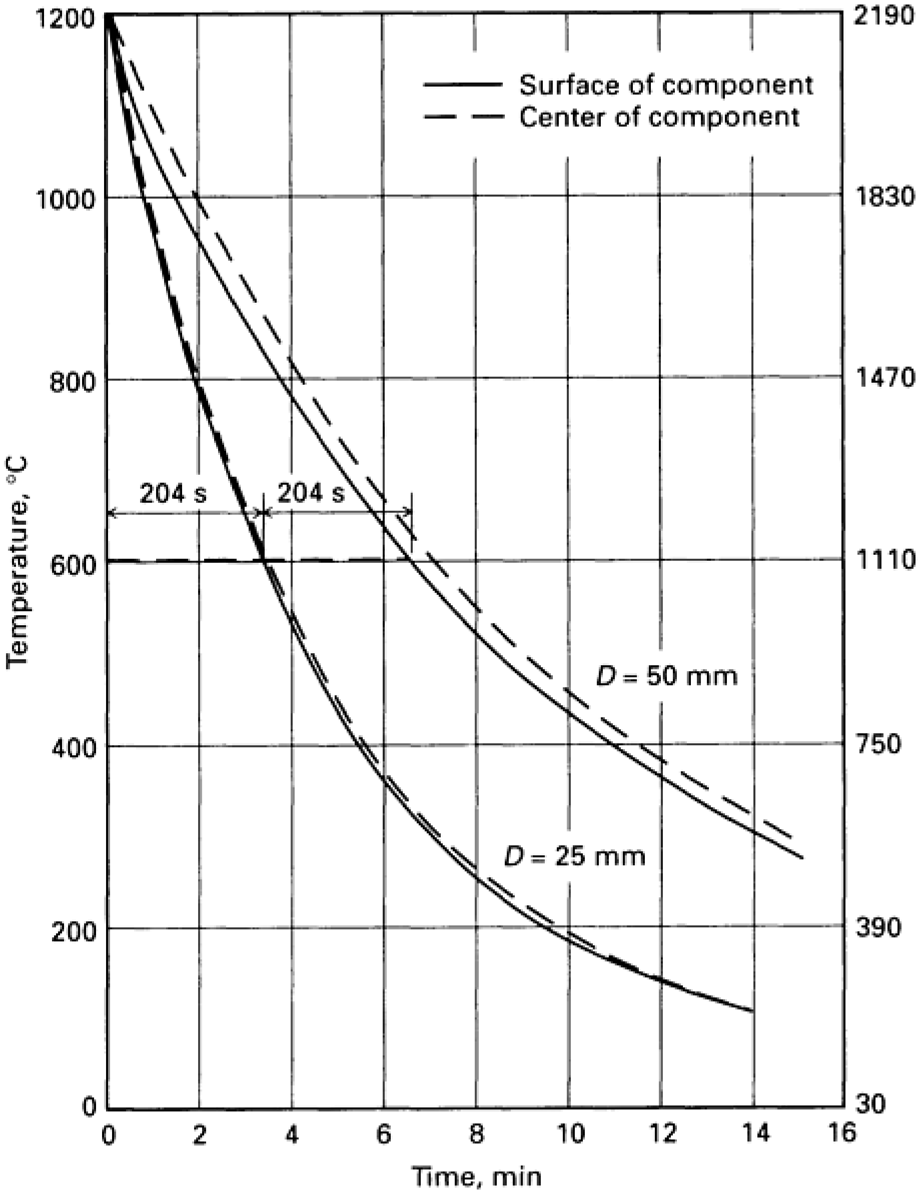

Fig. 10 Plot of temperature versus time showing the effect of varying diameter, *D*, on the cooling of tool steel slugs. Source: Ref 1

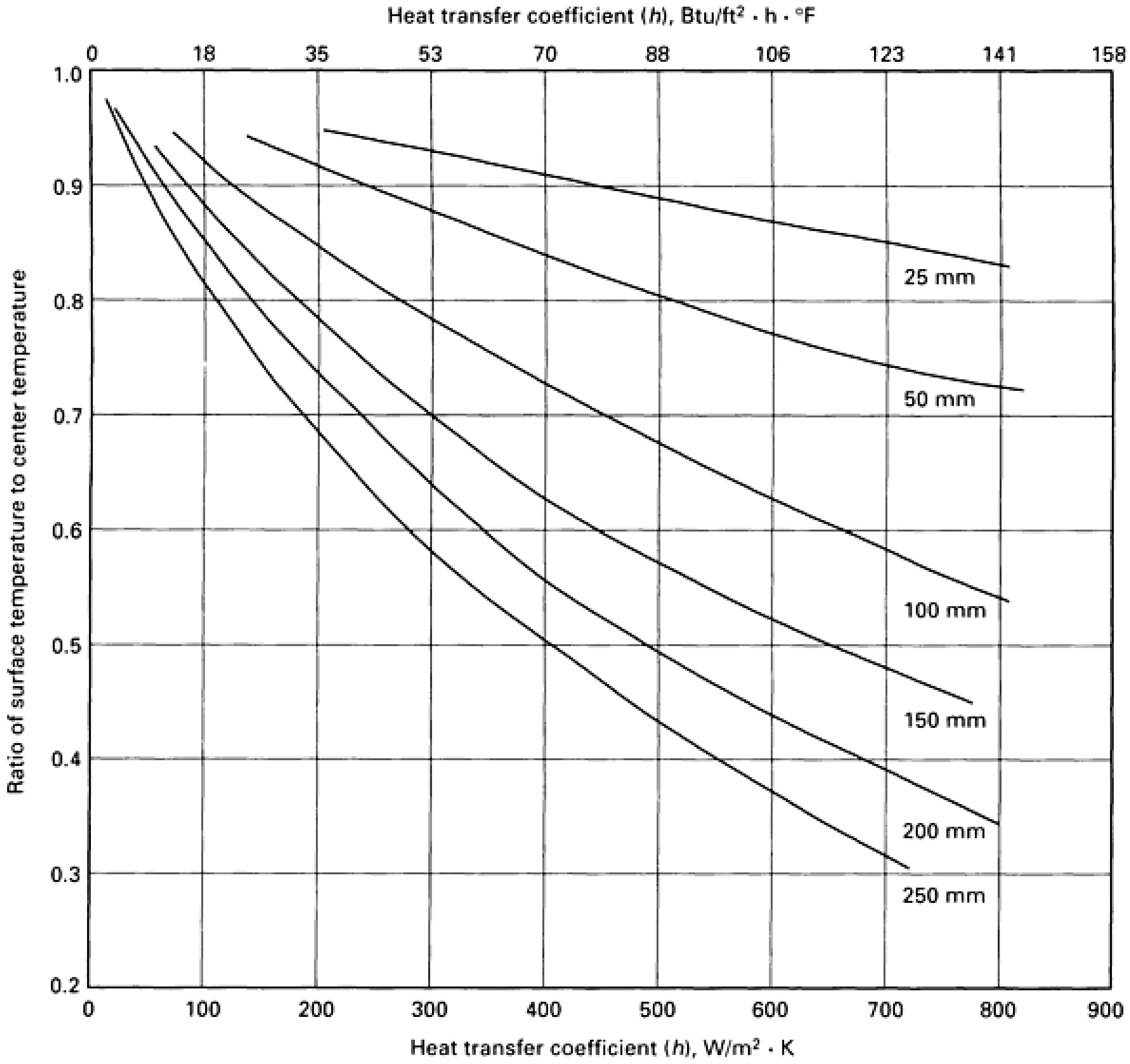

Fig. 11 Plot of surface-to-center temperature ratio versus the heat transfer coefficient to show the effect of varying tool steel slug diameters ranging from 25 to 250 mm (1 to 10 in.). Source: Ref 1

At low heat transfer coefficient values, gas parameters predominate over the cooling rate and negligible differences exist between the temperature at the surface and the temperature at the center of the component. As the heat transfer coefficient is increased, the component parameters begin to restrict the cooling rate of the component and large differences begin to develop between the temperature at the surface and the temperature at the center of the component. These temperature differences can cause distortion and cracking in large diameter components.

It is usually the cooling rate at the center of the component that is of most interest. The variation in center cooling rate in M2 tool steel over the temperature range 1200 to 600 °C (2190 to 1110 °F), is plotted for a range of heat transfer coefficients in Fig. 12.

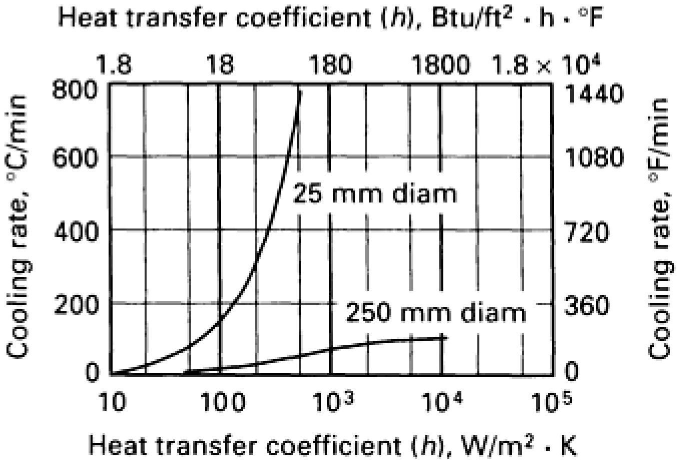

Fig. 12 Plot of cooling rate at the center of the slug versus the heat transfer coefficient of M2 tool steel to show effect of varying diameters over the temperature range of 1200 to 600 °C (2190 to 1110 °F). Source: Ref 1

For the large 250 mm (10 in.) diameter component, the center cooling rate increases only marginally with large increases in the heat transfer coefficient when compared to increases in the center cooling rate gained in a small component. For such large diameter components, even fast oil or salt quenching (*h* is approximately 1000 to 5000 $W/m^2 \cdot K$, or 200 to 900 $Btu/ft^2 \cdot h \cdot °F$) may not provide the center cooling rate required to develop the desired steel hardness properties.

Two important conclusions drawn from this discussion of how component parameters affect cooling rates are:

- High heat transfer coefficients can cause large variations in temperature between the center and surface of components (particularly as the diameter increases) that may result in cracking and/or distortion
- Even high heat transfer coefficients may not be able to cool the center of large diameter components fast enough to harden them adequately

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Fluidized-Bed Furnaces

Fluidized-bed furnaces offer another method of heat treating tool steels (see also the article "Fluidized-Bed Equipment" in this Volume). This method uses a solid rather than a liquid or gas for the heat transfer medium. In general, the furnace is composed of a layer of small mobile particles of an inert refractory (for example, aluminum oxide or silica sand) in a container which is heated and fluidized by a flowing stream of gas. Objects to be heat treated are immersed directly into the bed of particles.

A fluid bed results when a gas is passed upward through a bed of small solid particles at a rate fast enough to lift these particles and to create turbulence. This motion of particles, similar to that of a fluid, is shown in Fig. 13. When gas is forced upward through small holes in a supporting plate, two forces meet to raise the particles: the buoyancy of the gas and the retarding force known as aerodynamic drag.

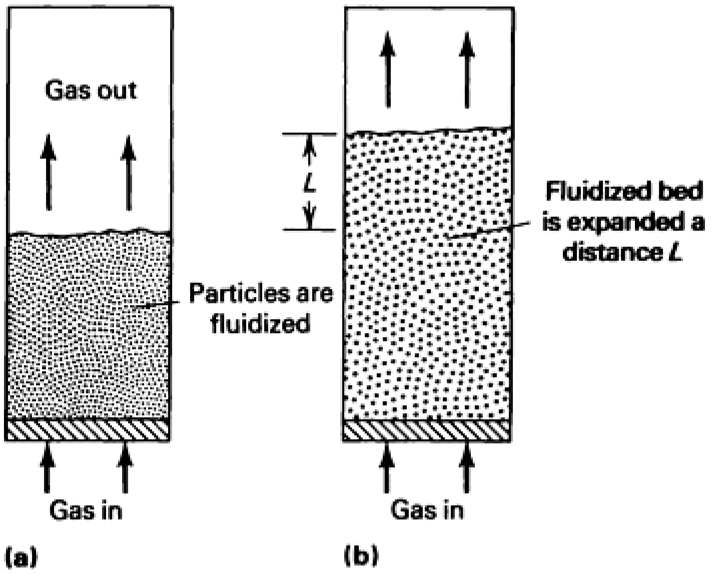

Fig. 13 Schematic showing principle of the fluidized-bed furnace. (a) Initially, the gas flows upward through the permeable base to agitate the particles as the pressure is gradually increased. (b) Eventually, the gas flow is sufficient to lift the small particles of refractory materials and to transform the particle movement into a violent turbulent motion. Although the particles are actually solid, the fluidized bed simulates the motion of a liquid. Source: Ref 2

Most fluidized-bed furnaces are used at temperatures below 1095 °C (2000 °F), although some manufacturers have furnaces capable of treating components to temperatures through 1205 °C (2200 °F). This temperature limitation is related to the exposure damage or wear and tear on the retort materials. Fluidized beds have been designed to perform a wide variety of heat-treating tasks including stress relieving, preheating, hardening, quenching, annealing, and tempering as well as a variety of surface treatments such as carburizing, nitriding, and steam tempering. This discussion will deal primarily with aspects of neutral hardening of tool steels.

Heat transfer with fluidized-bed furnaces is particularly good and offers characteristics approaching that of molten salt bath furnaces. Heating properties of the fluid bed can be adjusted through a wide range because there are many parameters that can be varied. Some of the major variable parameters are:

- Particle properties (size, shape, bulk density, and absolute density)
- Properties of the gas used to fluidize the bed (density, viscosity, heat capacity, and thermal conductivity)
- System properties (flow of gas through the bed, total weight of the particles in a given bed, cross section and shape of the retort or bed container, and type of permeable plate used to support the particles)

One of the major attributes of the fluidized bed is the high rate at which heat can be transferred from the bed of particles to an immersed object. Coefficients of heat transfer on the order of 400 to 740 $W/m^2 \cdot K$ (70 to 130 $Btu/ft^2 \cdot h \cdot °F$) are possible. This heat flow rate is two to ten times higher than that provided by normal convection or radiation. In addition, the rate of heat transfer in the full bed is relatively independent of the emissivity of the object which is immersed and the temperature level. The turbulence of the fluidized bed is important in mixing and can effectively minimize thermal gradients within the bed.

Figure 14 illustrates the nature of heat transfer in a fluidized bed. Under curve 1, the bed is nonfluidized in a static state with low heat transfer rates that increase only slightly with velocity. After the minimum fluidization velocity (V_{mf}) is reached, the heat transfer coefficient, h, increases rapidly over a comparatively narrow velocity range (curve 2). At a certain optimum velocity (V_{opt}), the heat transfer coefficient reaches a maximum (h_{max}) and then tends to diminish as the fluidized bed attains more gas-like properties (curve 3). The actual heat transfer rate experienced in the fluidized bed depends on the fluidizing gas velocity and its thermal conductivity, the size and density of the bed particles, their thermophysical properties, and on the geometry and structural design features of the furnace. Generally, the principal

parameter, other than velocity, that affects the heat transfer coefficient is the particle size with the coefficient rising as the particle diameter is decreased. These parameters result in heat transfer coefficients as high as 570 W/m^2 · K (100 Btu/ft^2 · h · °F), which is up to five times that which can be obtained in a conventional open-fired furnace and is similar to that obtained in liquid baths. The comparison of the heating rate in a fluidized-bed furnace with other typical modes of heating is shown in Fig. 15.

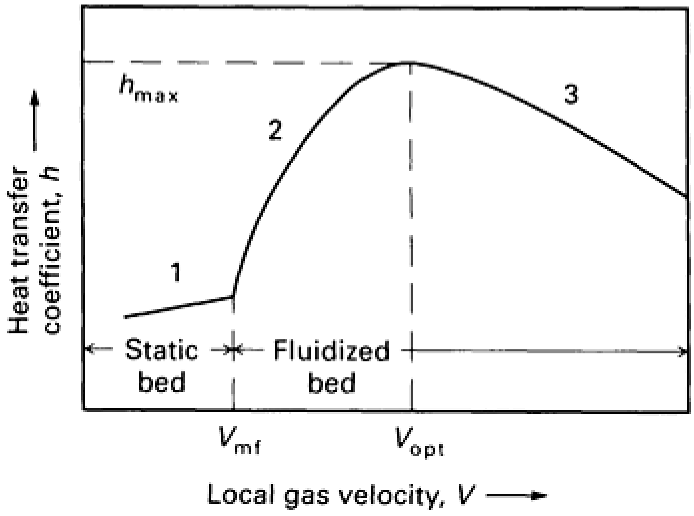

Fig. 14 Heat transfer coefficient rises with the increase in velocity of the fluidized bed until a peak value, h_{max}, is reached at the optimum velocity V_{opt}. Source: Ref 3

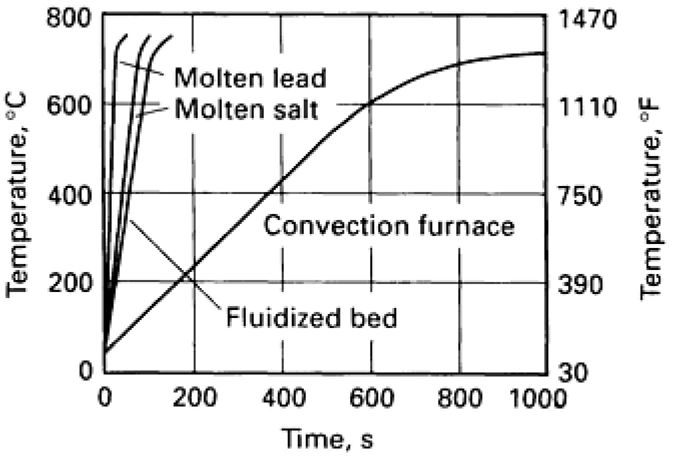

Fig. 15 Fluidized-bed heating compared with conventional immersion (molten salt and molten lead baths) and convection heating methods for 16 mm ($\frac{5}{8}$ in.) diam steel bars. Source: Ref 3

Fluidized-bed heat-treating furnaces are manufactured by several suppliers and are available in three fundamental configurations. Two of the configurations are fluidized by the products of combustion and are known as internally fired and externally fired types. For the third configuration, known as the indirectly heated type, the fluidization and the heating are accomplished independent of one another. The indirectly heated type is most often used for neutral hardening and therefore is more applicable to tool steel heat treating.

Because the heating and fluidization modes of an indirectly heated fluidized-bed furnace are independent of one another, this type of furnace is used where special atmospheres are required by the product. Literally, any gas may be used for fluidization and this type of furnace can accommodate a wide range of processes such as carburizing, carbonitriding,

steam treating, and bright annealing. An example of an indirectly heated fluidized-bed furnace is shown in Fig. 16. Although the furnace shown is heated electrically, it should be emphasized that a fluidized-bed furnace may also be fuel fired (simply by replacing the electric elements on the outside with a suitable burner system) or both fuel fired and electrically heated. In special configurations, furnaces may also be cooled to operate at subambient temperature conditions.

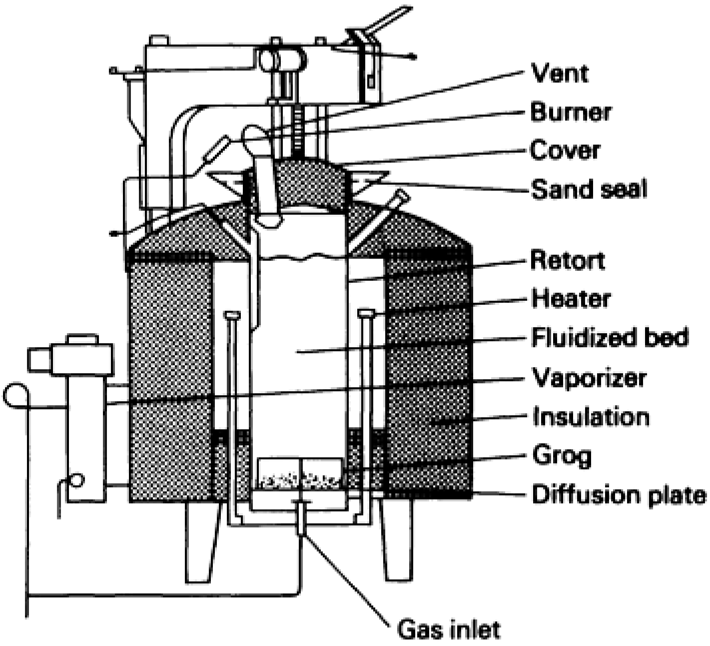

Fig. 16 Schematic of an indirectly heated fluidized-bed heat-treating furnace. The gas enters the furnace from the supply line on the bottom left. Source: Ref 4

The fluidized-bed particles offer some similarities to salt baths and can provide a supporting neutral environment. The fluidized particles do not collect on the work surface and therefore there is no dragout or subsequent cleaning required. The aluminum oxide or silica oxide particles can become contaminated but are typically not considered an environmental hazard as are lead and salt compounds used in the other heat treat methods. The workpiece, upon removal from the high-temperature bed, can, however, be exposed to surface contamination such as decarburization during transfer to a quenching media. Because multiple fluidized-bed furnaces or a combination of furnaces are typically used in conjunction with each other during tool steel heat treatment, such factors must be considered in the overall layout of a heat treat department.

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Heat Treating of Specific Classes of Tool Steels

Introduction

HEAT-TREATING PROCEDURES vary significantly among classes of tool steels and with intended application. The preferred heat-treating and hardening procedures, as well as mechanical properties and applications are discussed in this

article with respect to: water- and air-hardening tool steels, oil-hardening and high-carbon, high-chromium cold-work steels, low-alloy and special-purpose high-speed tool steels, and shock-resisting tool steels. Specific examples of heat-treating procedures for specific applications for hot-work tools are given.

Water-Hardening Tool Steels

Water-hardening tool steels containing 0.90 to 1.00% C are the most widely used. Carbon content affects heat-treating temperatures as indicated in Table 1, which outlines recommended heat-treating practices for these steels.

Table 1 Recommended heat-treating practices for water-hardening tool steels

Temperature		**Carbon content**	**Hardness after treatment**	Procedure
°C	**°F**			
Normalizing				
815	1500	0.60-0.75	. . .	**Heat through uniformly; hold for 15 min (light sections) to 1 h (heavy sections), then air cool**
790	1450	0.75-0.90		
870	1600	0.90-1.10		
870-925	1600-1700	1.10-1.40		
Annealing				
740-760	1360-1400	0.60-0.90	156-201 HB	**Heat through uniformly; hold for 1-4 h[a]; furnace cool to 510 °C (950 °F) at 22 °C/h (40 °F/h), then air cool**
760-790	1400-1450	0.90-1.40		
Hardening[b]				
790-845	1450-1550	0.60-0.80	65-68 HRC	**Hold at austenitizing temperature for 10-30 rain; quench in water or brine (very small pieces may be oil quenched)**
775-845	1425-1550	0.85-1.05		
760-830	**1400-1525**	**1.10-1.40**		

(a) Holding times vary from about 1 h, for light sections and small furnace charges, to about 4 h, for heavy sections and large furnace charges.

(b) For large tools and tools with intricate sections, preheating at 565 to 650 °C (1050 to 1200 °F) is recommended.

As a class, water-hardening tool steels are relatively low in hardenability, although they are arbitrarily classified and available as shallow-hardening, medium-hardening, and deep-hardening types. Their low hardenability is frequently an advantage, because it allows tough core properties in combination with high surface hardness. Low cost and adaptability to simple heat treatment are additional advantages offered by these steels.

Water-hardening tool steels are so termed because they are most commonly quenched in an aqueous medium. There are exceptions, however; for example, thin sections may be satisfactorily quenched in oil with less distortion and danger of cracking than if quenched in water or brine.

Example 1: Analysis of Maximum Diameter in Oil-Quenched Water-Hardening Steel Punch Yielding Minimum 60 HRC Hardness at Selected Austenitizing Temperatures.

In one plant, it was desirable to harden small-diameter punches in oil to reduce breakage and consequent downtime of the presses. A study was made to determine the maximum diameters of water-hardening tool steels that could be fully hardened to a minimum of 60 HRC by oil quenching. Results of the study, indicating the relationship between austenitizing temperature, type of steel, and punch diameter, are shown in Fig. 1.

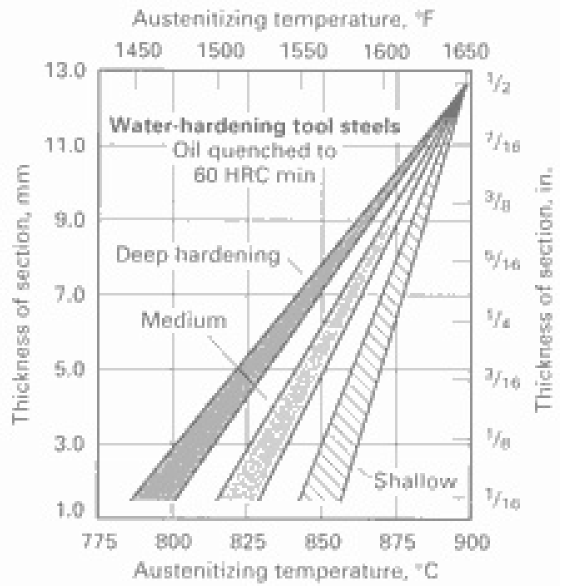


Fig. 1 Maximum section thicknesses of 3 classes of water-hardening tool steels that will develop minimum hardness of 60 HRC when oil quenched from various austenitizing temperatures

Experimentation proved that a greater degree of uniformity was obtained if the punches were normalized prior to hardening. Normalizing temperatures applied were: 870 °C (1600 °F) for punches up to 6.4 mm ($\frac{1}{4}$ in.) in diameter; 900 °C (1650 °F) for those over 6.4 mm ($\frac{1}{4}$ in.) in diameter. As indicated in Fig. 1, austenitizing temperature varied from 790 to 900 °C (1450 to 1650 °F), depending on punch diameter. The punches were austenitized by being heated vertically in a neutral salt bath. They were also quenched vertically, in a compounded oil containing additives. The quenching oil was maintained at 50 to 60 °C (120 to 140 °F) and circulated up and around workpieces at 190 L/main (50 gal/min).

Normalizing. Except in special instances where experience has proved it beneficial (as in the preceding example), normalizing is not recommended for water-hardening tool steels as received from the supplier. Normalizing is recommended for these steels after forging or before reheat treatment, for refining the grain and producing a more uniform structure. Recommended normalizing temperatures are given in Table 1; as indicated, optimum temperature varies with carbon content.

Decarburization during air cooling will be minimized if parts are heated in a protective atmosphere or a neutral salt bath. Parts heated in salt are additionally protected during the cooling period by the film of salt that adheres to their surfaces when they are removed from the salt bath. After parts have cooled, the film of salt can be easily removed (except from recesses such as tapped holes) by a water rinse. Additional information is available in the article "Normalizing of Steel" in this Volume.

Annealing. Tool steels of the W types are received from the supplier in the annealed condition. Thus, annealing by the user is usually unnecessary. Annealing is applied to forged or cold-worked carbon tool steel to soften it for easier machining, to relieve residual stress, and to produce a structure suitable for hardening. Annealing may be done in an atmosphere furnace (provided the furnace is of a type that can be cooled slowly to below 540 °C, or 1000 °F), in a vacuum, or in an ordinary air furnace after the piece has been protected against surface decarburization by being packed in a suitable container with an inert material. Protection against decarburization (but not against oxidation) may be obtained also by copper plating the surface or by applying a surface-protecting paint. (Not all of these paints are equally effective, and some are difficult to remove; the prospective user should investigate such a paint by trying it under his conditions of operation and then inspecting the treated part for decarburization.) The workpiece should be heated to the annealing temperature (Table 1) and held at temperature for from 1 h, for thin sections, to about 4 h, for heavy sections. When the steel has been placed in a pack to prevent surface reactions, a general rule of thumb is to allow the assembly to soak at temperature for 1 h per inch of pack cross section. Work should then be cooled in the furnace at a rate not exceeding 22 °C/h (40 °F/h), to 510 °C (950 °F). Below this temperature, cooling rate is not critical. Hardness after annealing should be in the range of 156 to 201 HB.

Stress relieving prior to hardening is sometimes employed to minimize distortion and cracking. The procedure consists of heating the work to 650 to 720 °C (1200 to 1325 °F) and cooling in air. Usually, stress relieving of water-hardening tool steel is limited to complex or severely cold-worked parts.

Example 2: Elimination of Cracking in a W2 Piston by Stress Relieving Prior to Hardening.

A piston of W2 steel for a pneumatic clay digger varied in section thickness by as much as 6 to 1. Cracking occurred in the cupped end section when the pistons were hardened by conventional practice. Stress relieving or preheating at 675 °C (1250 °F) prior to hardening eliminated this difficulty.

In most instances, stress relieving after hardening and grinding is not employed. Periodic stress relieving of tools that have been in service will reduce the stresses imposed by such service, and is believed to be beneficial in extending service life. Temperatures used for this purpose should never exceed those used for tempering the steel after hardening.

Austenitizing temperatures for water-hardening tool steels normally vary from 760 to 845 °C (1400 to 1550 °F), as indicated in Table 1. Higher temperatures are sometimes used for special purposes (Fig. 1). Hardenability increases as austenitizing temperature increases. The optimum time at austenitizing temperature is from 10 to 30 min. Preheating is unusual except for very large tools or those with intricate cross sections (such as the W2 piston cited in Example 2).

If surfaces are to be protected against scaling or decarburization, an atmosphere furnace, lead bath, or salt bath is required. It is particularly important to protect shallow-hardening steels against scaling and decarburization. Severe scaling can interfere with heat transfer during quenching and slow the required high rate of cooling. Decarburization will produce a soft surface on any tool steel, but in a deep-hardening steel it can be ground off until the underlying hard high-carbon area is reached. Grinding a shallow-hardening steel will frequently expose the soft core.

Atmospheres. Excellent results are obtained by austenitizing water-hardening tool steels in a slightly oxidizing atmosphere, as the data in Fig. 2, obtained in tests on type W2, indicate. Oxidizing atmospheres are inexpensive, and are usually produced by controlled direct-firing burners. The light scale that is produced is removed by the vigorous water or brine quench.

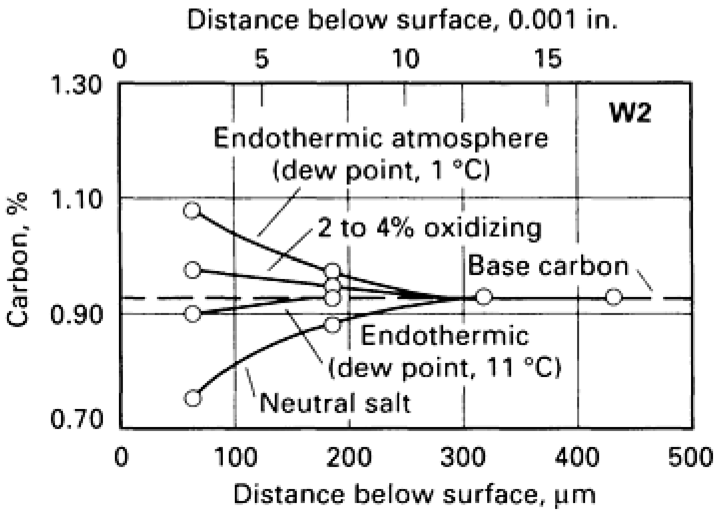


Fig. 2 Effect of furnace atmosphere on the surface carbon content of W2 tool steel. Specimens were heated at 790 °C (1450 °F) for 1 h, quenched in brine, annealed in lead at 705 °C (1300 °F), and machined in 0.13 mm (0.005 in.) cuts for analysis.

Endothermic atmospheres also are used, but close control is necessary to match the carbon potential of the atmosphere to the carbon content at the surface (Fig. 2). Also, endothermic installations are more expensive than the controlled-burner technique mentioned above.

Salt baths are widely used and frequently preferred over other heating mediums for hardening type W tool steels (see the article "Salt Bath Equipment" in this Volume).

Example 3: Advantages and Limitations of W1 and W2 Dies Heat Treated in Salt Baths.

In one plant, salt baths were found to be superior to atmosphere furnaces for heat treating die sections of W1 and W2 (0.90 to 1.05% C) because die sections could be hardened in limited areas by being suspended and only partly immersed in the salt bath, and because long sections, such as die wiper plates measuring 25 by 100 by 760 mm (1 by 4 by 30 in.), could be hardened in a salt bath with less distortion.

Salt baths are usually lower in initial cost than endothermic-atmosphere installations. Neutral salts such as No. 3 in Table 1 of the article entitled "Processes and Furnace Equipment for Heat Treating of Tool Steels" in this Volume, are commonly used. A salt of this type will operate satisfactorily in either steel-lined or ceramiclined pot furnaces, but maintenance cost will be less with ceramic linings. Immersed-electrode heating of these furnaces is recommended.

High-temperature salt baths will cause severe decarburization (see Fig. 2) if not closely controlled. A recommended method of rectification for control of these baths is indicated in the article, "Processes and Furnace Equipment for Heat Treating of Tool Steels" in this Volume.

Other disadvantages of salt baths are that salt dragout necessitates frequent replenishment of the bath, particularly when many small parts are being treated and that salt is sometimes difficult to remove from parts having complex shapes or tapped holes.

Lead baths also are used for austenitizing water-hardening steels and have advantages and limitations paralleling those of the salt bath, specifically with complex shapes and tapped holes, as described above. Both the Occupational Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA) have stringent regulations to avoid lead poisoning.

Fluidized-bed furnaces (see the article "Fluidized-Bed Equipment" in this Volume) represent a special class of atmosphere furnaces that exploit the excellent heat transfer properties of a ceramic medium that is liquefied via the

application of a gas flow. Fluidized-bed furnaces are extremely versatile furnaces because they have the capability to control blend gases that generate the desired carbon potential. In addition, fluidized-bed equipment can also be applied to processes such as ammonia gas nitriding and steam oxide surface coatings.

Quenching. To produce maximum depth of hardness in water-hardening tool steels, it is essential that they be quenched as rapidly as possible. In most instances, water or a brine solution consisting of 10% NaCl (by weight) in water is used. Occasionally, for an even faster quench, an iced brine solution is employed. Cooling rate is a function of size of workpiece as well as of quenching medium; for this reason, small pieces can be quenched in oil (Fig. 1). This is particularly useful when heat treating thin-section tools in an atmosphere furnace containing an integral oil quench.

Tempering. Water-hardening tool steels should be tempered immediately after hardening, preferably before they reach room temperature; about 50 °C (120 °F) is optimum. Salt baths, oil baths, and air furnaces are all satisfactory for tempering. However, working temperatures for both oil and salt are limited; the minimum for salt is about 165 °C (325 °F), and the maximum for oil is usually about 205 °C (400 °F).

All parts made of these steels should be tempered at temperatures not lower than 175 °C (350 °F). One hour at temperature is usually adequate; additional soaking time will further lower hardness. Figure 3 shows the effect of tempering temperature on hardness of water-hardening tool steels austenitized at 790, 815, and 845 °C (1450, 1500, and 1550 °F) and quenched in brine.

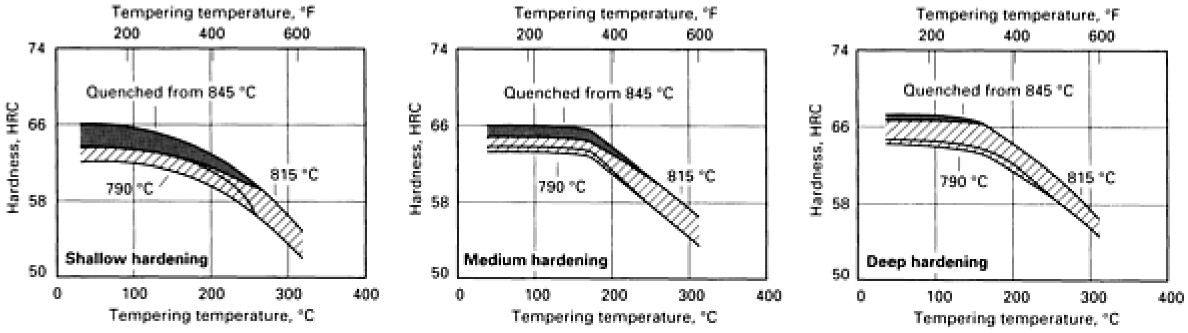


Fig. 3 Effect of tempering temperature on surface hardness of water-hardening tool steels austenitized at three different temperatures and quenched in brine. Specimens held for 1 h at the tempering temperature in a recirculating-air furnace. Cooled in air to room temperature. Data represent 20 25 mm (1 in.) diam specimens for each steel. Compositions of steels: shallow hardening, 0.90 to 1.00 C, 0.18 to 0.22 Mn, 0.20 to 0.22 Si, 0.18 to 0.22 V; medium hardening, 0.90 to 1.00 C, 0.25 Mn, 0.25 Si, no alloying elements; deep hardening, 0.90 to 1.00 C, 0.30 to 0.35 Mn, 0.20 to 0.25 Si, 0.23 to 0.27 Cr

Tools should be placed in a warm 95 to 120 °C (200 to 250 °F) furnace immediately after quenching and then brought to the tempering temperature with the furnace. This is particularly necessary when quenched tools are being accumulated for tempering in a single batch. Allowing quenched tools to stand at room temperature or placing them in a cold furnace will lead to cracking. Except for large pieces, the work will heat at about the same rate as the furnace. The low temperatures used in tempering eliminate the need for atmosphere control. A double temper is frequently used to temper any martensite that may have formed from retained austenite during quenching, and in the first tempering cycle.

The resistance to fracture by impact initially increases with tempering temperature to about 180 °C (360 °F) but falls off rapidly to a minimum at about 260 °C (500 °F). This is known as 500 °F embrittlement or tempered martensite embrittlement (see the article "Embrittlement of Steels" in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook*). For tools subjected to impact loading, tempering temperature should be selected to give an optimum combination of hardness and impact resistance.

Shock-Resisting Tool Steels

Recommended heat-treating practices for shock-resisting tool steels are outlined in Table 2. These steels may be obtained with several variations in composition, for specific applications (for example, S1 steel is available with 0.30 or 0.50% Mo or with up to 0.90% Si). The user of these nonstandard compositions should: (a) obtain from the manufacturer

information as to the modifications required in heat treatment, or (b) select a heat treatment recommended for the shock-resisting tool steel of standard composition that most closely resembles the modified steel. The latter procedure should be followed only after the treatment has been tried on test samples.

Table 2 Recommended heat-treating practices for shock-resisting tool steels

Steel	**Annealing**					**Hardening**							Quenched hardness, HRC
	Normalizing	**Temperature**[(a)]		**Cooling rate**[(b)]		**Annealed hardness, HB**	**Temperature**				**Holding time, min**	**Quenching medium**	
							Preheat		**Austenitizing**				
		°C	**°F**	**°C/h**	**°F/h**		**°C**	**°F**	**°C**	**°F**			
S1	Not rec	790-815	1450-1500	22	40	183-229	. . .	. . .	900-955	1650-1750	15-45	O	**57-59**
S2	Not rec	760-790	1400-1450	22	40	192-217	650[(c)]	1200[(c)]	845-900	1550-1650	5-20	B, W	**60-62**
S4	Not rec	760-790	1400-1450	22	40	192-229	650	1200	870-925	1600-1700	5-20	B, W	**61-63**
									900-925	1650-1700	5-20	O	**57-59**
S5	Not rec	775-800	1425-1475	14	25	192-229	760	1400	870-925	1600-1700	5-20	O	**58-61**
S6	Not rec	800-830	1475-1525	14	25	192-229	760	1400	915-955	1675-1750	10-30	O	**56-60**
S7	**Not rec**	**815-845**	**1500-1550**	**14**	**25**	**187-223**	**650-705**	**1200-1300**	**925-955**	**1700-1750**	**15-45**[(d)]	**A, O**	**60-61**

Not rec, not recommended.

(a) Lower limit of range should be used for small sections, upper limit for large sections. Holding time varies from about 1 h, for light sections and small furnace charges, to about 4 h, for heavy sections and large charges; for pack annealing, hold for 1 h per inch of pack cross section.

(b) Maximum. Rate is not critical after work is cooled to about 510 °C (950 °F).

(c) Preferable for large tools to minimize decarburization.

(d) For open furnace heat treatment. For pack hardening, hold for $\frac{1}{2}$ h per inch of pack cross section.

Normalizing is not recommended for the shock-resisting tool steels.

Annealing. The high-silicon types (S2, S4, S5, and S6) are susceptible to graphitization and decarburization. Annealing these types at temperatures higher than those indicated in Table 2 may produce a softer structure, but it will also increase the danger of graphitization. The silicon types should not be soaked at temperature. Surfaces should be protected against decarburization by heating in a protective atmosphere or a vacuum furnace, by the use of pack annealing, or by the application of proprietary paints.

Pack annealing consists of surrounding parts with inert material inside a closed container, heating the container to the recommended temperature, and slow cooling. The selection of a packing medium for use with shock-resisting tool steels is difficult; the same general practice has produced different results in different plants. Dry silica sand is usually satisfactory for type S1, and a combination of new and used carburizing compound is usually satisfactory for S2, S4, and S5. Burned-off cast iron chips, spent pitch coke, lime, and mica are sometimes used, also. Cast iron chips decrease in carbon content and should not be used indefinitely; lime and mica should be used carefully, because they are insulators. Excessive thicknesses of inert material should not be packed around parts, because this complicates handling and lengthens heating time. Wrapping parts tightly in brown paper before surrounding them with packing material helps to keep the surfaces clean. Additional information is available in the article "Introduction to Heat Treating of Tool Steels" in this Volume.

Proprietary paints are available that are intended to protect steel surfaces from decarburization during annealing. The use of such paints is simpler than the use of a pack anneal, but not all of these paints are effective. Moreover, considerable difficulty may be experienced in removing such paints after heat treatment. The prospective user should test any such paint on a sample of steel prior to adopting it in practice.

Stress relieving before hardening is seldom required for shock-resisting tool steel, except for extremely intricate parts of widely varying section thickness (to minimize distortion and cracking) and parts subjected to excessive stock removal (to relieve stresses induced by machining). Treatment of such parts, which involves no microstructural transformation, consists of heating them to 650 °C (1200 °F), (soaking should be avoided), furnace cooling to about 510 °C (950 °F), and then removing them from the furnace to cool in air.

Stress relieving of tools after tempering is seldom done. In some instances, however, increased tool life has been obtained by removing tools from service and stress relieving them (at a temperature no higher than the original tempering temperature) before returning them to service.

Example 4: Doubling the Tool Life of Shock-Resistant Tool Steels Used in Swaging Stainless Steels with Stress Relief.

In one plant, shock-resisting steel tools used for swaging stainless steel would sink a definite amount after a time in service. If kept in service, these tools would crack after swaging about 40,000 parts. However, by withdrawing the tools after sinking had ceased and stress relieving them at 230 °C (450 °F) for 1 h per inch of cross section, tool life was more than doubled.

Austenitizing temperatures for shock-resisting tool steels vary from 815 to 955 °C (1500 to 1750 °F). Preheating is not mandatory, but it is sometimes desirable for large tools, to minimize distortion, shorten time at the austenitizing temperature, and speed up production.

These steels may be austenitized in electric or fuel-fired furnaces or in salt or lead baths. Generally, for austenitizing temperatures below 870 °C (1600 °F), a slightly oxidizing environment is best, whereas above 870 °C (1600 °F) a reducing atmosphere is required. If a semimuffle fuel-fired furnace is used, the desired atmosphere can be obtained at low cost by adjustment of burners. However, if electrically heated or full-muffle fuel-fired furnaces are used, a prepared atmosphere from an external source is required.

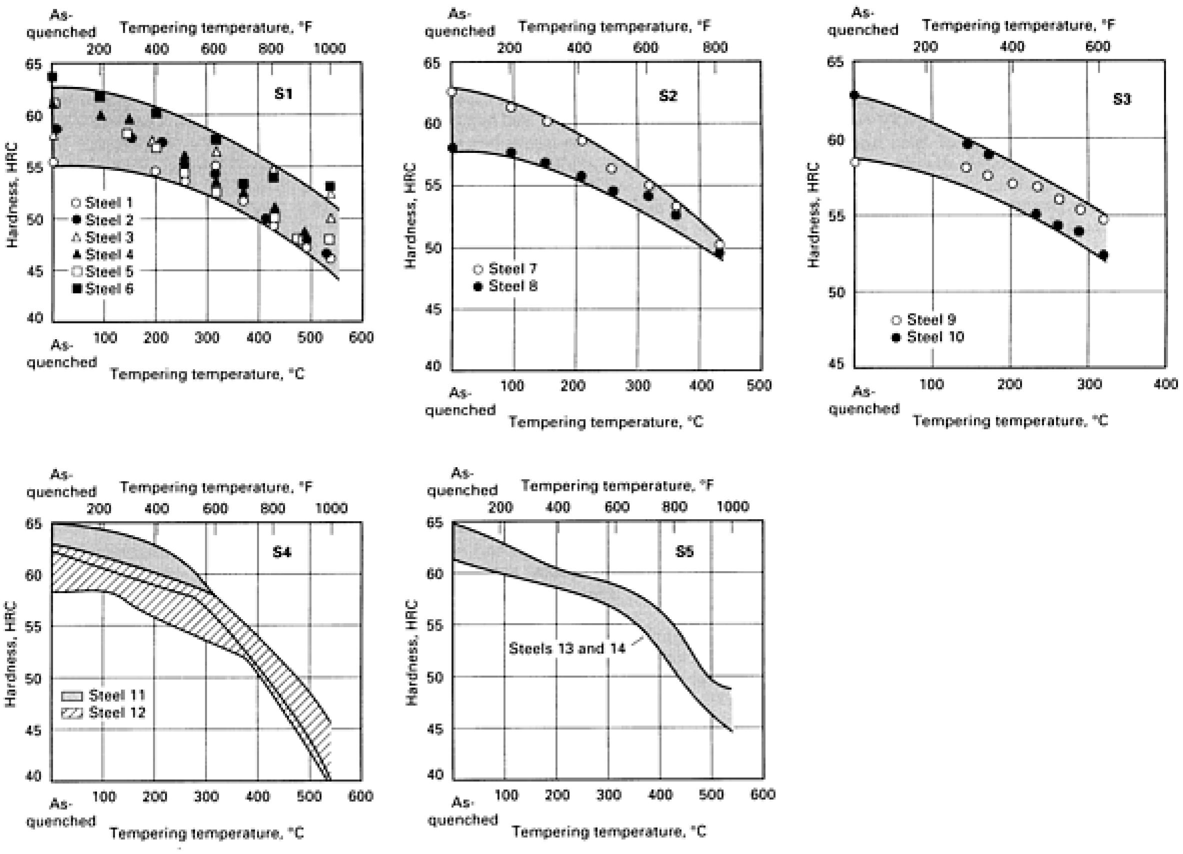
Neutral salt baths are a practical means of heating the type S steels. A salt mixture such as No. 3 in Table 1 of the article, "Processes and Furnace Equipment for Heat Treating of Tool Steels" in this Volume, is satisfactory for types S2, S4, and S5, whereas a mixture such as No. 2 in that table will be more suitable for heating S1. A recommended method of controlling these salts to prevent decarburization of the work is indicated in the discussion of rectification in the article, "Processes and Furnace Equipment for Heat Treating of Tool Steels."

If atmosphere furnaces or neutral salt baths are not available, the shock-resisting steels can be heated in a pack of neutral material such as burned pitch coke or cast iron chips. Packing mediums must be free of oil or other contaminants. Before being placed in the pack, tools should be wrapped with heavy brown paper, to prevent packing material from adhering to them as they are removed for quenching.

Types S2, S4, and S5 should be quenched soon after they reach the austenitizing temperature; types S1 and S7 are soaked at temperature for 15 to 45 min before being quenched (Table 2). Types S1 and S7 have the highest hardenability of these steels. The other types, although lower in hardenability than S1 and S7, are higher in hardenability than the W steels.

Tempering. Both the tungsten and the silicon types of shock-resisting tool steel resist softening from tempering to a greater degree than carbon tool steels. Secondary hardening does not occur in these steels, except to a minimal degree in some compositions of the tungsten type.

The effect of tempering temperature on the hardness of various types and compositions of the S steels is shown in Fig. 4.



Steel		Composition, %					Quenching		
							Temperature		Medium
No.	Type	C	Si	W or Mo	Cr	V	°C	°F	
1	S1	0.43	. . .	2.00 W	1.30	0.25	955	1750	. . .

2	S1	0.53	. . .	2.00 W	1.65	0.25	900	1650	**. . .**
3	S1	0.50	. . .	2.75 W	1.25	0.20	925	1700	**. . .**
4	S1	0.55	. . .	2.50 W	1.50	0.35	925	1700	**. . .**
5	S1	0.50	0.75	2.50 W	1.15	0.20	955	1750	**Oil**
6	S1	0.58	0.95	2.25 W	1.25	0.25	925	1700	**Oil**
7	S2	0.50	1.10	0.50 Mo	. . .	0.20	855	1575	**Water**
8	S2	0.50	1.10	0.50 Mo	. . .	0.20	900	1650	**Oil**
9	S3	0.50	. . .	1.00 W	1.00	. . .	870	1600	**Oil**
10	S3	0.50	. . .	1.00 W	1.00	. . .	815	1500	**Water**
11	S4	0.54-0.60	1.90-2.00	. . .	0-0.34	0-0.25	845-900	1550-1650	**Water**
12	S4	0.54-0.60	1.90-2.00	. . .	. . .	. . .	870-955	1600-1750	**Oil**
13	S5	0.50	1.60	0.25 Mo	. . .	. . .	870	1600	**Oil**
14	**S5**	**0.60**	**2.00**	**0.40 Mo**	**0.28**	**0.20**	**900**	**1650**	**Oil**

Fig. 4 Effect of tempering temperature on surface hardness of shock-resisting tool steels

Tools made of shock-resisting steel should be tempered immediately after quenching, or cracking is likely to result, especially if they are quenched in water or brine.

Example 5: Study Conducted to Determine Maximum Elapsed Time Required Between Quenching and Tempering Treatments to Prevent Cracking.

One plant made an extensive study on how much time could be safely permitted between quenching and tempering of tools made of shock-resisting steels. Results of this study are given in Table 3.

Table 3 Allowable time between quenching and tempering of shock-resisting tool steels, for prevention of cracking

Values determined by an extensive study conducted in one plant. Allowable time may vary significantly with size and shape of part.

Steel	**Austenitizing temperature**	**Quenching medium**	Allowable time prior to tempering, min

	°C	°F		tempering, min
S1	900	1650	Oil	**30**
S1	980	1800	Oil	**15**
S2	845	1550	Brine	**10**
S2	900	1650	Brine	**5**
S3	815	1500	Brine	**10**
S3	870	1600	Brine	**5**
S4	870	1600	Brine	**10**
S4	925	1700	Brine	**5**
S4	900	1650	Oil	**30**
S4	955	1750	Oil	**15**
S5	870	1600	Oil	**30**
S5	**925**	**1700**	**Oil**	**15**

In this same plant, tool records indicate that double tempering is beneficial for tools made from the S steels. The first tempering operation is done at a temperature 30 to 55 °C (50 to 100 °F) lower than that of the second and final tempering operation.

Surface treatments such as carburizing and carbonitriding are often applied to S1 steel. Types S4 and S5 do not take an effective carburized case.

Oil-Hardening Cold-Work Tool Steels

Recommended heat-treating practices for oil-hardening cold-work tool steels is summarized in Table 4.

Table 4 Recommended heat-treating practices for oil-hardening cold-work tool steels

Steel	Normalizing temperature[(a)]	Annealing			Hardening			
		Temperature[(b)]	Cooling rate[(c)]	Annealed hardness,	Temperature	Holding time,	Quenching medium	Quenched hardness,

					rate[c]		HB	Preheat		Austenitizing		min	medium	HRC
	°C	°F	°C	°F	°C/h	°F/h		°C	°F	°C	°F			
O1	870	1600	760-790	1400-1450	22	40	183-212	650	1200	790-815	1450-1500	10-30	Oil	**63-65**
O2	845	1550	745-775	1375-1425	22	40	183-212	650	1200	760-800	1400-1475	5-20	Oil	**63-65**
O6	870	1600	765-790	1410-1450	11	20	183-217	. . .	. . .	790-815	1450-1500	2-5	Oil	**63-65**
O7	900	1650	790-815	1450-1500	22	40	192-217	650	1200	790-830	1450-1525	10-30	Water	**64-66[d]**
										845-885	**1550-1625**	**10-30**	**Oil**	**64-66[d]**

(a) Holding time, after uniform through heating, varies from about 15 min, for small sections, to about 1 h, for large sections. Work is cooled from temperature in still air.

(b) Lower limit of range should be used for small sections, upper limit for large sections. Holding time varies from about 1 h, for light sections and small furnace charges, to about 4 h, for heavy sections and large charges; for pack annealing, hold for 1 h per inch of pack cross section.

(c) Maximum. Rate is not critical after cooling to below 540 °C (1000 °F).

(d) Sections larger than 38 mm ($1\frac{1}{2}$ in.) will be softer.

Normalizing is desirable and sometimes necessary for parts that have been forged or heated previously to temperatures much higher than the proper austenitizing temperature, because it produces a more uniformly refined grain structure. Recommended normalizing temperatures are given in Table 4. Work should be held at temperature for 15 min to 1 h, depending on section size; prolonged soaking is not desirable. When tools are to be hardened after normalizing, precautions must be taken in order to avoid decarburization during normalizing. If tools are to be subsequently machined, annealing is recommended in preference to normalizing.

Annealing. Finished or semifinished tools made from oil-hardening cold-work steels should be protected from decarburization or carburization during annealing. This can be accomplished by the use of dry exothermic furnace atmospheres. More often, however, it is accomplished by pack annealing, wherein work to be annealed is packed in a box and surrounded with inert protective material, such as clean cast iron chips or 6-to-8 mesh spent pitch coke. Pack annealing permits the use of an open furnace; also, slow heating and cooling occur naturally in the packed box. However, it is important that the work be soaked long enough to permit it to reach the annealing temperature. Recommended annealing temperatures, cooling rates, and expected hardness values are given in Table 4.

Type O1 steel may also be cycle annealed (Table 5). Cycle annealing offers little advantage for large loads, but with individual tools that can be conveniently handled in liquid baths or other conventional furnaces, it enables substantial savings in time.

Table 5 Cycle annealing treatments for four types of tool steel

Steel	Treatment
O1	**Heat to 730 °C (1350 °F), hold for 4 h; heat to 780 °C (1440 °F), hold for 2 h; cool to 690 °C (1275 °F), hold for 6 h; air cool**
A2	**Heat to 900 °C (1650 °F), hold for 2 h; cool to 760 °C (1400 °F), hold for 6 h; air cool**
A6	**Heat to 815 °C (1500 °F), hold for 2 h; cool to 650 °C (1200 °F), hold for 6 h; air cool**
D2	**Heat to 900 °C (1650 °F), hold for 2 h; cool to 775 °C (1425 °F), hold for 6 h; air cool**

Stress Relieving. In most instances, stress relieving of finished tools prior to final hardening does not noticeably lessen distortion during hardening. If extreme dimensional accuracy after hardening is required, tools should be stress relieved after rough machining but before final light machining. A recommended stress-relieving treatment consists of heating to 650 to 675 °C (1200 to 1250 °F), holding at temperature for 1 h per inch of thickness, and then air cooling.

Preheating of the O steels will minimize distortion during subsequent hardening. It is almost always required for tools that are to be austenitized in liquid baths. Recommended preheating temperatures are listed in Table 4. Open furnaces can be used for preheating, but if scale-free and oxide-free hardening is required, preheating must be done with atmosphere control.

Austenitizing. Recommended austenitizing temperatures for oil-hardening coldwork tool steels are given in Table 4. Work that has been preheated may either be transferred to an austenitizing furnace or be heated to the austenitizing temperature in the same furnace in which it was preheated.

Decarburization and scaling can be effectively minimized in liquid salt or lead baths, and in furnaces with controlled atmospheres (such as endothermic gas, dissociated ammonia, and argon or other inert gases). However, in all of these there is some danger of decarburization if conditions are not controlled. Oxides in the molten baths or excess water vapor in the various gases will cause decarburization. The atmospheres of gas-fired or oil-fired semimuffle furnaces can be adjusted to contain from 2 to 4% O_2, a condition that will eliminate decarburization but not oxidation. Types O1 and O2 can be satisfactorily austenitized in such an atmosphere, but it is not recommended for types O6 and O7. All type O steels may be austenitized in semimuffle furnaces if packed in inert materials such as spent pitch coke and clean cast iron chips. Adequate time must be allowed to ensure that packed work reaches prescribed temperature. If salt baths are used, a salt mixture such as No. 3 in Table 1 of the article, "Processes and Furnace Equipment for Heat Treating of Tool Steels" in this Volume, is recommended. For a suitable method of controlling this bath, see the discussion of rectification in that article.

Quenching. The optimum temperature range for quenching baths consisting of conventional oils is 40 to 60 °C (100 to 140 °F); agitation is recommended. Quenching oils that contain additives (fast oils) increase the cooling rate of the steel and permit more latitude in the operating temperature of the bath. Tools may be quenched in these oils at 80 °C (180 °F) without loss of hardness.

Martempering. If control of distortion is particularly important, martempering is sometimes advantageous. In martempering, the work is quenched in a bath of oil or molten salt that is usually held about 15 to 30 °C (25 to 50 °F) above the temperature (M_s) at which martensite starts to form from austenite on cooling, and is held in the bath long

enough to allow it to attain substantially equalized temperature throughout. The work is then removed from the bath and air cooled. The slow cooling through the martensitic transformation range permits the transformation of austenite to martensite to take place uniformly throughout the piece, thus minimizing distortion. Figure 5 presents a comparison of the dimensional changes in tools made of O1 steel that were oil quenched with those in tools of the same steel martempered at 230 °C (450 °F) for 10 min; the martempered tools exhibited markedly less distortion.

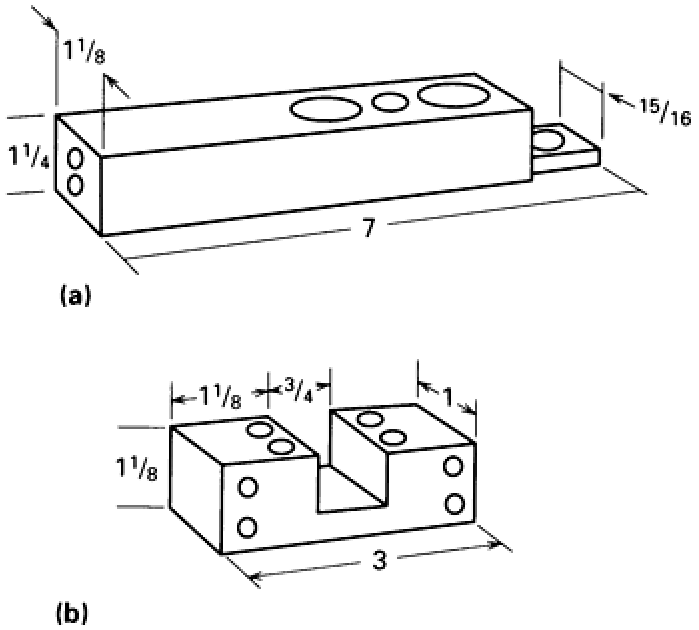


Fig. 5 Dimensional changes in O1 tools. Tools sketched, made of O1 steel, were used for comparison of dimensional changes resulting from martempering at 230 °C (450 °F) for 10 min, and from oil quenching. Five tools of each design, processed by each method, were measured on 5 different days. (a) Maximum change in flatness along the 180 mm (7 in.) dimension was 0.25 mm (0.020 in.) after oil quenching and 0.005 mm (0.0002 in.) after martempering. (b) Maximum change of the 19 mm ($\frac{3}{4}$ in.) slot width was 0.1 mm (0.0039 in.) after oil quenching and 0.33 mm (0.0012 in.) after martempering.

Tempering. The O steels should be tempered immediately after quenching (preferably before they reach room temperature). These steels usually are not tempered below 120 °C (250 °F) or above 540 °C (1000 °F); the most commonly used temperature range is from 175 to 205 °C (350 to 400 °F). Tempering times vary with section size. Often, a time at temperature of 1 h per inch of thickness (minimum dimension of heaviest section) or per inch of diameter, with a minimum of 1 h, is used.

Typical hardness values obtained with various tempering temperatures for oil-hardening tool steels are given in Fig. 6. The upper curve in each graph represents results from austenitizing at the higher side of the range of temperatures indicated, and the lower curve represents results from austenitizing at the lower side.

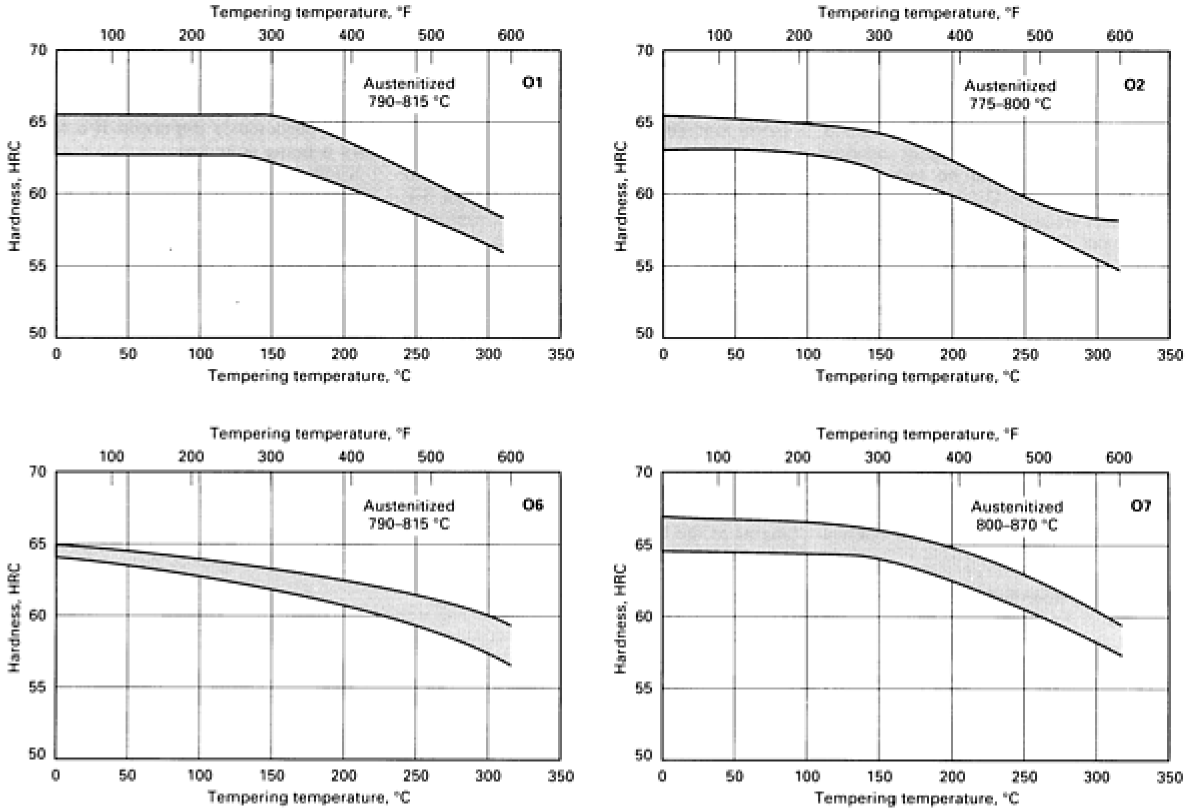


Fig. 6 Hardness as a function of tempering temperature, for oil-hardening cold-work tool steels. Steels O1, O2, and O6 were austenitized at the temperatures indicated, and then oil quenched. For O7 steel, large uniform sections were austenitized at 800 to 830 °C (1475 to 1525 °F) and water quenched, and other sections were austenitized at 830 to 870 °C (1525 to 1600 °F) and oil quenched. Duration of tempering was 1 h.

Conventional tools made from the O steels are seldom subjected to multiple tempering or subzero treatment. However, for some special tools, such as gages, where dimensional stability is critical, multiple tempering is desirable. In such instances the workpieces should be cooled to below 65 °C (150 °F) prior to each retempering. Subzero cooling to -75 °C (-100 °F) or lower is also helpful in achieving dimensional stability.

Medium-Alloy Air-Hardening, and High-Carbon High-Chromium, Cold-Work Tool Steels

Recommended heat-treating practices for medium-alloy air-hardening cold-work tool steels (group A) and high-carbon high-chromium cold-work tool steels (group D) are summarized in Table 6.

Table 6 Recommended heat-treating practices for medium-alloy air-hardening, and high-carbon high-chromium, cold-work tool steels

Steel	Normalizing temperature[(a)] °C (°F)	Annealing			Hardening			Quenching medium	Quenched hardness, HRC
					Temperature		Holding time, min		
		Temperature[(b)]	Cooling rate[(c)]	Annealed hardness, HB	Preheat	Austenitizing			

		°C	°F	°C/h	°F/h	HB	°C	°F	°C	°F			
Medium-alloy air-hardening cold-work tool steels													
A2	Not rec	845-870	1550-1600	22[d]	40[d]	201-229	790	1450	925-980	1700-1800	20-45[e]	A	**62-65[f]**
A3	Not rec	845-870	1550-1600	22	40	207-229	790	1450	955-1010	1750-1850	25-60[e]	A	**. . .**
A4	Not rec	740-760	1360-1400	14[g]	25[g]	200-241	675	1250	815-870	1500-1600	15-90	A	**61-64[f]**
A5	Not rec	740-760[h]	1360-1400[h]	14	25	229-255	595	1100	790-845	1450-1550	15-45	A	**62-63[f]**
A6	Not rec	730-745	1350-1375	14	25	217-248	650	1200	830-870	1525-1600	20-45	A	**59-63[f]**
A7	Not rec	870-900	1600-1650	14[d]	25[d]	235-262	815	1500	955-980	1750-1800	30-60[e]	A	**64-67[f]**
A8	Not rec	845-870	1550-1600	22	40	192-223	790	1450	980-1010	1800-1850	20-45[e]	A	**60-62[f]**
A9	Not rec	845-870	1550-1600	14	25	212-248	790	1450	980-1025	1800-1875	20-45[e]	A	**56-58[f]**
A10	790 (1450)	765-795	1410-1460	8	15	235-269	650	1200	790-815	1450-1500	30-60	A	**62-64[f]**
High-carbon high-chromium cold-work tool steels													
D1	Not rec	870-900	1600-1650	22	40	207-248	815	1500	970-1010	1775-1850	15-45[e]	A	**61**
D2	Not rec	870-900	1600-1650	22	40	217-255	815	1500	980-1025	1800-1875	15-45[e]	A	**64**
D3	Not rec	870-900	1600-1650	22	40	217-255	815	1500	925-980	1700-1800	15-45[e]	O	**64**
D4	Not rec	870-900	1600-1650	22	40	217-255	815	1500	970-1010	1775-1850	15-45[e]	A	**64**
D5	Not rec	870-	1600-	22	40	223-255	815	1500	980-	1800-	15-45[e]	A	**64**

		900	1650						1025	1875			
D7	**Not rec**	**870-900**	**1600-1650**	**22**	**40**	**235-262**	**815**	**1500**	**1010-1065**	**1850-1950**	**30-60**[(e)]	**A**	**65**

Not rec, not recommended.

(a) Holding time, after uniform through heating, varies from about 15 min, for small sections, to about 1 h, for large sections. Work is cooled from temperature in still air.

(b) Lower limit of range should be used for small sections, upper limit for large sections. Holding time varies from about 1 h, for light sections and small furnace charges, to about 4 h, for heavy sections and large charges; for pack annealing, hold for 1 h per inch of pack cross section.

(c) Maximum rate, to 540 °C (1000 °F) unless footnoted to indicate otherwise.

(d) To 705 °C (1300 °F).

(e) For open furnace heat treatment. For pack hardening, hold for $\frac{1}{2}$ h per inch of pack cross section.

(f) Hardness varies with austenitizing temperature.

(g) To 650 °C (1200 °F).

(h) One manufacturer recommends cooling from 760 to 540 °C (1400 to 1000 °F), then reheating to 730 °C (1350 °F) and cooling.

Normalizing. Except for type A10 (see Table 6), normalizing is not recommended for any of the steels in groups A and D.

Annealing. These steels are usually supplied in the annealed condition by the manufacturer. However, they should be annealed after forging and prior to rehardening. Annealing is required also for previously hardened or welded tools that are to be reworked.

Recommended annealing temperatures for the various types are given in Table 6. Tools should be heated slowly and uniformly to the annealing temperature. Slow heating is particularly important if a hardened tool is being annealed.

Cycle, or isothermal, treatments may be employed for annealing some A and D steels (Table 5).

Stress Relieving. Tools made of A and D steels that cannot be ground after hardening are sometimes stress relieved after rough machining. This is particularly advisable for delicate tools and tools that vary markedly in cross section. Stress relieving is used also on tools that are machined to final shape, if these tools can be straightened after stress relieving and before final heat treatment. There is little advantage in stress relieving completed tools if they cannot be straightened prior to hardening, because a good preheat will relieve stresses, and the distortion which occurs in either case will remain uncorrected. Recommended temperatures for stress relieving are:

A2, A7	650-675 °C	**(1200-1250 °F)**
A4, A5, A6	675-705 °C	**(1250-1300 °F)**
D1-D7	**675-705 °C**	**(1250-1300 °F)**

Usually, tools can be stress relieved at these temperatures without surface protection. Tools are commonly held at temperature for 1 h/in. of cross section (minimum of 1 h) and then air cooled.

Preheating. Steels of the A and D groups are usually preheated before being austenitized for hardening. Preheating reduces subsequent distortion in the hardened parts by minimizing nonuniform dimensional changes during austenitizing. Preheating simpler tools made of grades A4, A5, A6, and A10 can often be eliminated if they are austenitized in a furnace instead of a liquid bath, because these steels are austenitized at lower temperatures.

Recommended preheating temperatures are listed in Table 6. Holding time at temperature is usually 1 h per inch of maximum cross section. Preheating temperatures of 790 to 815 °C (1450 to 1500 °F) are used for tools made from A2, A3, A7, A8, or A9, or from any of the D steels. For these higher temperatures, a liquid bath or a protective furnace atmosphere is required in order to prevent scaling and decarburization.

Austenitizing. Steels of groups A and D can be austenitized in molten salt baths or in various types of furnaces using gaseous atmospheres. Because of their lower austenitizing temperatures, types A4, A5, A6, and A10 may also be austenitized in molten lead, or in open furnaces with oxidizing atmospheres. However, the latter methods are not satisfactory for the other A steels or for the D steels, because of their higher austenitizing temperatures.

If salt baths are used, salt mixtures such as No. 2 or No. 3 in Table 1 of the article, "Processes and Furnace Equipment for Heat Treating of Tool Steels," are recommended; the choice between the two depends on required working temperature range. These mixtures may be rectified (for the prevention of decarburization) by the method indicated in that article.

Procedures for austenitizing two different parts made of D2 steel by salt bath and by endothermic atmosphere furnace processes are shown in Table 7.

Table 7 Procedures for salt bath and endothermic atmosphere austenitizing of D2 inserts

Bending die inserts[a]	
Salt bath[b]	**Preheat in air furnace at 650 °C (1200 °F) for $1\frac{1}{2}$ h[c]; austenitize at 1010 °C (1850 °F) for 35 min[c]; air cool; remove salt**
Endothermic atmosphere[d]	**Charge directly into furnace at 705 °C (1300 °F) and preheat for $1\frac{1}{2}$ h[c]; austenitize at 1010 °C (1850 °F) for 2 h; air cool[c]**
Trim die inserts[e]	
Salt bath[b]	**Preheat in air furnace at 650 °C (1200 °F), 4 h[c], then in salt bath at 845 °C (1550 °F), 1 h[c][f]; austenitize at 1010 °C (1850 °F) for 1 h[c]; air cool[c]; remove salt**
Endothermic	**Charge directly into furnace at 705 °C (1300 °F), and preheat for 4 h[c]; raise furnace temperature, and**

atmosphere[d]	austenitize at 1010 °C (1850 °F) for 4 h; air cool[c]

(a) After austenitizing, inserts 200 by 305 by 38 mm (8 by 12 by $1\frac{1}{2}$ in.) were double tempered (2 h at 510 °C or 950 °F, air cool; 2 h at 510 °C or 950 °F, air cool) and then nitrided for 48 h at 510 °C (950 °F).

(b) Salt bath furnace was immersed-electrode type, 380 by 760 by 915 mm (15 by 30 by 36 in.) deep.

(c) Manual loading requires $1\frac{1}{2}$ min per piece.

(d) Furnace was radiant-tube type, 610 by 915 by 455 mm (24 by 36 by 18 in.) high.

(e) After austenitizing, die inserts were double tempered (4 h at 190 °C or 375 °F, air cool; 4 h at 190 °C or 375 °F, air cool).

(f) Second preheat was necessary because of faster heating rate of salt bath.

In some instances, austenitizing will cost more with atmosphere furnaces than with salt baths, and in other instances the reverse will be true. Atmospheres that have proved suitable for austenitizing the A and D steels are endothermic, dry dissociated ammonia, and dry hydrogen.

Endothermic gas produced by catalytic combination of air and fuel gas is the most widely used atmosphere. This relatively inexpensive gas can be adjusted for desired carbon potential and controlled by dew point.

Dry dissociated ammonia (dew point, -50 °C, or -60 °F) and dry hydrogen (dew point, -75 °C, or -100 °F) are used in applications in which complete freedom from discoloration is required. Vacuum, which excludes all atmosphere, can also be used to austenitize the A and D steels; it is particularly suitable for these steels because their air-hardening characteristics permit slow cooling rates.

Like the O steels, the A and D steels may be packed and then austenitized in semi-muffle furnaces. The packing materials and heat-treating procedures employed are similar to those described in the previous section on austenitizing of the O grades.

Steels of groups A and D must be held at their austenitizing temperatures long enough to obtain required carbide solution if they are to attain maximum hardness. However, hardening from excessively high austenitizing temperatures will increase the retained austenite. Although retained austenite can be decreased by repeated tempering or subzero cooling (or both), it should be avoided.

Quenching. Steels of groups A and D, except D3, will attain maximum hardness by cooling in still air, unless sections are extremely large. However, the hardenability of these steels varies with different types, as indicated in Table 8.

Table 8 Hardenability in still air of several A and D tool steels

Steel	Center hardening		Surface hardening	
	Size of section that fully hardens at center	Hardness, HRC	Size of section that fully hardens at surface	Hardness, HRC

A2, A4	75 mm (3 in.) diam	59-61	100 mm (4 in.) diam	**59-61**
A5	. . .	. . .	100 mm (4 in.) diam	**62-63**
A6	180 mm (7 in.) cube	59-60	180 mm (7 in.) cube	**60-61**
D1, D2, D5	**100 mm (4 in.) cube**	**60-61**	**125 × 125 × 255 mm (5 × 5 × 10 in.)**	**61-62**

Depending on section size, hardenability, and complexity of shape, the following methods are used to obtain increasingly accelerated cooling of nominally air-hardening steels:

- Cool in still air--that is, atmospheric air undisturbed by artificial circulation
- Cool in fan air--that is, the current of air discharged from a fan
- Cool in air blast--that is, the discharge from a high-pressure line
- Oil quench to black--that is, quench in oil until the steel is below the temperature at which it glows dull red, then cool to room temperature in air
- Oil quench by conventional practice

Tempering practices for A and D steels parallel those described for O steels in the preceding section. Tempering is usually begun when the work reaches a temperature of about 50 to 65 °C (120 to 150 °F). However, these steels retain some austenite at this temperature range. To maximize transformation of austenite to martensite, cooling to room temperature, or to subzero temperature (see the article "Cold Treating and Cryogenic Treatment of Steel" in this Volume), is sometimes applied.

Opinions vary greatly as to the merits of subzero cooling, because it increases the probability of cracking during the cooling cycle. The more usual practice is to begin tempering when parts reach about 50 to 65 °C (120 to 150 °F) and then double or triple temper. Multiple tempering is effective in decreasing the amount of austenite retained in A and D steels and is a common practice in heat treating them. The general precautions and tempering practices outlined for O steels in the preceding section are followed for the A and D steels. However, because most of the steels in groups A and D (except A4, A5, and A6) soften less rapidly than the group O steels with an increase in tempering temperature (Fig. 7 and 8), higher tempering temperatures can be used for the A and D steels. A minimum tempering temperature of 205 °C (400 °F) is a common requirement for A2, A7, and D steels. Tempering temperatures as high as 550 °C (1025 °F) are frequently used, and even higher temperatures are used for special requirements.

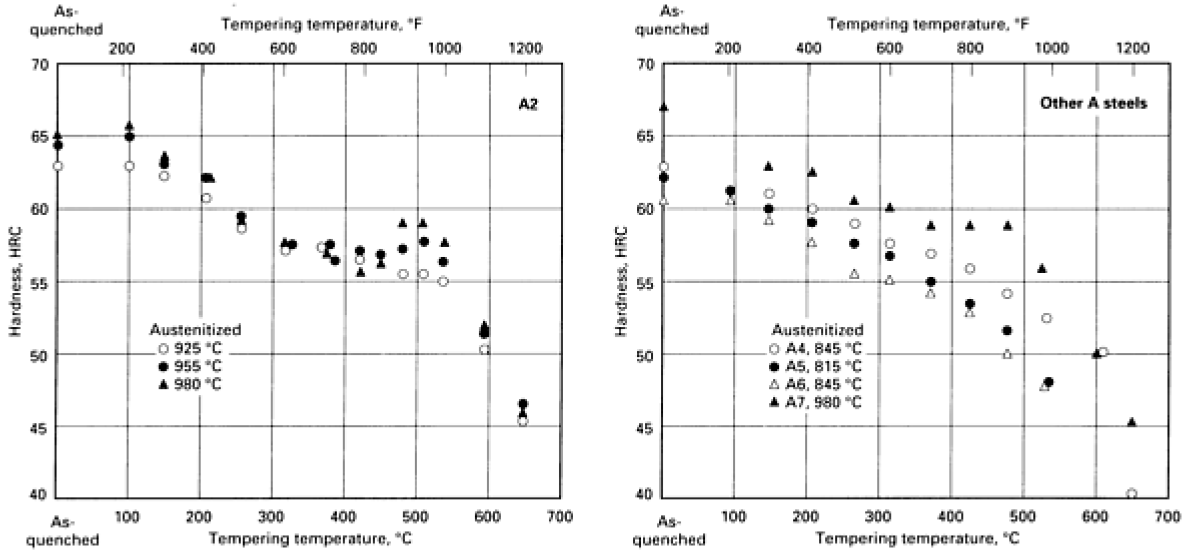


Fig. 7 Effect of tempering temperature on hardness of medium-alloy air-hardening steels

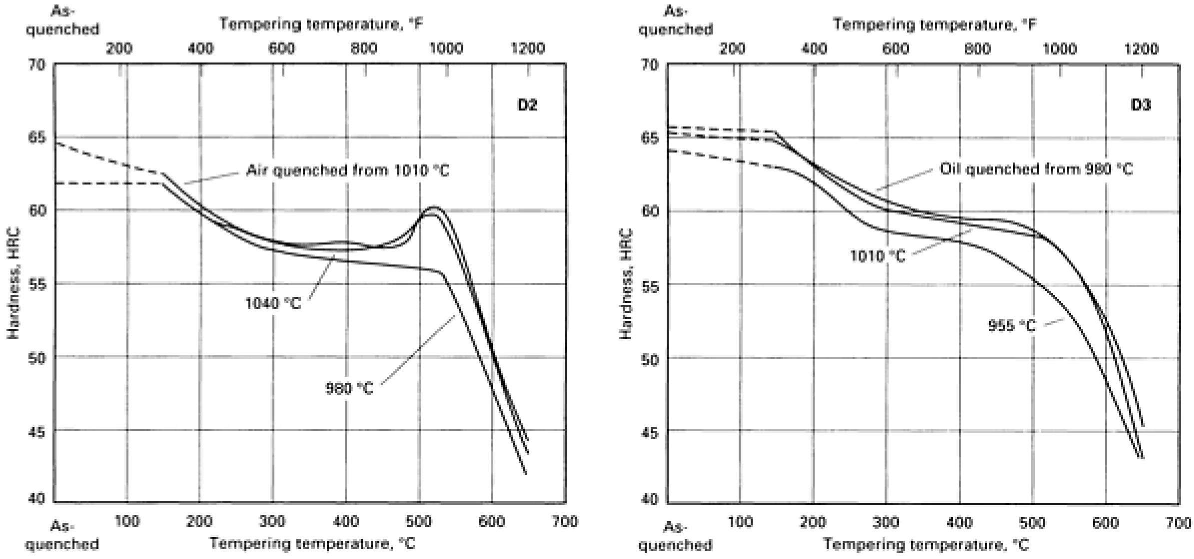


Fig. 8 Relation between tempering temperature and hardness for D2 and D3 tool steels. Steels were austenitized in an air furnace; a recirculating pit-type furnace was used for tempering. Curves representing steel from three suppliers; average of 5 hardness measurements made on each specimen from each supplier. Specimens were 25 mm (1 in.) in diam and 38 mm ($1\frac{1}{2}$ in.) long.

It will be noted in Fig. 7 and 8 that certain steels (notably A2 and D2) exhibit higher hardness after being tempered at about 540 °C (1000 °F) than after being tempered at temperatures 55 to 110 °C (100 to 200 °F) lower. This reversal in the usual relationship is known as secondary hardening, and is caused by transformation of retained austenite during tempering at the higher temperatures, near 540 °C (1000 °F). When a steel can be tempered to the same hardness at more than one temperature (for instance, D2 to 58 to 59 HRC), it is advisable to select the highest tempering temperature that will produce the desired hardness. This will yield added toughness and may prevent tool breakage in service.

Nitriding. The A steels (particularly A2 and A7) and the D steels are often nitrided after being hardened and tempered. Nitriding may be done either in a salt bath or in an atmosphere of dissociated ammonia. High tempering temperatures of 510 to 540 °C (950 to 1000 °F) are used on steels that are to be nitrided. Excessively high nitriding temperatures, with a

recommended range of 510 to 540 °C (950 to 1000 °F), will reduce hardness of the base metal and should not be used. Austenitizing at a higher temperature when hardening prior to nitriding will minimize loss of hardness during nitriding of some D steels (note graph for D2 in Fig. 8). For details, see the article "Gas Nitriding" in this Volume.

Hot-Work Tool Steels

Nominal compositions of chromium, tungsten, and molybdenum types of hotwork tool steels are given in Table 1 of the article entitled "Introduction to Heat Treating of Tool Steels " in this Volume. The steels in the group denoted in Table 1 as "Other Alloy Tool Steels" are included here in the discussion of hot-work tool steels, because they are also used extensively for hot-work applications. Table 9 summarizes the heat-treating practices commonly employed for this composite group of tools steels.

Table 9 Recommended heat-treating practices for hot-work tool steels

Steel	**Normalizing temperature[(a)] °C (°F)**	**Annealing**					Hardening					
							Temperature			**Holding time, min**	**Quenching medium**	Quenched hardness, HRC
		Temperature[(b)]		**Cooling rate[(c)]**		**Annealed hardness, HB**	**Preheat, °C (°F)**	**Austenitizing**				
		°C	**°F**	**°C/h**	**°F/h**			**°C**	**°F**			
Chromium hot-work tool steels												
H10	Not rec	845-900	1550-1650	22	40	192-229	815 (1500)	1010-1040	1850-1900	15-40[(d)]	A	**56-59**
H11	Not rec	845-900	1550-1650	22	40	192-229	815 (1500)	995-1025	1825-1875	15-40[(d)]	A	**53-55**
H12	Not rec	845-900	1550-1650	22	40	192-229	815 (1500)	995-1025	1825-1875	15-40[(d)]	A	**52-55**
H13	Not rec	845-900	1550-1650	22	40	192-229	815 (1500)	995-1040	1825-1900	15-40[(d)]	A	**49-53**
H14	Not rec	870-900	1600-1650	22	40	207-235	815 (1500)	1010-1065	1850-1950	15-40[(d)]	A	**55-56**
H16	Not rec	870-900	1600-1650	22	40	212-241	815 (1500)	1120-1175	2050-2150	2-5	A, O	**55-58**
H19	Not rec	870-900	1600-1650	22	40	207-241	815 (1500)	1095-1205	2000-2200	2-5	A, O	**52-55**
Tungsten hot-work tool steels												

H20	Not rec	870-900	1600-1650	22	40	207-235	815 (1500)	1095-1205	2000-2200	2-5	A, O	**53-55**
H21	Not rec	870-900	1600-1650	22	40	207-235	815 (1500)	1095-1205	2000-2200	2-5	A, O	**43-52**
H22	Not rec	870-900	1600-1650	22	40	207-235	815 (1500)	1095-1205	2000-2200	2-5	A, O	**48-57**
H23	Not rec	870-900	1600-1650	22	40	212-255	815 (1500)	1205-1260	2200-2300	2-5	O	**33-35**[e]
H24	Not rec	870-900	1600-1650	22	40	217-241	815 (1500)	1095-1230	2000-2250	2-5	A, O	**44-55**
H25	Not rec	870-900	1600-1650	22	40	207-235	815 (1500)	1150-1260	2100-2300	2-5	A, O	**46-53**
H26	Not rec	870-900	1600-1650	22	40	217-241	870 (1600)	1175-1260	2150-2300	2-5	A, O, S	**63-64**
Molybdenum hot-work tool steels												
H41	Not rec	815-870	1500-1600	22[f]	40[f]	207-235	730-845 (1350-1550)	1095-1190	2000-2175	2-5	A, O, S	**64-66**
H42	Not rec	845-900	1550-1650	22	40	207-235	730-845 (1350-1550)	1120-1220	2050-2225	2-5	A, O, S	**54-62**
H43	Not rec	815-870	1500-1600	22[g]	40[g]	207-235	730-845 (1350-1550)	1095-1190	2000-2175	2-5	A, O, S	**54-58**
Other alloy tool steels												
6G	Not rec	790-815	1450-1500	22[h]	40[h]	197-229	Not req	845-855	1550-1575	. . .	O[i]	**63 min**[j]
6F2	Not rec	780-795	1440-1460	22[k]	40[h]	223-235	Not req	845-870	1550-1600	. . .	O[i]	**63 min**[j]
6F3	Not rec	760-775	1400-1425	22[l]	40[h]	235-248	Not req	900-925	1650-1700	. . .	A[m]	**63 min**[j]
6F4	Not rec	705	1300	[n]	[n]	262-285	815	1010-	1850-	. . .	O, A	**38-41**[e]

							(1500)	1020	1870			
6F5	Not rec	845	1550	(o)	(o)	262-285	Not req	870	1600	. . .	O, A	**58-59**
6F6	Not rec	845 (pack)	1550 (peak)	(p)	(p)	196	650-705 (1200-1300)(q)	925-955(q)	1700-1750(q)	. . .	O(r)	**(s)**
6F7	845-870 (1550-1600)	670	1240	22	40	260-300	730 (1350)	915	1675	. . .	A	**54-55**
6H1	Not rec	845	1550	22(t)	40(t)	202-235	760-790 (1400-1450)	900-940	1650-1725	. . .	A	**48-49**
6H2	**Not rec**	**815-845**	**1500-1550**	**22**	**40**	**202-235**	**705-760 (1300-1400)**	**980-1065**	**1800-1950**	**. . .**	**O, A**	52-55

A, air; O, oil; S, salt; Not rec, not recommended; Not req, not required.

(a) Holding time, after uniform through heating, varies from about 15 min, for small sections, to about 1 h, for large sections. Work is cooled from temperature in still air.

(b) Lower limit of range should be used for small sections, upper limit for large sections. Holding time varies from about 1 h, for light sections and small furnace charges, to about 4 h, for heavy sections and large charges; for pack annealing, hold for 1 h per inch of pack cross section.

(c) Maximum rate, to 425 °C (800 °F) unless footnoted to indicate otherwise.

(d) For open furnace heat treatment. For pack hardening, hold for $\frac{1}{2}$ h per inch of pack cross section.

(e) Temper to precipitation harden.

(f) To 540 °C (1000 °F).

(g) To 480 °C (900 °F).

(h) To 370 °C (700 °F).

(i) To 205 to 175 °C (400 to 350 °F), then air cool.

(j) Temper immediately.

(k) For isothermal annealing, furnace cool to 650 °C (1200 °F), hold for 4 h, furnace cool to 425 °C (800 °F), then air cool.

(l) For isothermal annealing, furnace cool to 670 °C (1240 °F), hold for 4 h, furnace cool to 425 °C (800 °F), then air cool.

(m) (p) Cool with forced-air blast to 205 to 175 °C (400 to 350 °F), then cool in still air.

(n) Air cool from annealing temperature.

(o) Furnace cool, at 22 °C (40 °F), (max) per h, to 425 °C (800 °F), reheat to 595 ± 14 °C (1100 ± 25 °F), furnace cool to 425 °C (800 °F), then air cool.

(p) Furnace cool at 17 °C (30 °F) per h to 540 °C (1000 °F), reheat to 790 °C (1450 °F), furnace cool at 11 °C (20 °F) per h to 540 °C (1000 °F), then air cool.

(q) Heat in pack or in controlled atmosphere.

(r) To 50 °C (125 °F).

(s) Pack heating, 59 to 60 HRC; atmosphere heating, 54 to 55 HRC.

(t) For isothermal annealing. hold at 845 °C (1550 °F) for 2 h, furnace cool to 745 °C (1375 °F), hold for 4 to 6 h, then air cool.

Normalizing. Because these steels as a group are either partially or completely air-hardening, normalizing is not recommended except for the high-nickel steel 6F7. After forging or before reheat treating, 6F7 may be normalized by heating to 845 to 870 °C (1550 to 1600 °F), preferably in a controlled atmosphere, and cooling in still air.

Annealing. Recommended annealing temperatures, cooling practices, and expected hardness values are given in Table 9. Heating for annealing should be slow and uniform to prevent cracking, especially when annealing hardened tools. Heat losses from the furnace usually determine the rate of cooling; large furnace loads will cool at a slower rate than light loads. For most of these steels, furnace cooling to 425 °C (800 °F), at 22 °C max (40 °F max) per h, and then air cooling, will suffice.

For types 6F2, 6F3, and 6H1, an isothermal anneal (Table 9) may be employed to advantage for small tools that can be handled in salt or lead baths or for small loads in batch-type furnaces; however, isothermal annealing has no advantage over conventional annealing for large die blocks or large furnace loads of these steels.

To minimize scaling and decarburization, small parts are usually pack annealed, while large and heavy die blocks are more commonly annealed in controlled-atmosphere furnaces.

Packing material should preferably be spent cast iron chips or spent pitch coke-petroleum coke heated to 1205 °C (2200 °F) in a semiclosed container to drive off gas and moisture. Lime, sand, or mica is sometimes used, but under such material if mixed with a small amount of charcoal or other carburizing material, the steel may be decarburized. Packing material should be dry and free of all oxidizing materials, should separate all metal surfaces, and should fill the container. Containers should be sealed after packing. Holding time at the annealing temperature is 1 h per inch of container thickness. The H steels must have a neutral packing material, because they are extremely susceptible to both carburization and decarburization.

In controlled-atmosphere furnaces, the work should be supported so that it does not touch the bottom of the furnace. This will ensure uniform heating and permit free circulation of the atmosphere around the work. Workpieces should be supported so that they will not sag or distort under their own weight.

Grades 6F4 and 6F7 may be annealed without packing or controlled atmosphere if light scaling is not objectionable, because they are annealed at lower temperatures (Table 9).

Stress Relieving. It is sometimes advantageous to stress relieve tools made of hot-work steel after rough machining but prior to final machining, by heating them to 650 to 730 °C (1200 to 1350 °F). This treatment minimizes distortion during hardening, particularly for dies or tools that have major changes in configuration or deep cavities. However, closer dimensional control can be obtained by hardening and tempering after rough machining and prior to final machining, provided that the final hardness obtained by this method is within the machinable range.

Preheating prior to austenitizing is nearly always recommended for all hot-work steels except 6G, 6F2, 6F3, and 6F5. These four steels may or may not require preheating, depending on size and configuration of the workpieces. Recommended preheating temperatures for all the other types are given in Table 9.

Die blocks or other tools for open furnace treatment should be placed in a furnace that is not over 260 °C (500 °F). Work that is packed in containers may be safely placed in furnaces at 370 to 540 °C (700 to 1000 °F). Once the workpieces (or container) have attained furnace temperature, they are heated slowly and uniformly, at 65 to 110 °C (150 to 200 °F) per h, to the preheating temperature (Table 9) and held for 1 h per inch of thickness (or per inch of container thickness, if packed). Thermocouples should be placed adjacent to the pieces in containers. Controlled atmospheres or other protective means must be used above 650 °C (1200 °F) to minimize scaling and decarburization. A slightly reducing atmosphere is especially recommended for preheating of H41.

For certain parts--for example, intricate die-casting dies--preheating is omitted. Distortion of such parts is sometimes lessened by packing them and heating them slowly and uniformly throughout the entire range to the quenching temperature.

Austenitizing temperatures recommended for the hardening of hot-work tool steels are given in Table 9. Rapid heating from the preheating temperature to the austenitizing temperature is preferred for types H16 through H43 and for type 6F4.

Except for steels H10 through H14 (see Table 9), time at the austenitizing temperature should only be sufficient to heat the work completely through; prolonged soaking is not recommended. Time cycles for several specific conditions are indicated in the next section of this article entitled "Examples of Heat-Treating Procedure for Hot-Work Tools."

The equipment and method employed for austenitizing are frequently determined by the size of the workpiece. For tools weighing less than about 230 kg (500 lb), any of the methods would be suitable. However, larger tools or dies would be difficult to handle in either a salt bath or a pack.

Tools or dies made of hot-work steel must be protected against carburization and decarburization when being heated for austenitizing. Carburized surfaces are highly susceptible to heat checking. Decarburization causes decreased strength, which may result in fatigue failures; and on die-casting dies, the molten casting metal will weld on to decarburized surfaces and may cause washout because of poor wear resistance of the decarburized surface. However, the principal detrimental effect of decarburization is to mislead the heat treater as to the actual hardness of the die. To obtain specified hardness of the decarburized surface, the die is tempered at too low a temperature. The die then goes into operation at excessive internal hardness and breaks at the first application of load.

An endothermic atmosphere produced by a gas generator is probably the most widely used protective medium. The dew point is normally held from 2 to 7 °C (35 to 45 °F) in the furnace, depending on carbon content of the steel and operating temperature. A dew point of 3 to 4 °C (38 to 40 °F) is ideal for most steels of type H11 or H13 when austenitized at 1010 °C (1850 °F).

The packing of work in spent pitch coke before heating it for austenitizing has been used extensively in small shops where it has not been feasible to invest in special equipment. This procedure is generally used for small dies. New pitch coke is generally heated to 1040 to 1205 °C (1900 to 2200 °F) to burn off any combustibles that may be present as well as to remove any excessive moisture. The spent pitch coke is then sifted to remove the fines (the coke should also be sifted before re-use). Normal procedure for this method is to wrap the workpiece in plain brown wrapping paper and place it in

a heat-resistant metal box in the bottom of which is about 50 mm (2 in.) of spent pitch coke. The workpiece should be covered and surrounded with approximately 50 to 100 mm (2 to 4 in.) of spent pitch coke. The cover is then placed on the box and sealed with a refractory paste. The box is then ready to be placed in a furnace, which need not be provided with controlled atmosphere.

Quenching. Hot-work steels range from high to extremely high in hardenability. Most of them will achieve full hardness by cooling in still air; however, even with those types having the highest hardenability, sections of die blocks may be so large that insufficient hardening results. In such instances, an air blast or an oil quench is required to achieve full hardness. Hot-work steels are never water quenched. Recommended quenching media are listed in Table 9.

If blast cooling is used, air should be blasted uniformly on the surface to be hardened. All air must be dry. When being air quenched, dies or other tools should not be placed on concrete floors or in locations where water vapor may strike them.

Some of the hot-work steels (especially the tungsten and molybdenum types) will scale considerably during cooling to room temperature in air. An interrupted quench reduces this scaling by eliminating the long period of contact with air at elevated temperature, but it also increases distortion. The procedure is best carried out by quenching from the austenitizing temperature in a salt bath held at 595 to 650 °C (1100 to 1200 °F), holding in the quench until the workpiece reaches the temperature of the bath, and then withdrawing the piece and allowing it to cool in air. An alternative, but less precise, procedure is to quench in oil at room temperature or slightly above and judge by color (faint red) when the workpiece has reached 595 to 650 °C (1100 to 1200 °F); the piece is then quickly withdrawn and permitted to cool to room temperature in air. While cooling, the pieces should be placed in a suitable rack, or be supported by wires, in such a manner that air is permitted to come in contact with all surfaces.

Steel H23 requires a different type of interrupted quench, because ferrite precipitates rapidly in this steel at 595 °C (1100 °F) and M_s is below room temperature. Type H23 should be quenched in molten salt at 165 to 190 °C (325 to 375 °F) and then air cooled to room temperature. This steel will not harden in quenching but will do so by secondary hardening during the tempering cycle.

Parts quenched in oil should be completely immersed in the oil bath, held until they have reached bath temperature, and then transferred immediately to the tempering furnace. Oil bath temperatures may range from 55 to 150 °C (130 to 300 °F), but should always be below the flash point of the oil. Oil baths should be circulated and kept free of water.

Tempering. Hot-work tool steels should be tempered immediately after quenching, even though sensitivity to cracking in this stage varies considerably among the various types (for example, air-quenched 6F4 may be safely kept at room temperature for several hours before tempering, whereas 6G, 6F2, and 6F3 are susceptible to cracking if they are cooled substantially below 175 °C, or 350 °F, before tempering).

Hot-work steels are usually tempered in air furnaces of the forced-convection type. Salt baths are used successfully for smaller parts, but for large complex parts salt bath tempering may induce too severe a thermal shock and cause cracking. The effect of tempering temperature on hardness of hot-work tool steels is shown in Fig. 9(a), 9(b), and 9(c).

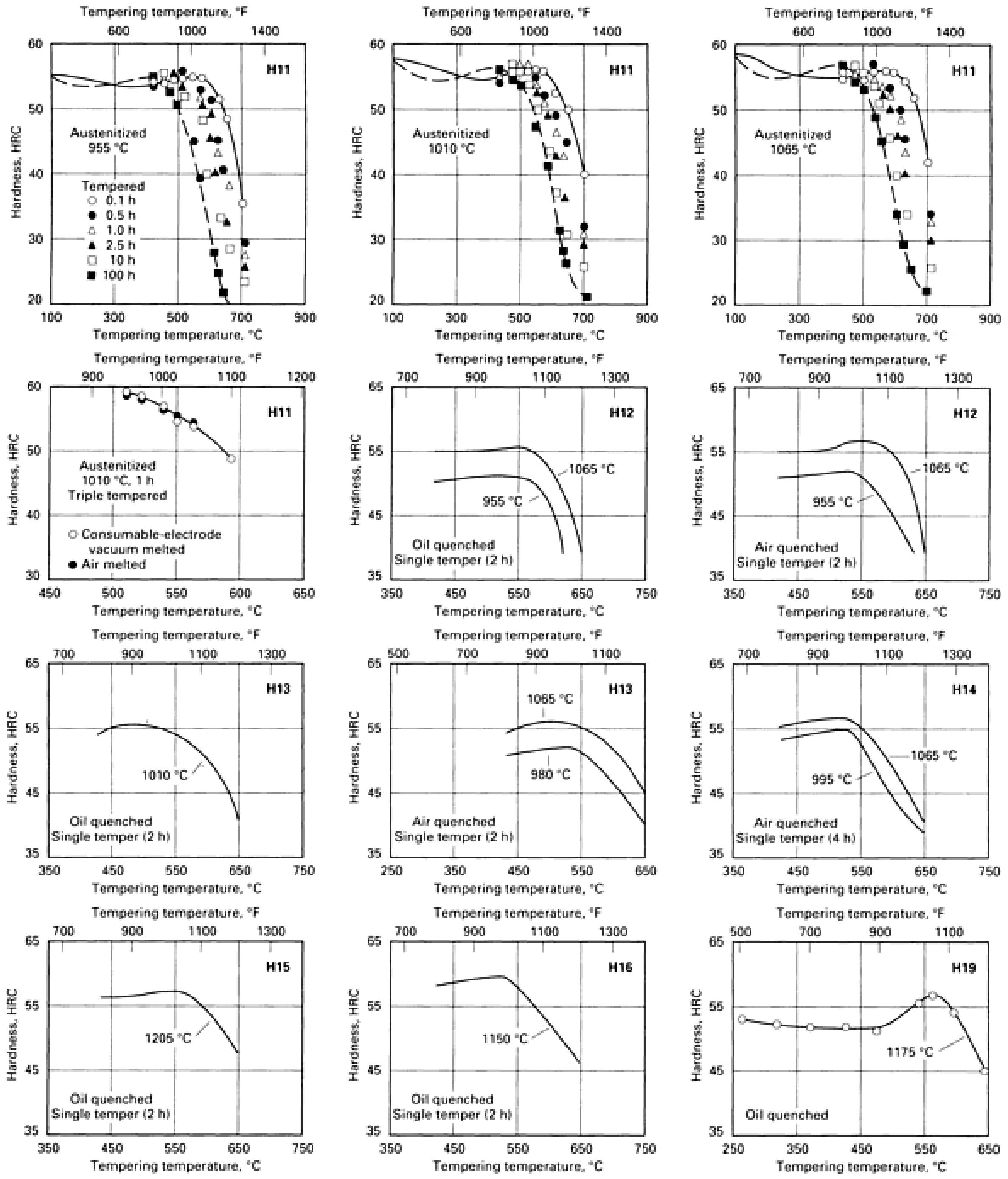


Fig. 9(a) Effect of temperature on hardness of chromium hot-work tool steels

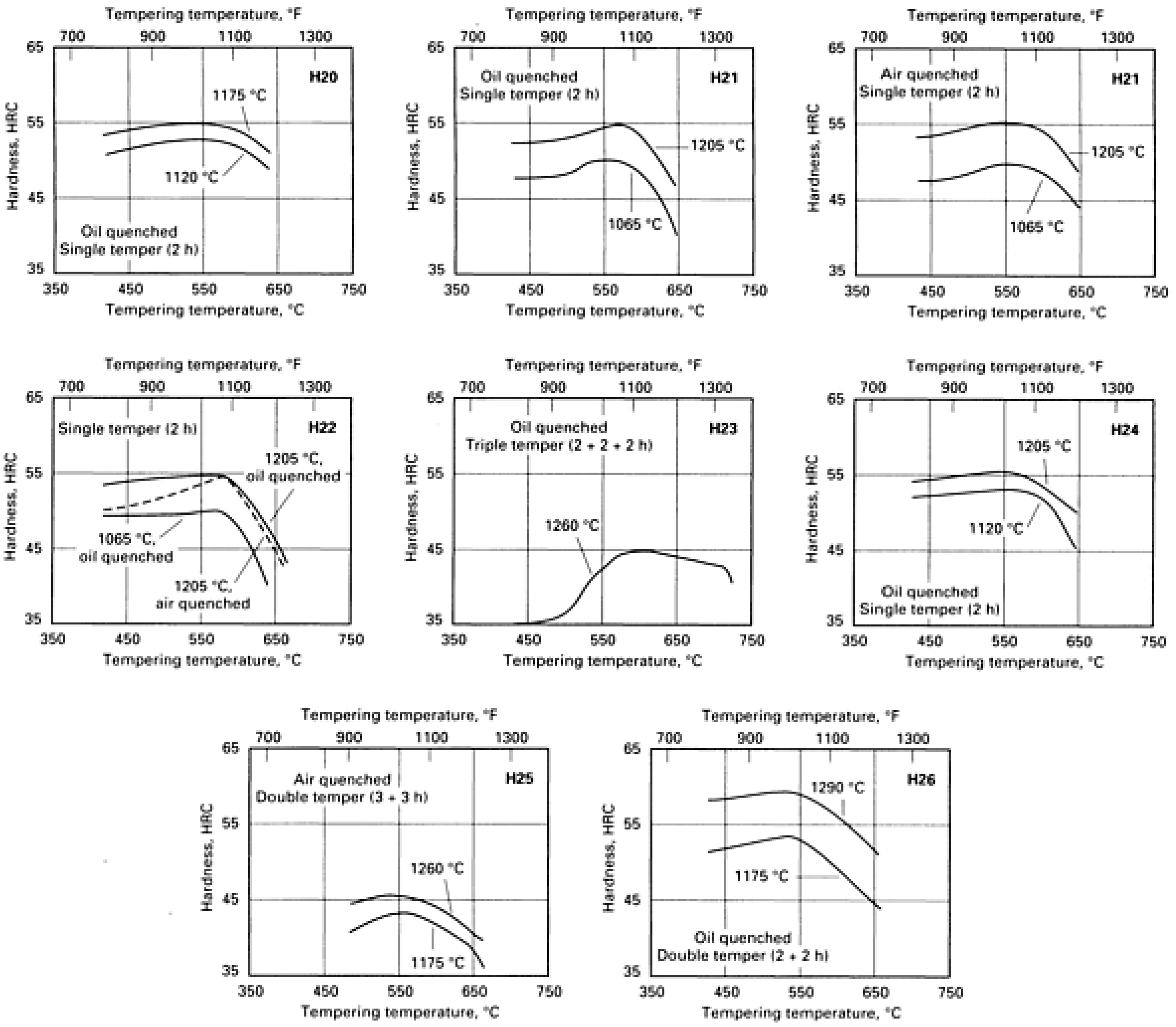


Fig. 9(b) Effect of temperature on hardness of tungsten hot-work tool steels

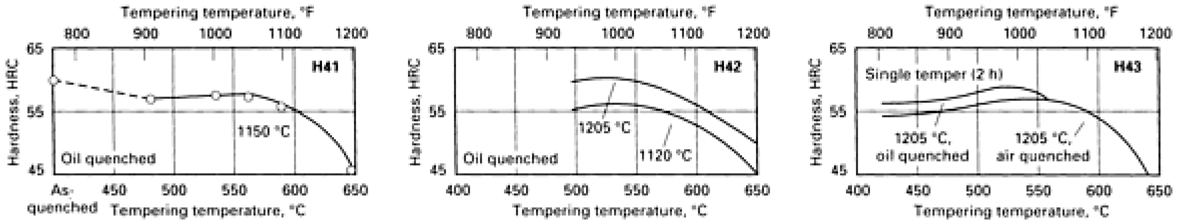


Fig. 9(c) Effect of temperature on hardness of molybdenum hot-work tool steels

Multiple tempering ensures that any retained austenite that transforms to martensite during the first tempering cycle is tempered before a tool is placed in service. Multiple tempering also minimizes cracks due to stress originating from the hardening operation.

Multiple tempering has proved particularly advantageous for large or sharp-cornered die blocks that are not permitted to reach room temperature before the first tempering operation.

Example 6: Heat Treatment of Selected Hot-Work Steels.

In one plant where many die blocks are heat treated, standard practice is as follows. When the dies have air cooled to 52 °C (125 °F), they are placed in a tempering furnace maintained at 565 °C (1050 °F). After the dies have reached furnace temperature, they are soaked for 1 h per inch of thickness. The dies are then air cooled to room temperature. Second and third tempering operations are carried out in the same manner, except that temperature may be increased as required in order to obtain desired hardness.

Most of the hot-work steels have secondary hardening characteristics; H23 is the most pronounced in this respect (Fig. 9(a), 9(b), and 9(c)). As with A2 and D2 (discussed previously), these secondary-hardening hot-work steels should be tempered at the highest temperature at which the desired hardness can be produced.

Surface Hardening. Although tools and dies made of the hot-work steels usually have sufficient hardness to perform the tasks for which they were designed, they are occasionally surface hardened to acquire improved resistance to wear or heat for special applications. The two principal processes that have been used for this purpose are carburizing and nitriding.

Carburizing is usually limited to hot-work steels having a carbon content of 0.35% or lower. Type H12 has been reported to achieve a carburized surface hardness of 60 to 62 HRC. The carburized case should be shallow--for example, 0.4 mm (0.015 in.) maximum--or severe embrittlement will occur. The greater the thermal shock (or gradient) present in service--as in die casting--the shallower the case must be.

Nitriding. Gas or liquid nitriding is sometimes applied to the hot-work steels to increase resistance to heat or wear, or both. For instance, dies for hot extrusion are sometimes nitrided to increase service life. One disadvantage of nitriding, however, is the difficulty it imposes on the reworking of tools or dies. Another disadvantage is that it may accentuate heat checking. Hot-work steels should be hardened and tempered before being nitrided, but should be neither decarburized nor carburized.

The quality and depth of the nitrided case are influenced by the chemical composition of the steel and by the time and temperature of nitriding. The presence of nitride-forming elements such as chromium and vanadium is helpful to the attainment of a satisfactory case. The fact that most of the hot-work steels reach a secondary hardening peak when tempered in the vicinity of 540 °C (1000 °F) is beneficial, because nitriding is usually accomplished in a range of 510 to 540 °C (950 to 1000 °F) over a period of 15 to 24 h. The nitrided case, in addition to being very hard, may be brittle. Brittleness increases with depth of case; hence, shallow, 0.08 to 0.2 mm (0.003 to 0.008 in.), nitrided cases are usually applied.

Examples of Heat-Treating Procedure for Hot-Work Tools

Tools and dies made of hot-work steel extend over an extremely wide range of sizes and weights (sometimes up to several tons, as in the largest die blocks). Therefore, details of heat-treating techniques may vary considerably. The following examples give details of procedures that have proved successful in practice:

Example 7: Heat Treating of an H21 Hot Extrusion Die.

A typical method for heat treating a 75 mm (3 in.) thick, 200 mm (8 in.) OD, 75 mm (3 in.) hole, hot extrusion die made of H21 steel comprises the following:

- Preheat at 815 to 845 °C (1500 to 1550 °F), either in a slightly oxidizing atmosphere or in neutral salt
- Transfer to furnace (6 to 12% reducing atmosphere or neutral salt bath) operating at 1175 °C (2150 °F). Hold in furnace for approximately 20 min after the die has reached 1175 °C (2150 °F)
- Cool in still air to about 65 °C (150 °F)
- Temper at 565 °C (1050 °F) for 4 h
- Cool to near room temperature
- Retemper at 650 °C (1200 °F) for 4 h
- Air cool

Example 8: Heat Treating of an H11 Mandrel.

Mandrels made of H11, used in conjunction with the H21 die in Example 7, above, are heat treated as follows:

- Preheat at 760 °C (1400 °F) in a slightly oxidizing atmosphere
- Transfer to atmosphere furnace (1 to 3% excess O_2) operating at 1010 °C (1850 °F) and hold for 20 min plus 5 min for each inch of thickness
- Air cool to near room temperature (oil quenching can also be used)
- Temper (or, preferably, double temper) for desired hardness

Example 9: Heat Treating of an H13 Die Block.

One plant employs the following procedure for heat treating die blocks made of H13 that weigh less than 23 kg (50 lb):

1. Insert eyebolt to facilitate handling
2. Wrap die block in waxed paper and place in a heat-resistant container on a bed of spent pitch coke 75 to 100 mm (3 to 4 in.) deep
3. Seal cover on container with asbestos paste
4. Place container in furnace (not atmosphere-controlled) operating at 760 °C (1400 °F); bring to furnace temperature and hold for 4 h
5. Raise furnace temperature at 30 °C (50 °F) per h to 1010 °C (1850 °F) and hold charge at this temperature for 6 h
6. Remove die block from container by use of eyebolt
7. Cool in still air to 345 °C (650 °F) (temperature-indicating crayons may be used), then place in furnace operating at 345 °C (650 °F) and cool in furnace at 30 °C (50 °F) per h to 95 °C (200 °F). (If the die block has no sharp corners or major changes in configuration, the interrupted cooling may be omitted)
8. Remove from furnace and cool in air to 40 °C (100 °F)
9. Place in tempering furnace operating at 565 °C (1050 °F), bring to furnace temperature and hold for 8 h, air cool to room temperature and check hardness
10. Repeat step 9, except that it may be necessary to increase tempering temperature so that final hardness will be 46 to 49 HRC

Example 10: Heat Treating of an H13 Die Block.

The following procedure has proved successful for heat treating large die blocks, 1590 kg (3500 lb), made of H13 steel:

1. Load die block into electrically heated bell-type furnace. The sequence of operations begins when furnace temperature reaches 95 °C (200 °F)
2. Raise furnace temperature at 30 °C (50 °F) per h to 370 °C (700 °F)
3. Introduce nitrogen atmosphere to furnace and increase furnace temperature at 55 °C (100 °F) per h to 790 °C (1450 °F); hold for 1 h, then shut off nitrogen, introduce endothermic atmosphere--dew point, 3 to 4 °C (38 to 40 °F)--and hold for an additional 5 h
4. Increase furnace temperature at 55 °C (100 °F) per h to 1040 °C (1900 °F) and hold for 6 h
5. Remove die block and air cool to 65 °C (150 °F)
6. Place die block in tempering furnace operating at 205 °C (400 °F); bring to furnace temperature and hold for 7 h
7. Increase furnace temperature at 40 °C (100 °F) per h to 565 °C (1050 °F) and hold for 16 h
8. Air cool to room temperature. Hardness is about 46 to 48 HRC
9. Temper die block a second time, repeating steps 6, 7, and 8 but increasing final temperature to 580 °C (1075 °F) because a finished hardness of 42 to 43 HRC is desired
10. Temper a third time, repeating steps 6, 7, and 8 without modification

Example 11: Heat Treatment of a Premium Grade H13 Die

(Ref 1). Most aluminum die casting dies fail by thermal fatigue of the die surface. Repeated cyclic stressing caused by alternate heating and cooling of the die surface leads to formation of a pattern of check-like cracks that are indicated as protrusions of the die casting surface and eventually expand and merge to cause further failure of the die.

Die life varies widely (20,000 to 2,000,000 shots are typical) depending on the aggressiveness of the process conditions, whether the die is preheated prior to being put into service, the metallurgy of the steel used, and the heat treat microstructure.

Hot-work die steels containing 5% Cr are normally used (H13 is the most common in the United States) because they have:

- A good combination of toughness and strength for safety and service
- Good hardenability in thick sections
- Good hot hardness and strength to resist cyclic stressing at operating temperatures up to 400 °C (750 °F)
- Good resistance to tempering during service which gradually lowers the surface hardness and the fatigue strength

Carbide precipitation, other than that produced during tempering, is known to be deleterious to the fatigue life of H13 tool steel. Fast quenching rates required to suppress intermediate precipitation of carbides (such as proeutectoid grain-boundary carbide, pearlite, or bainite) also produce large thermal gradients within the tool which can cause distortion or even cracking. The larger the tool, the greater the risk of cracking.

Austenitizing temperature was approximately 1040 °C (1900 °F) for the continuous cooling test. Test results are shown in Fig. 10.

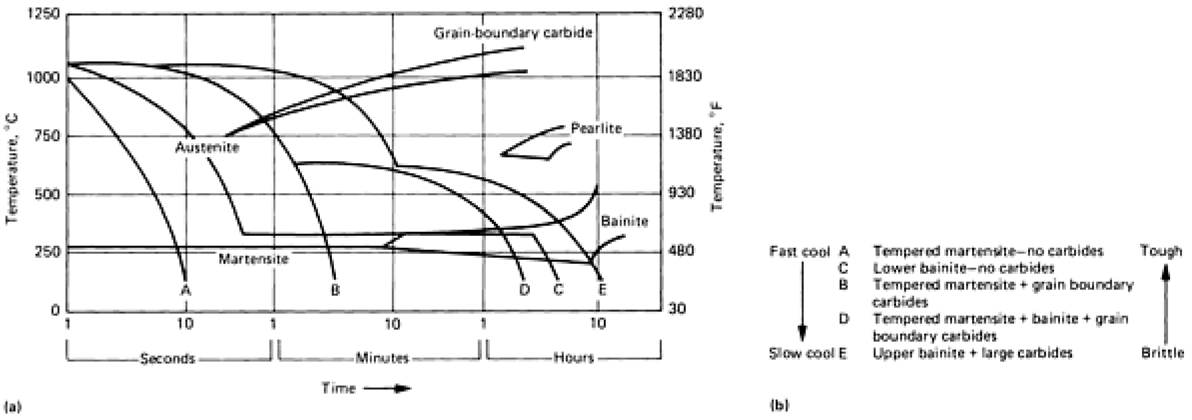


Fig. 10 Effect of intermediate cooling rates on the microstructure and toughness of H13 tool steel austenitized at 1075 °C (1970 °F). (a) Continuous cooling transformation (CCT diagram) showing variation in microstructure with varying cooling rates. (b) Variation in toughness as a function of carbides ejected from austenite. Hardness maintained at constant value. Source: Ref 1

After tempering to 46 HRC, the H13 bars were finish machined to produce specimens for impact energy testing.

As shown in Fig. 11, the results of the 12 treatments processed by continuous cooling indicate that three regimes of toughness occur. The slowest cooling rates of 2 to 4 °C/min (4 to 7 °F/min) produce structures with some pearlite and heavy grain-boundary carbides. These structures result in low toughness values of 3 to 8 J (2 to 6 ft · lbf) at room temperature for the Charpy V-notch test. Increasing the cooling rate to 10 to 31 °C/min (17 to 56 °F/min) eliminates the pearlite and provides martensitic/bainitic matrices but considerable quantities of grain-boundary carbide remain. These faster cooling rates produce room-temperature Charpy V-notch toughness values of 16 to 20 J (12 to 15 ft · lbf). The fastest cooling rates result in greatly reduced grain-boundary carbide precipitation and virtually 100% martensitic matrices. These structures have room-temperature Charpy V-notch toughness values of 24 to 26 J (18 to 19 ft · lbf).

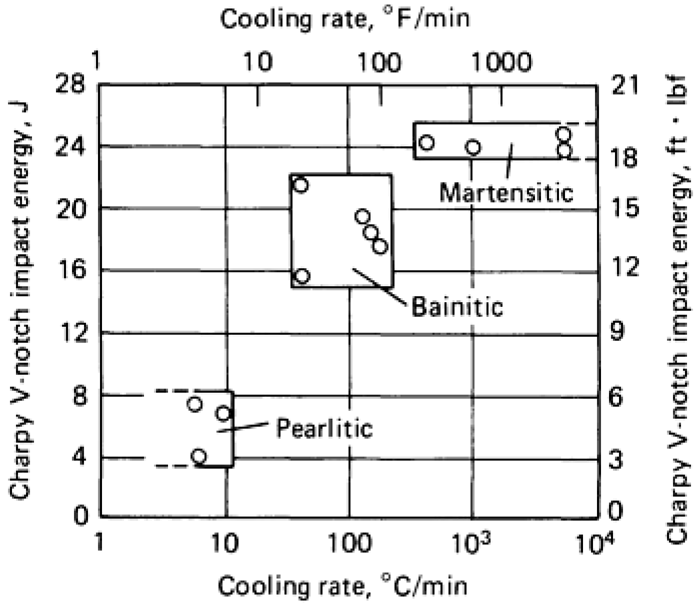


Fig. 11 Plot of impact energy versus cooling rate showing three distinct regions of toughness obtained for 12 treatments of premium H13 tool steel. Note that all test values lie inside these three regions.

This study clearly shows that increasing the quenching rate increased the impact strength but the effect is nonlinear.

Structures containing pearlite rates should be avoided by quenching at rates faster than 9.5 °C/min (17 °F/min) until below the nose of the pearlite curve. This results in bainite/martensite structures with some grain-boundary carbides and an anticipated notch impact strength of 15 to 22 J (11 to 16 ft · lbf).

Faster quenching at rates of over 58 °C/ min (105 °F/min) will give a martensite structure with less grain-boundary carbide. The small increase in impact strength to 23 to 26 J (17 to 19 ft · lbf) may not be considered worth the increased risk of cracking and distortion.

Example 12: Heat Treating of a 6F3 Forging Die.

In one plant, dies, 495 by 215 by 150 mm ($19\frac{1}{2}$ by $8\frac{1}{2}$ by 6 in.), used for forging pitman arms are heat treated to a final hardness of 40 to 42 HRC by the following procedure:

1. Preheat at 260 °C (500 °F)
2. When dies have attained furnace temperature, raise temperature at 55 to 85 °C (100 to 150 °F) per h to 915 °C (1675 °F); use controlled atmosphere above 760 °C (1400 °F)
3. Hold at 915 °C (1675 °F) for 6 h
4. Air-blast cool to 175 °C (350 °F) (temperature-indicating crayons used)
5. Place in tempering furnace operating at 175 to 205 °C (350 to 400 °F). When dies have attained furnace temperature, raise temperature at 85 °C (150 °F) per h to 595 °C (1100 °F) and hold for 9 h
6. Air cool to room temperature; check hardness
7. Retemper, repeating steps 5 and 6 except for final temperature, which will depend on hardness obtained from first tempering

6F2, 6F4, and H12 Components Used in Forging of Pinions. The following three examples indicate the procedures employed in one plant for heat treating 6F2, 6F4, and H12 components used for hot upset forging of pinions.

Example 13: Heat Treating of a 6F2 Heading Tool and Gripper Die.

Final hardness of 40 to 42 HRC is obtained on this tool by preheating, austenitizing, quenching, tempering, and retempering as follows:

1. Preheat at 260 °C (500 °F)
2. When dies have attained furnace temperature, raise temperature at 55 to 85 °C (100 to 150 °F) per h to 855 °C (1575 °F)
3. Hold at 855 °C (1575 °F) for 1 h per inch of thickness
4. Quench in oil at 55 °C (130 °F), to 175 °C (350 °F) (temperature-indicating crayons used); transfer as quickly as possible to tempering furnace
5. Place in tempering furnace operating at 175 to 205 °C (350 to 400 °F). When dies have attained furnace temperature, raise temperature at 55 to 85 °C (100 to 150 °F) per h to 595 °C (1100 °F) and hold for 1 h per inch of thickness
6. Cool in still air to room temperature; check hardness
7. Retemper, repeating steps 5 and 6 except for final temperature, which depends on hardness obtained from first tempering

Example 14: Heat Treating of a 6F4 Slab Insert.

These inserts, requiring final hardness of 39 to 41 HRC, are heat treated as follows:

1. Preheat at 260 °C (500 °F)
2. When inserts have attained furnace temperature, raise temperature at 55 to 85 °C (100 to 150 °F) per h to 815 °C (1500 °F) (use controlled atmosphere above 760 °C, or 1400 °F)
3. Solution treat at 1020 °C (1870 °F) for 1 h per inch of thickness
4. Cool in still air to room temperature. Note: When these inserts were quenched to only 95 °C (200 °F), threads broke out of the die during tapping
5. Precipitation harden by heating at 260 °C (500 °F) until temperature of insert equals furnace temperature, raising furnace temperature at 55 to 85 °C (100 to 150 °F) per h to 450 °C (840 °F), holding at 450 °C (840 °F) for 3 h plus 1 h per inch of thickness (minimum time, 4 h), and air cooling to room temperature

Example 15: Heat Treating of an H12 Punch Insert.

Heat treating to a desired final hardness of 40 to 42 HRC comprises the following procedure:

1. Preheat at 260 °C (500 °F)
2. When inserts have attained furnace temperature, raise temperature at 55 to 85 °C (100 to 150 °F) per h to 870 °C (1600 °F) (use controlled atmosphere above 760 °C, or 1400 °F)
3. Raise furnace temperature to 1010 °C (1850 °F); hold inserts at 1010 °C (1850 °F) for 1 h per inch of thickness
4. Quench inserts in still air until they are cool enough to be hand-held. Transfer immediately to the tempering furnace
5. Place in tempering furnace operating at 260 °C (500 °F). When inserts have attained furnace temperature, raise temperature at 55 to 85 °C (100 to 150 °F) per h to 595 °C (1100 °F). Hold at 595 °C (1100 °F) for 1 h per inch of thickness
6. Cool in still air and check hardness
7. Retemper, repeating steps 5 and 6 except for final temperature, which will depend on the hardness that was obtained from the first tempering cycle
8. Temper for a third time, if time permits

Reference cited in this section

1. D.L. Cocks, "Longer Die Life From H13 Die Casting Dies by the Practical Application of Recent Research Results," Paper presented at a conference on Tool Materials for Molds and Dies: Application and Performance, St. Charles, IL, 30 Sept to 2 Oct 1987

High-Speed Tool Steels

High-speed tool steels are used primarily for cutting tools, such as broaches, chasers, cutters, drills, hobs, reamers, and taps. Nominal compositions of these steels are given in Table 1 of the article, "Introduction to Heat Treating of Tool Steels," in this Volume. Recommended heat-treating practices are summarized for two standard groups of high-speed steels and one intermediate group in Table 10 of this article; note that normalizing of high-speed tool steels is not recommended.

Table 10 Recommended heat-treating practices for high-speed tool steels

Steel	**Normalizing**	**Annealing**					Hardening						
		Temperature[(a)]		**Cooling rate**[(b)]		**Annealed hardness, HB**	**Temperature**				**Holding time, min**	**Quenching medium**	Quenched hardness, HRC
							Preheat		**Austenitizing**[(c)]				
		°C	**°F**	**°C/h**	**°F/h**		**°C**	**°F**	**°C**	**°F**			
Tungsten high-speed tool steels, standard group													
T1	Not rec	870-900	1600-1650	22	40	217-255	815-870	1500-1600	1260-1300	2300-2370	2-5	O, A, S	**63-65**
T2	Not rec	870-900	1600-1650	22	40	223-255	815-870	1500-1600	1260-1300	2300-2370	2-5	O, A, S	**64-66**
T4	Not rec	870-900	1600-1650	22	40	229-269	815-870	1500-1600	1260-1300	2300-2370	2-5	O, A, S	**64-66**
T5	Not rec	870-900	1600-1650	22	40	235-285	815-870	1500-1600	1275-1300	2330-2370	2-5	O, A, S	**64-66**
T6	Not rec	870-900	1600-1650	22	40	248-302	815-870	1500-1600	1275-1300	2330-2370	2-5	O, A, S	**64-66**
T8	Not rec	870-900	1600-1650	22	40	229-255	815-870	1500-1600	1260-1300	2300-2370	2-5	O, A, S	**64-66**
T15	Not rec	870-900	1600-1650	22	40	241-277	815-870	1500-1600	1205-1260	2200-2300	2-5	O, A, S	**65-67**
Molybdenum high-speed tool steels, standard group													

M1	Not rec	815-870	1500-1600	22	40	207-235	730-845	1350-1550	1175-1220	2150-2230	2-5	O, A, S	**64-66**
M2	Not rec	870-900	1600-1650	22	40	212-241	730-845	1350-1550	1190-1230	2170-2250	2-5	O, A, S	**65-66**
M3	Not rec	870-900	1600-1650	22	40	223-255	730-845	1350-1550	1205-1230	2200-2250	2-5	O, A, S	**64-66**
M4	Not rec	870-900	1600-1650	22	40	223-255	730-845	1350-1550	1205-1230	2200-2250	2-5	O, A, S	**64-66**
M6	Not rec	870	1600	22	40	248-277	790	1450	1175-1205	2150-2200	2-5	O, A, S	**63-66**
M7	Not rec	815-870	1500-1600	22	40	217-255	730-845	1350-1550	1175-1220	2150-2230	2-5	O, A, S	**64-65**
M10	Not rec	815-870	1500-1600	22	40	207-255	730-845	1350-1550	1175-1220	2150-2230	2-5	O, A, S	**64-66**
M30	Not rec	870-900	1600-1650	22	40	235-269	730-845	1350-1550	1205-1230	2200-2250	2-5	O, A, S	**64-66**
M33	Not rec	870-900	1600-1650	22	40	235-269	730-845	1350-1550	1205-1230	2200-2250	2-5	O, A, S	**64-66**
M34	Not rec	870-900	1600-1650	22	40	235-269	730-845	1350-1550	1205-1230	2200-2250	2-5	O, A, S	**64-66**
M36	Not rec	870-900	1600-1650	22	40	235-269	730-845	1350-1550	1220-1245	2230-2270	2-5	O, A, S	**64-66**
M41	Not rec	870-900	1600-1650	22	40	235-269	730-845	1350-1550	1190-1215	2170-2220	2-5	O, A, S	**64-66**
M42	Not rec	870-900	1600-1650	22	40	235-269	730-845	1350-1550	1165-1190	2130-2170	2-5	O, A, S	**63-66**
M43	Not rec	870-900	1600-1650	22	40	248-269	730-845	1350-1550	1150-1175	2100-2150	2-5	O, A, S	**63-66**
M44	Not rec	870-900	1600-1650	22	40	248-285	730-845	1350-1550	1200-1225	2190-2240	2-5	O, A, S	**63-66**
M46	Not rec	780-900	1600-1650	22	40	235-269	730-845	1350-1550	1190-1220	2170-2230	2-5	O, A, S	**63-66**

M47	Not rec	870-900	1600-1650	22	40	235-269	730-845	1350-1550	1175-1205	2150-2200	2-5	O, A, S	**63-66**
High-speed tool steels, intermediate group													
M50	Not rec	830-845	1525-1550	22	40	197-235	730-845	1350-1550	1095-1120	2000-2050	2-5	O, A, S	**63-65**
M52	**Not rec**	**830-845**	**1525-1550**	**22**	**40**	**197-235**	**730-845**	**1350-1550**	**1120-1175**	**2050-2150**	**2-5**	**O, A, S**	**63-65**

O, oil; A, air; S, salt; Not rec, not recommended.

(a) Pack annealing is recommended, for minimum decarburization. Steels should be held at temperature for 1 h per inch of thickness of the container.

(b) Maximum. Rate is not critical after work (in pack, if employed) has been furnace cooled to 650 °C (1200 °F).

(c) If steels are austenitized in a salt bath, austenitizing temperatures should be 14 °C (25 °F) lower than those in the ranges given.

The market for tungsten high-speed steels is basically limited to Europe. Molybdenum high-speed steels are the materials of choice in the United States for machine tool applications.

Recommended Heat-Treating Procedures Based on Steel Group and Type

Steels in the intermediate group, M50 and M52, are less expensive than standard high-speed steels and may occasionally be used in place of standard high-speed steels.

The intermediate high-speed steels do not resist tempering to the same extent as M2, and therefore, they cannot be expected to perform as well as high-speed steels in applications where red hardness is important. For example, in such applications as lathe tools and drills, where the tool is in continuous contact with the workpiece and high surface temperatures are the rule, M50 and M52 steels would not be expected to perform as well as standard high-speed steels. When contact with the workpiece is intermittent or surface temperatures are low, in such applications as hack and band saw blades, blanking dies, and some special woodworking tools, M50 and M52 steels may perform adequately. M50 steel is also used in ball and roller bearing races used at elevated temperatures. Other applications include woodworking tools, hydraulic pump assemblies, pump pistons, and pump vanes. If greater abrasion resistance is required, but not as much as afforded by standard high-speed steels, then M52 may be a logical choice.

Annealing. High-speed steel must be fully annealed after forging or when rehardening is required. To minimize decarburization, pack annealing in tightly closed containers is recommended. The packing material can be dry sand or lime to which a small amount of charcoal has been added; burned cast iron chips also are satisfactory. Because the packing material acts to insulate the container and thereby slow down heating, the container should be filled in such a way with the steel to be annealed that a minimum amount of packing material is required.

After the steel has reached the annealing temperature range (Table 10), it should be held at temperature for 1 h per inch of thickness of the container and should then be slowly cooled in the furnace (at a rate not exceeding 22 °C, or 40 °F per h) until it reaches a temperature of 650 °C (1200 °F), when a faster rate of cooling is permissible.

Preheating. Austenite begins to form at about 760 °C (1400 °F), and preheating for hardening to slightly above this temperature will minimize stresses that might be set up because of the transformation. If the prevention of partial decarburization is important, a preheating temperature of 705 to 790 °C (1300 to 1450 °F) generally will be used. When this is not a problem, preheating at 815 to 900 °C (1500 to 1650 °F) is satisfactory.

Double preheating--in one furnace at 540 to 650 °C (1000 to 1200 °F) and in another at 845 to 870 °C (1550 to 1600 °F)--is often recommended to minimize thermal shock and to increase the productivity of the equipment.

If a single preheat is used, the T types of high-speed steels are preferably preheated at 815 to 870 °C (1500 to 1600 °F), and the remaining M types at 730 to 845 °C (1350 to 1550 °F). It is common practice to preheat for twice the length of time required at the austenitizing temperature. Accordingly, to ensure a uniform flow of work, the capacity of the preheating installation is generally twice that of the austenitizing installation.

Although preheating is recommended for all high-speed steels, small tools and those that do not incorporate sharp notches or abrupt changes in section, such as small tool bits and solid drill rod blanks, may be placed directly into the austenitizing furnace with reasonable safety. If consumable carbonaceous muffles are used, the preheating temperature must not exceed about 650 °C (1200 °F), because the type of atmosphere they provide is ineffective in preventing decarburization at higher temperatures. Decarburization is detrimental to a heat-treated tool requiring finished edges and surfaces.

Austenitizing. High-speed steels depend on the solution of various complex alloy carbides during austenitizing to develop their heat-resisting qualities and cutting ability. These carbides do not dissolve to an appreciable extent unless the steel is heated to temperatures near the melting point. Therefore, exceedingly accurate temperature control is required in austenitizing high-speed steel. Steels containing about 3% or more vanadium may be held at the austenitizing temperature approximately 50% longer than the lower-vanadium types. The relatively pure vanadium carbide phase inherent in the microstructure of the high-vanadium steels is virtually insoluble at temperatures below the melting point and acts to restrict grain growth, thus permitting longer soaking times without detriment. It should be noted that the tungsten, molybdenum chromium, and cobalt contents rather than the vanadium content are the key factors in determining the soaking time required in austenitizing. However, the recommended austenitizing temperatures for these steels should not be exceeded.

Single-point tools intended for heavy-duty cutting often can be effectively austenitized at 8 to 17 °C (15 to 30 °F) above the nominal austenitizing temperature. The higher temperature increases alloy solution, temper resistance, and hot hardness, but it also results in some sacrifice in toughness. To prevent rapid wear-out of fine-edged tools such as taps and chasers, austenitizing temperatures of 1040 to 1080 °C (1905 to 1975 °F) are recommended. Punches and dies that do not require maximum hardness may be austenitized for maximum toughness at temperatures 55 to 110 °C (100 to 200 °F) below the nominal temperature.

Other adjustments in austenitizing temperature depend on the type of heating equipment employed. Full-muffle furnaces employing a controlled atmosphere rich in carbon monoxide are usually operated at the higher temperature of the recommended range. Salt baths usually are operated 15 to 30 °C (30 to 50 °F) below the top of the range.

The effect of austenitizing temperature on the as-quenched hardness of M2 steel is shown in Fig. 12. Below 1175 °C (2150 °F), M2 cannot develop full hardness on quenching, because of insufficient carbide solution. At temperatures above approximately 1230 °C (2250 °F), the as-quenched hardness of M2 decreases because of too much carbon and alloy solution and an excess of retained austenite in the as-quenched steel.

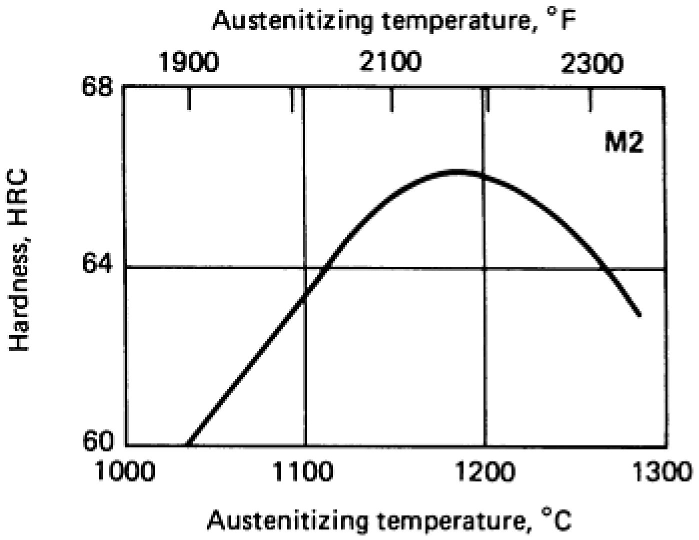


Fig. 12 Effect of austenitizing temperatures on the as-quenched hardness of M2 steel

Figure 13 illustrates the improved toughness of M2, as measured by the Izod unnotched impact test, that results from the use of lower-than-normal austenitizing temperatures. Numerous investigators have shown that the optimum means for attaining maximum toughness in high-speed steel is through reduced austenitizing temperatures rather than by full austenitizing and over-tempering to an equivalent hardness level.

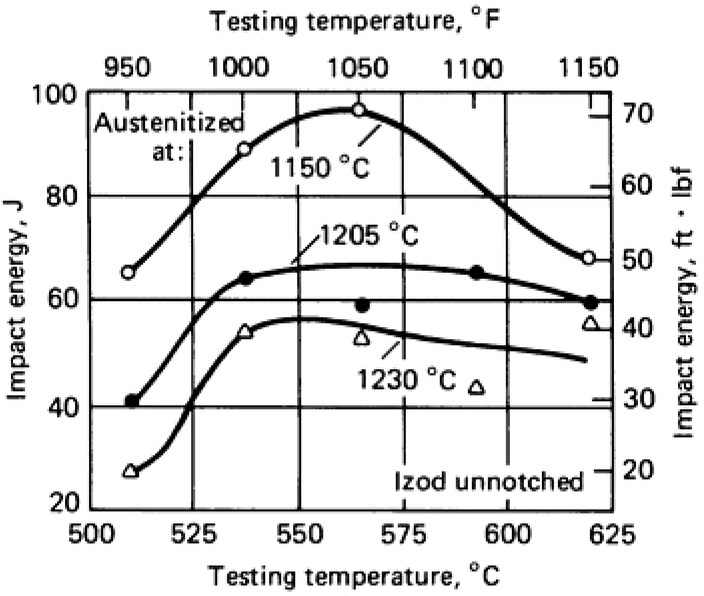


Fig. 13 Effect of austenitizing and tempering temperatures on impact strength of M2 steel

Figure 14 illustrates the sacrifice in high-temperature hardness of M2 that results from the use of reduced austenitizing temperatures.

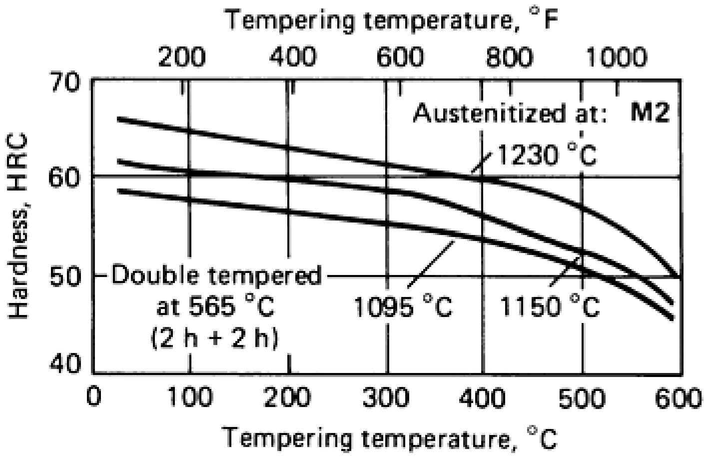


Fig. 14 Effect of austenitizing temperature on high-temperature hardness of M2 steel

Quenching. High-speed steels can be quenched in air, oil, or molten salt. However, except for thin tools, which are air quenched between plates to keep them straight, it is customary to quench in oil from muffle or semimuffle furnaces and in molten salt from a high-temperature salt bath. After its temperature has been equalized in the salt quench, the tool is air cooled. For large cutters heated in a furnace, an interrupted oil quench is often used to minimize quenching strains and prevent cracking. This consists of cooling the cutters in the oil only until they lose color (about 540 °C, or 1000 °F) and then cooling in air. Cooling rates ranging from 335 to 555 °C/min (600 to 1000 °F/min) are required to develop desirable microstructures (no carbide precipitation on grain boundaries) when cooling from austenitizing temperatures down to 760 °C (1400 °F).

After quenching, high-speed steel tools usually possess high residual stress, and to prevent cracking, it is good practice to transfer them from the quenchant to a tempering furnace before they have cooled to below 65 °C (150 °F). This is particularly important for large or intricate tools, for which a delay between quenching and tempering or permitting the work to cool to too low a temperature will usually induce cracking. If the work cannot be transferred to a tempering furnace at once, it should be put in a holding furnace maintained at 120 to 205 °C (250 to 400 °F) until a tempering furnace is available.

Vacuum furnaces equipped or modified to enhance quenching capabilities have found increasing use in high-speed steel hardening applications. Ongoing vacuum furnace technology developed since 1985 has been incorporated into the production of section sizes up to 75 mm (3 in.) with increases in the mechanical properties of high-speed steels over conventional vacuum furnace equipment produced components. Vacuum hardening has advantages over salt hardening in terms of environmental safety, and energy costs. With proper fixturing (see the article "Heat-Resistant Materials for Furnace Parts, Trays, and Fixtures" in this Volume), vacuum hardening can also minimize distortion.

Bainitic hardening has been used in a few applications. To produce a primary bainitic structure, this treatment is performed by arresting the quench from the austenitizing temperature at approximately 260 °C (500 °F), holding for 4 h, then cooling to room temperature. This produces a structure with about 55% bainite and the remainder retained austenite. Subsequent tempering at normal tempering temperature transforms the retained austenite and tempers the bainite to a Rockwell C hardness 1 to 3 points lower than normal for the selected tempering temperature.

Partial Hardening to Improve Machinability. Annealed high-speed steel may be partially hardened to approximately 270 to 300 HB to improve machinability. At these hardnesses, high-speed steels, including the sulfurized types, are less likely to tear in shaving or back-off operations. Typical heat treating to achieve this result consists of heating to 855 to 870 °C (1575 to 1600 °F), holding for at least 1 h, quenching in oil, and tempering at 635 to 665 °C (1175 to 1225 °F) to obtain the desired hardness. If the austenitizing temperature does not exceed 870 °C (1600 °F), this treatment will not cause grain coarsening in the final hardening operation.

Certain machining operations, such as drilling and rough milling, should be performed in the annealed condition to obtain maximum tool life.

Tempering. As shown in Fig. 15 for an M2 steel austenitized at 1220 °C (2225 °F), the hardness of high-speed steel is directly affected by tempering temperature and time. From the slope of the curves in Fig. 15, it can be seen that M2 undergoes secondary hardening at temperatures above approximately 370 °C (700 °F) and that secondary hardening proceeds at higher temperatures up to about 595 °C (1100 °F), depending on time at temperature. These temperatures approximate the practical limits for most tempering operations; lower temperatures do not evoke the secondary hardening response, and higher temperatures produce hardnesses considerably lower than are usually desired.

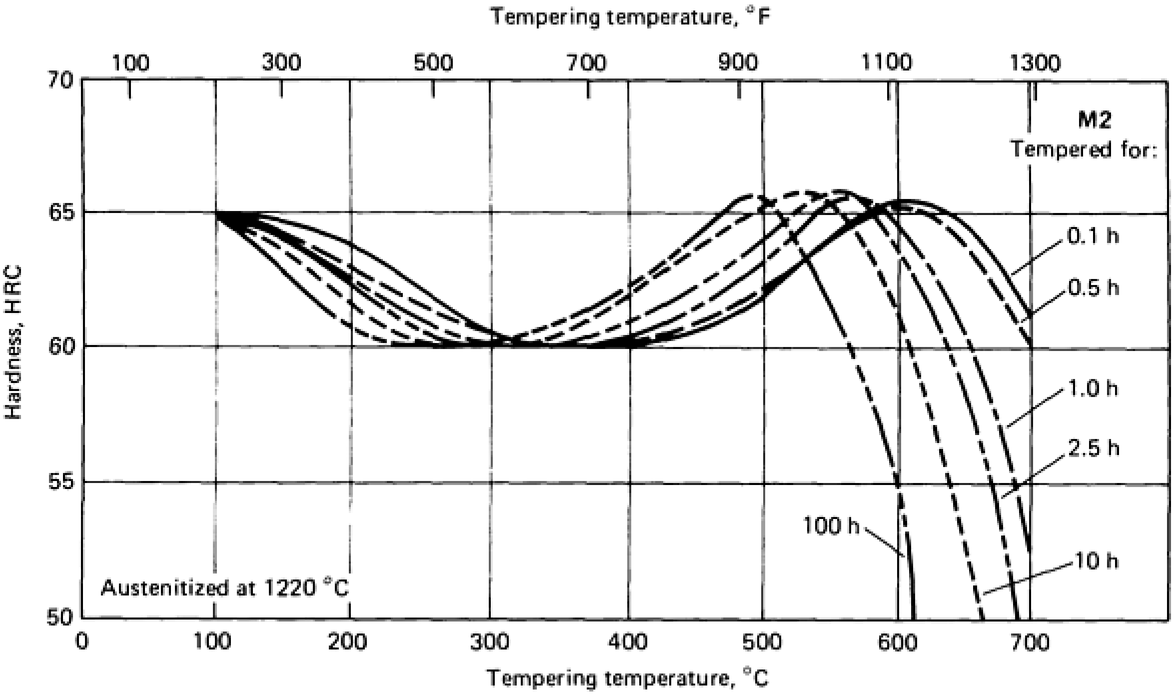


Fig. 15 Effect of tempering temperature and time on hardness of M2 high-speed steel

Emphasizing the practical time-temperature range, the response of several M and T types of high-speed steel to tempering at 425 to 705 °C (800 to 1300 °F) for periods ranging from $\frac{1}{2}$ to 10 h is indicated in Fig. 16.

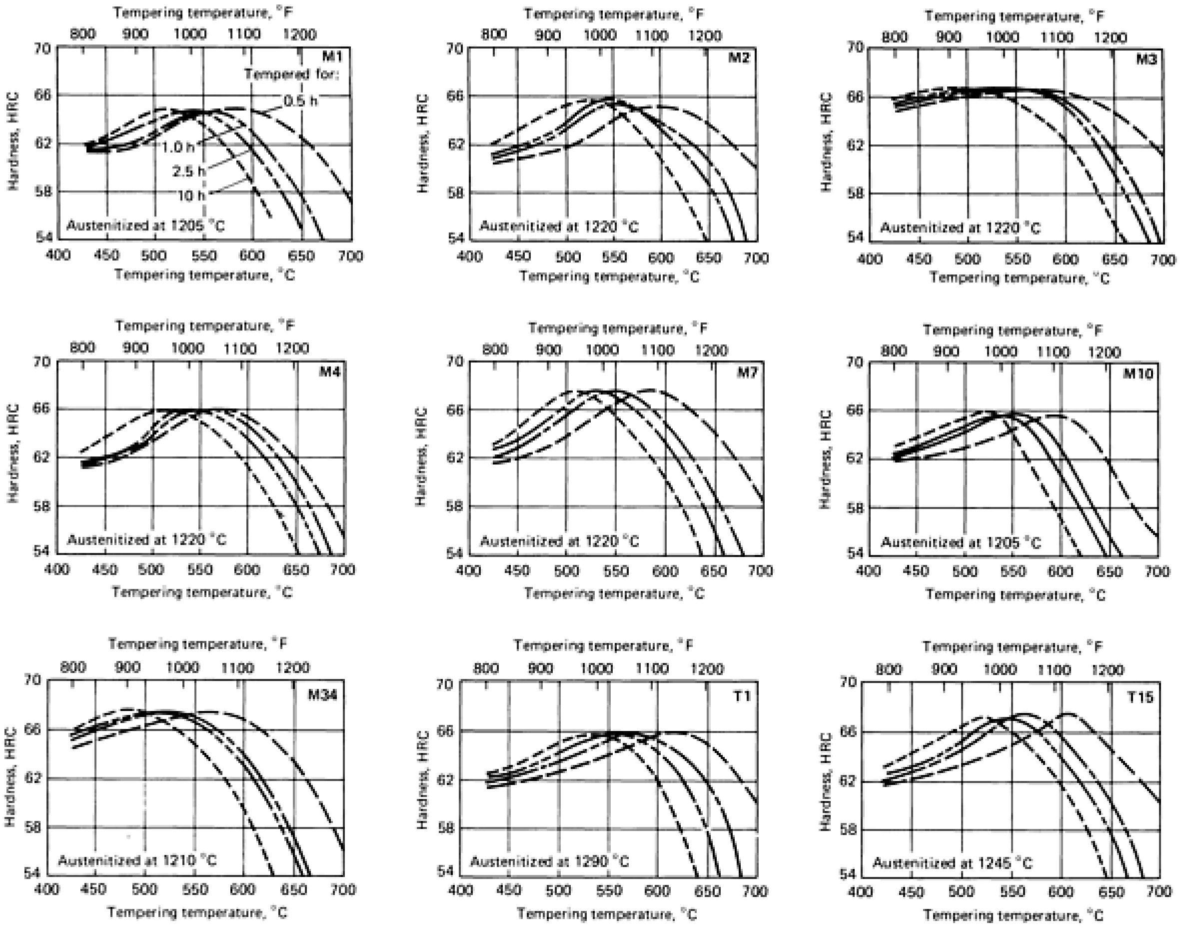


Fig. 16 Effect of tempering at temperatures from 425 to 705 °C (800 to 1300 °F) for periods of $\frac{1}{2}$ to 10 h on hardness of high-speed steels

The effect of austenitizing temperature on the tempering characteristics of several high-speed steels tempered from 480 to 675 °C (900 to 1250 °F) is shown graphically in Fig. 17. For all of the steels for which data are plotted, the highest austenitizing temperature results in maximum solution of alloy carbides--which, during subsequent tempering, produces the maximum response to secondary hardening.

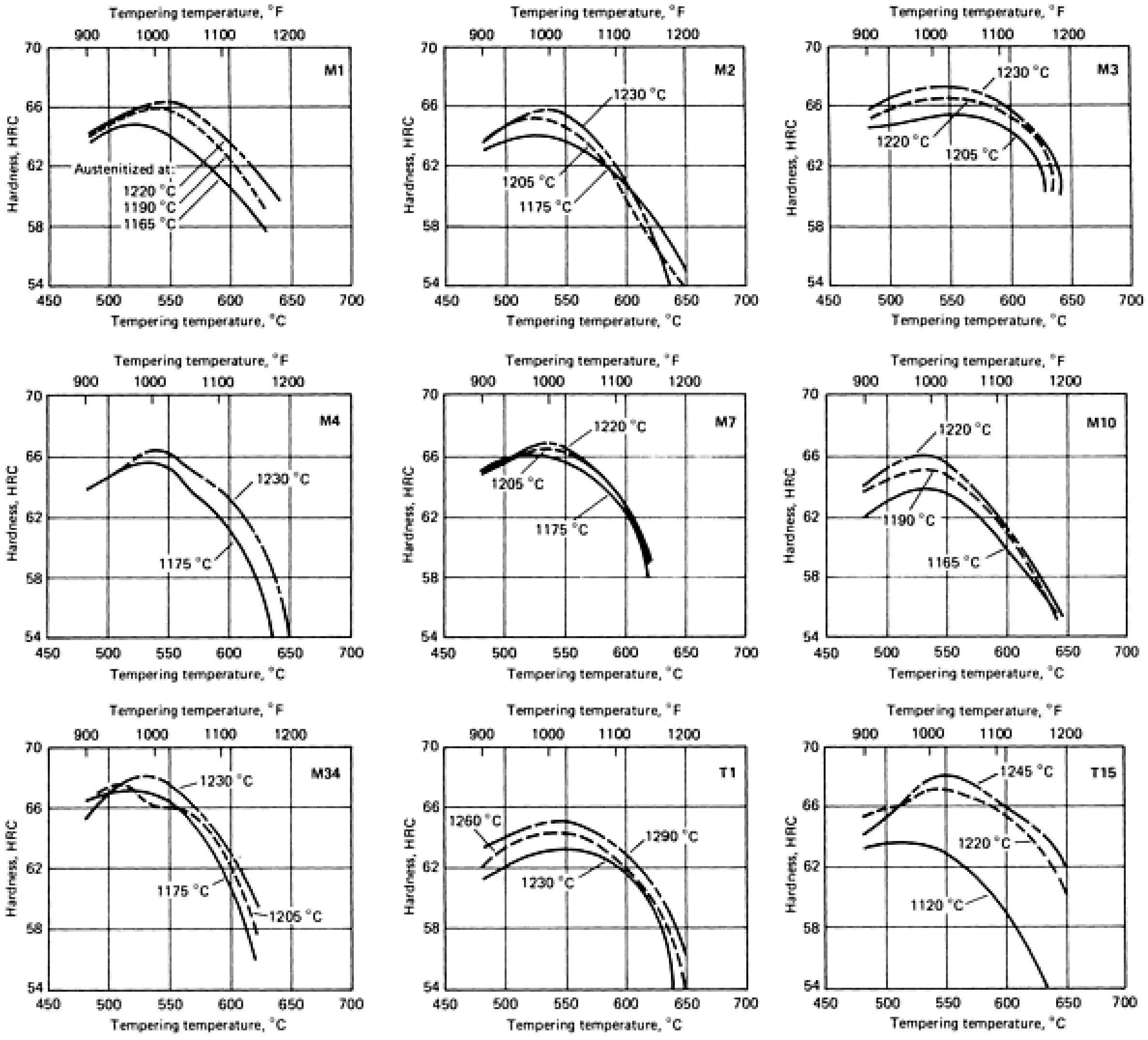


Fig. 17 Effect of austenitizing and tempering temperatures on hardness of high-speed steels. Steels were double tempered (2 h + 2 h).

High-speed steels normally are subjected to a minimum of two separate tempering treatments within the range of 540 to 595 °C (1000 to 1100 °F). The actual tempering temperature depends on tool type (for example, drills typically require temperatures of 540 to 555 °C, or 1000 to 1030 °F, and taps typically require temperatures of 560 to 580 °C, or 1040 to 1080 °F). The duration of each treatment is usually 2 h or more at temperature. This process ensures attaining consistent martensitic structures, because the amount of retained austenite in the as-quenched condition will vary significantly because of variations in heat chemistry, prior thermal history, hardening temperature, and quenching conditions.

It is essential that the time-temperature combination of the first tempering operation be adequate to condition the retained austenite. Consequently, the first tempering treatment is sometimes longer and at a slightly higher temperature than the second, because the latter is used to temper the freshly formed martensite that develops on cooling from the first temper. Moreover, multiple tempering gains in importance in attaining an acceptable structure if short tempering times are used. The hardness of single and double tempered M2 steel austenitized at various temperatures, as affected by tempering temperature, is shown in Fig. 18.

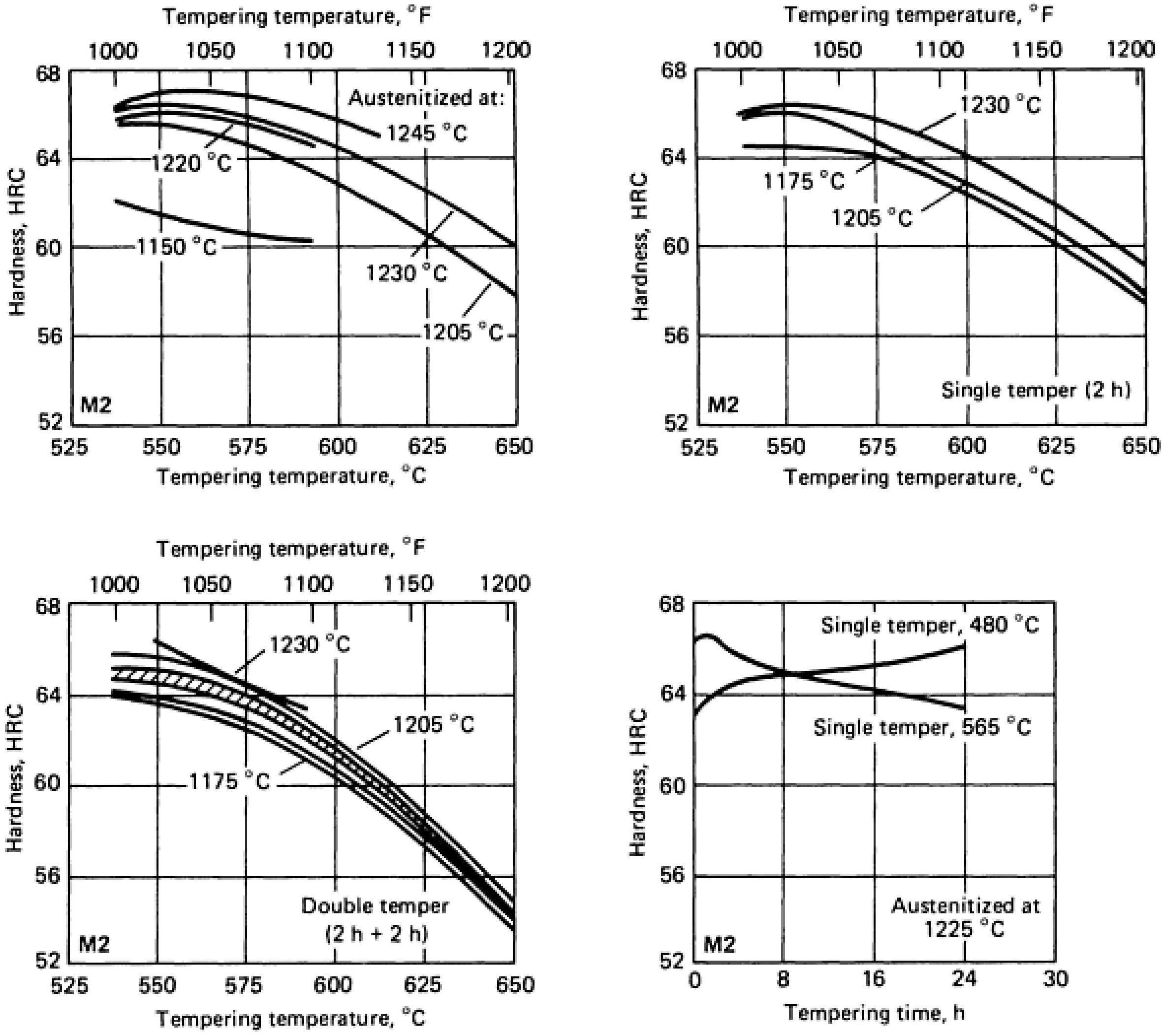


Fig. 18 Effect of austenitizing temperature and tempering conditions on hardness of M2 high-speed tool steel

Tempering at too low a temperature or for too short a time, or both, may not adequately condition the 20 to 30% retained austenite present after initial quenching, and the steel will still retain abnormally large quantities of austenite after cooling from the initial temper. This austenite will not transform until the steel is cooled from the second temper, and a third temper is then required to temper the martensite so formed. It should be noted that the second temper provides a negligible increase in hardness. In order to carry these reactions as near to completion as possible, high-speed steel should always be cooled to room temperature between tempers. The beneficial effect of multiple tempering on mechanical properties of T1 high-speed steel is shown in Table 11.

Table 11 Effects of single and double tempering on mechanical properties of T1

Time at tempering temperature	**Hardness, HRC**	**Bend strength, MPa (ksi)**	Torsion-impact strength, J (ft · lbf)
Single tempering at 565 °C (1050 °F)			
6 min	65.1	2150 (312)	**22 (16)**

1 h	65.7	1860 (270)	**41 (30)**
$2\frac{1}{2}$ h	65.0	2810 (408)	**65 (48)**
5 h	64.5	2590 (376)	**65 (48)**
Double tempering at 565 °C (1050 °F)			
$2\frac{1}{2}$ h + $2\frac{1}{2}$ h	**64.5**	**3130 (454)**	**85 (63)**

Forced-air furnaces are generally conceded to be the most desirable for tempering high-speed steel, because the heat is transmitted from the heating elements to the work by convection; consequently, the transfer of heat is gradual, and there is little danger of the work cracking as the result of thermal shock. It is advisable to place the work in a tempering chamber maintained in the temperature range of 205 to 260 °C (400 to 500 °F) and to bring the work up to the tempering temperature slowly with the furnace. This is particularly important for large or intricate tools, because too rapid a heating rate may lead to cracking.

The very rapid heating rates of molten lead or salt baths, and the attendant thermal shock, usually militate against their successful use for tempering high-speed steel tools of other than simple shape and design, unless they are preheated to about 315 °C (600 °F) before being introduced into the bath.

Refrigeration treatment may be employed to transform retained austenite. The application of a refrigeration treatment is recommended for high-alloy high-speed steels such as M42, M3 (class 2), and CPM Rex 60. Best results are obtained when the refrigeration treatment is performed after the quenching operation. The hardened or hardened and tempered tool is cooled to at least -85 °C (-120 °F) and then tempered or retempered at normal tempering temperatures. Carburized surfaces will respond satisfactorily to the -85 °C (-120 °F) treatment, even when they have been tempered prior to refrigeration.

Nitriding. Liquid nitriding is preferred to gas nitriding for high-speed steel cutting tools because it is capable of producing a more ductile case with a lower nitrogen content.

Although any of the liquid nitriding baths or processes may be used to nitride high-speed steel, the commercial bath consisting of 60 to 70% sodium salts and 30 to 40% potassium salts is most commonly employed. The nitriding cycle for high-speed steel is of relatively short duration, seldom exceeding 1h; in all other respects, however, the procedures and equipment are similar to those used for low-alloy steels.

The cyanide baths employed in liquid nitriding introduce both carbon and nitrogen into the surface layers of the nitrided case. Normally, the highest percentages of both elements are found in the first 0.025 mm (0.001 in.) surface layer. For carbon and nitrogen gradients, see the section on liquid nitriding.

The effect of time in a liquid nitriding bath at 565 °C (1050 °F) on the nitrogen content of the first 0.025 mm (0.001 in.) surface layer of a T1 high-speed steel is shown in Table 12. A nitrogen content of 0.06% was obtained in the first 3 min at temperature, and it gradually increased to 1.09% at the end of a 6-h cycle at this temperature.

Table 12 Effect of nitriding time on surface nitrogen content of T1 high-speed tool steel

Nitrogen content of first 0.025 mm (0.001 in.) layer

Time at 565 °C (1050 °F)	Nitrogen, %

3 min	**0.06**
10 min	**0.093**
30 min	**0.15**
90 min	**0.26**
3 h	**0.58**
6 h	**1.09**

As shown in Table 13, carbon also was absorbed by the steel, at nitriding temperatures as low as 455 °C (850 °F). In a 30-min nitriding cycle, the carbon content of the first 0.025 mm (0.001 in.) surface layer increased with an increase in the nitriding temperature. However, it was reported that only a portion of the carbon was absorbed by the steel, most of the carbon being mechanically attached to the surface, filling microscopic pits. (This pitting is not dangerous under normal conditions, because the pits are shallower than ordinary grinding or machining marks.)

Table 13 Carbon content of nitrided T1 high-speed tool steel

Carbon content of the first 0.025 mm (0.001 in.) surface layer of steel originally containing 0.705% C. Some of the carbon was in pits on the surface, rather than diffused into the steel.

Nitriding			Surface carbon, %
Temperature		**Time, min**	
°C	**°F**		
455	850	30	**0.85**
510	950	30	**0.99**
565	1050	30	**1.18**

High-speed steel tools that are nitrided in fresh baths or for short times show steep nitrogen and hardness gradients. To avoid these steep gradients, which are believed responsible for the brittleness of the case after such treatments, the use of longer immersion time, higher temperature, or a thoroughly aged bath is recommended. To avoid brittleness of case when relatively short immersion times are used, the cyanate content of the bath should exceed 6%. These conditions often will lower the surface hardness as well as the hardness gradient.

Figure 19 compares the hardness gradients obtained on specimens of T1 high-speed steel nitrided at 565 °C (1050 °F) for 90 min in a new bath and for various lengths of time in an aged bath.

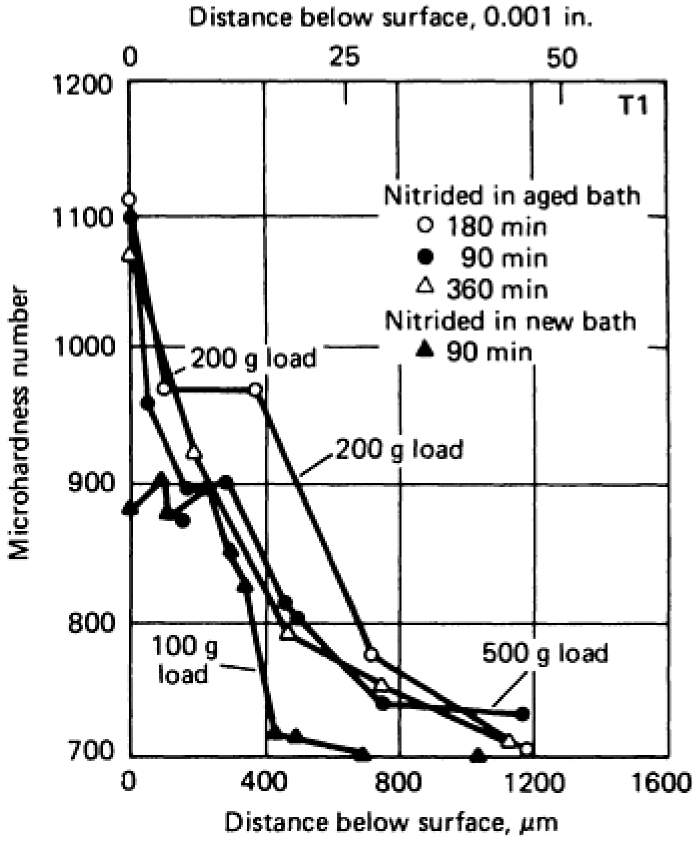


Fig. 19 Effect of bath condition and immersion time on hardness gradients in type T1 high-speed steel specimens nitrided at 565 °C (1050 °F)

Nitriding of decarburized high-speed steel tools should be avoided, because it results in a brittle surface condition. For those surfaces that have been softened from grinding, nitriding is frequently employed as an offsetting corrective measure.

Liquid nitriding provides high-speed steel tools with high hardness and wear resistance and a low coefficient of friction. These properties enhance tool life in two somewhat related ways. The high hardness and wear resistance lower the abrading action of chips and work on the tool, and the low frictional characteristics serve to create less heat at and behind the tool point, in addition to assisting in the prevention of chip pickup (see the article "Wrought Tool Steels" in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook*).

Plasma nitriding (also known as ion nitriding, glow-discharge nitriding, and the glow-discharge deposition process) is a heat treatment that uses a large electrical potential to ionize (break down) a treatment gas into ions which are attracted to the surface of the workpiece. When the reaction is properly controlled, the hardened case obtained is similar to a liquid nitride case.

Detailed information is available in the article "Plasma (Ion) Nitriding" in this Volume.

Steam treating produces a nonuniform, soft layer of iron oxide on the surface of finished high-speed steel tools. This layer, approximately 0.005 mm (0.0002 in.) thick, has lubricant-retaining and antigalling properties, and in some applications will improve tool life by reducing tool-edge buildup. The oxide layer is removed from the tool after a short interval of operation; during this interval, the cutting surfaces of the tool develop a burnished surface that adds further to antigalling characteristics.

Steam treatment requires a special furnace with a sealed retort from which all air can be displaced by steam, which is admitted at controlled rates. The presence of excessive levels of moisture in the furnace prior to the admission of the steam will cause rusting and an unsatisfactory surface finish.

A typical processing cycle involves placing the work in the special furnace, heating to approximately 370 °C (700 °F), and equalizing. After a suitable equalizing time, which depends on the load, the steam is admitted at controlled rates for approximately $\frac{1}{2}$ h. The furnace is then partly sealed to develop positive steam pressure, and the temperature is raised to 525 °C (975 °F). The steam can then be shut off and the work removed from the furnace and cooled normally.

The treatment produces a blue-black film whose appearance is improved by subsequent dipping in oil. This treatment may sometimes be combined with normal tempering treatments, because the type of film produced is relatively insensitive to temperature up to approximately 580 °C (1075 °F). Steam treating offers an additional advantage for tools hardened in salt baths, because it effectively reduces the pitting that can result from adhering salt.

Carburizing is not recommended for high-speed steel cutting tools because of the extreme brittleness of the case so produced. However, it is suitable for applications requiring extreme wear resistance in the absence of impact or highly concentrated loading, such as are encountered with certain types of cold-work dies made from high-speed steel. At the same level of hardness, the carburized layer does not have the heat resistance of normal high-speed steel because carbides in the microstructure are predominantly Fe_3C, rather than the complex alloy carbides characteristic of high-speed steel.

Carburizing cycles for high-speed steel consist of packing in a carburizing medium, heating to approximately 1040 to 1065 °C (1900 to 1950 °F) long enough to develop the depth of case desired, and air cooling. The usual holding time at carburizing temperature is from 10 to 60 min, to produce a case 0.05 to 0.25 mm (0.002 to 0.010 in.) deep. Deeper cases should be avoided because of the extreme brittleness which develops. This treatment carburizes the surface and serves as the austenitizing treatment for hardening the entire piece. The carburized layer will harden to 65 to 70 HRC at the surface.

Hardening of Specific Machine Tools

High-speed tool steels are used extensively as materials for broaches, chasers, milling cutters, drills, taps, reamers, form tools, hobs, thread rolling dies, threading dies, tool bits, and bearing components.

Broaches require maximum edge hardness because of the continuous cutting action and light chip load to which they are subjected. This indicates a minimum hardness of 65 HRC for the standard grades and 66 HRC for the premium grades of high-speed steel.

Broaches should be suspended vertically in the hardening furnace to avoid undue distortion, and should be quenched under controlled and uniform cooling conditions. Broaches should be straightened while still warm from the hardening operation, and should be cooled to at least 65 °C (150 °F) before tempering. These precautions are particularly important for large diameters.

Chasers, because they usually are quite small, present no particular problem in hardening with regard to straightness or residual stress. Hardness recommendations for chasers depend largely on the type of application and the pitch of the thread. Recommended hardnesses for chasers used to cut threads in steel are listed in Table 14.

Table 14 Recommended hardness values for chasers and taps used to cut threads in steel

Threading tool	Hardness, HRC			
	Fine-pitch threads	**Coarse-pitch threads**	**Acme threads**	Pipe threads
Chasers	61-63	64-65	60-62	...
Taps	**63-65**	**63-65**	**62-64**	**62-64**

For cutting cast iron or plastics, chasers should be heat treated to the maximum attainable hardness, because these materials are cut without any significant cutting force but require maximum abrasion resistance. For Acme threads, however, it is sometimes advisable to underharden.

Milling Cutters. Fine-tooth cutters and those with fragile forms should be hardened to 63 to 64 HRC. Heavy-duty milling cutters and cutters for use on soft, abrasive materials should be hardened to the maximum hardness obtainable for the particular type of steel.

Drills. Hardening techniques for drills vary, depending on the diameter of the drill. Straightness of these tools is extremely important. Various jigging methods are employed, but it is usually advisable to heat treat drills vertically suspended by their shanks in order to reduce distortion in the hardening operation. Straightening is best accomplished in the as-hardened condition before tempering. In tempering, the tempering furnace must not be overloaded, and all drills must receive the correct tempering temperature and time at temperature.

Specific recommendations for the hardness of drills for cutting steel are as follows:

- Most drills 5 mm ($\frac{3}{16}$ in.) in diameter and smaller are usually hardened to 63 to 65 HRC. (Drills of this size used for plastics, aluminum, or magnesium may have hardness as high as 65 HRC)
- Drills over 5 mm ($\frac{3}{16}$ in.) in diameter, to 63 to 65 HRC
- Heavy-duty drills normally use grades of high-speed steel providing hardnesses equal to or higher than those noted above. (These drills generally are designed for maximum rigidity and require maximum abrasion resistance)

Taps, like drills, are slender in section and require hardening techniques that minimize distortion; this generally means hardening in the vertical position suspended in suitable jigs. Taps should be straightened in the as-hardened condition before tempering. Tempering of these tools must be carefully controlled to allow adequate heating time. Specific hardness recommendations for taps that are to be used to cut steel are listed in Table 14.

Reamers encounter a minimum chip load but require maximum wear resistance. For this reason, they are always hardened to the maximum hardness attainable for each grade of steel.

Form tools of all types also should have maximum hardness. In general, a minimum of 65 HRC is necessary, and for the premium grades hardnesses ranging from 68 to 70 HRC are frequently desirable.

Hobs. Because of their shaving action, hobs require maximum edge hardness. They may become oval in shape if they are not placed in the hardening furnace in the vertical position. Such placement may require special fixtures. Techniques and temperatures in both hardening and tempering must be accurately controlled if tools of this type are to be produced successfully and economically.

The hardness of fragile tooth forms may have to be reduced to 62 to 64 HRC to avoid breakage, although the lower hardness results in a shorter production life.

Thread rolling dies are usually made of A2 or D2 steel, although dies made of high-speed steel frequently afford superior results, particularly in rolling the harder materials. For fragile thread forms, thread rolls should be hardened to 60 to 62 HRC. For heavier thread forms and those used to roll high-strength materials, hardnesses of 63 to 65 HRC are recommended; however, at these higher hardnesses, dies are more susceptible to breakage.

Threading Dies. Most threading dies are made of carbon steel; however, button and acorn dies justify the use of high-speed steel. The relation between hardness and thread form for threading dies is the same as that recommended for taps and chasers.

Tool Bits. Standard tool bits, as well as cheeking tools, offset-head bits, and other special types, all require maximum hardness. Standard-duty tool bits should be hardened to 65 to 66 HRC, whereas tool bits made from the higher-alloy high-speed steels should be hardened to 67 to 69 HRC when possible.

Bearing Components. The heat treatment of M50 high-speed steel bearing components for aerospace applications must be capable of producing a part with high hardness, uniformly fine grain size, and dimensional stability over a wide temperature range.

M50 steel has a nominal composition of 0.83C-4.0Cr-4.0Mo-1.0V with a M_s temperature of approximately 163 to 166 °C (325 to 330 °F). The time-temperature transformation (TTT) diagram for M50 is illustrated in Fig. 20.

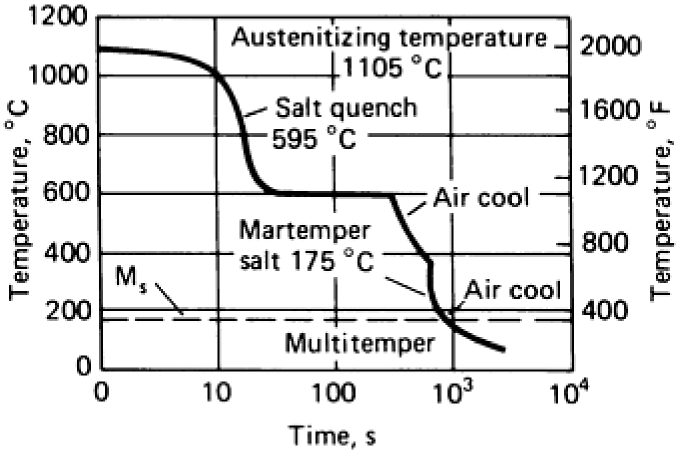


Fig. 20 TTT diagram for M50 steel

Virtually any cooling rate capable of cooling the austenitized part to 205 °C (400 °F) or below in 15 min will produce high hardness. To minimize distortion, residual stress and crack susceptibility, a cooling similar to the idealized rate shown in Fig. 20 is desirable.

The following practices and procedures are recommended for heat treating M50 bearing components to provide optimum bearing properties:

- M50 can be satisfactorily heat treated in vacuum or protective atmosphere furnace. However, most bearing manufacturers prefer to heat treat these bearing components in a neutral molten salt bath or baths
- Parts should be preheated prior to the austenitizing cycle to minimize the required soak time at the high austenitizing temperature. If a single preheat is employed, a bath temperature of 815 to 870 °C (1500 to 1600 °F) with a cycle of 5 to 15 min is recommended. If multiple preheat baths are available, recommended bath temperatures and cycles are listed in Table 15.
- The high-temperature bath cycle is the most critical operation in heat treating M50 steel. Following preheating, parts should be austenitized at 1105 to 1120 °C (2025 to 2050 °F) for 3 to 10 min, depending on cross section and gross load weight. Optimum cycles in the austenitizing bath may be established empirically by varying the soak cycle in the high-temperature bath in $\frac{1}{2}$-min increments and evaluating resultant grain size and hardness. Grain size is more easily measured on as-quenched samples; however, hardness should be checked on parts subsequent to final tempering operations. Ideally, the cycle will be as short as possible to minimize grain growth while producing desired hardness
- Following austenitizing, parts should be quenched in 540 to 595 °C (1000 to 1100 °F) molten salt for 5 to 10 min. The quench minimizes internal stresses and the core-to-surface thermal differential prior to subsequent air cooling and martempering operations
- Parts should be subjected to a 175 to 190 °C (350 to 375 °F) martemper bath for 5 to 15 min following quench or quench/air cool operations. The martemper bath, which operates between 15 and 30 °C (25 and 50 °F) above the M_s temperature for M50, equalizes core-to-surface thermal differentials and facilitates subsequent transformation of austenite into martensite with minimal residual stress, distortion, or cracking potential. To avoid undesirable intermediate transformation products, the interval between austenitizing and martempering should not exceed 15 min
- Following martempering, parts should be air cooled to room temperature prior to washing, tempering, or

subzero treatment. The air-cooling equipment and conditions should provide uniform cooling of parts from the 175 to 190 °C (350 to 375 °F) martempering bath to room temperature within 30 to 60 min. Shorter cooling rates may result in increased residual stress, distortion, or susceptibility to stress cracking

- M50 steel requires multiple tempers to provide maximum toughness and dimensional stability. Parts should be subjected to a minimum of three tempers of 540 to 550 °C (1000 to 1025 °F) for 2 to 4 h, with cooling to room temperature between each temper. Failure to cool to below 40 °C (100 °F) between tempers may result in retained austenite. Tempering may be performed either in neutral molten salts or in atmosphere or air furnaces
- Subjection to subzero temperatures prior to and/or after initial tempering enhances transformation of retained austenite to martensite. Common deep-freeze cycles for M50 are -70 to -85 °C (-90 to -120 °F) for 2 to 4 h. Use of lower temperatures provides little if any added benefit. The deep-freeze cycle provides maximum benefit when employed before tempering; however, it is not recommended for parts not subjected to martempering or parts susceptible to cracking. When parts are subzero treated before tempering, caution should be exercised to ensure that the total elapsed time between martempering and tempering does not exceed 5 h. Use of prior stress-relief cycles reduces effectiveness of deep-freeze operation. When equipment, time constraints, or part design are unfavorable for performing deep freezing prior to tempering, the parts should be subjected to deep freeze between the first and second tempering operations
- Parts requiring re-treating should be annealed prior to rehardening to minimize susceptibility to developing duplex/nonuniform grain

Table 15 Recommended bath temperatures and cycle times for preheated M50 bearing steel

Cycles	**Temperature**		Time[(a)], min
	°C	**°F**	
Two preheat baths			
1	675-730	1250-1350	**10-15**
2	815-870	1500-1600	**5-15**
Three preheat baths			
1	675-730	1250-1350	**10-15**
2	815-870	1500-1600	**5-15**
3	**955-1010**	**1750-1850**	**5-10**

(a) Time predicated on relative load size/bath capacity

Low-Alloy Special-Purpose Tool Steels

Nominal compositions of the low-alloy special-purpose tool steels are given in Table 1 of the article entitled "Introduction to Heat Treating of Tool Steels" in this Volume. These steels are similar in composition to the water-hardening tool steels,

except that the addition of chromium and other elements provides the L steels with greater wear resistance and hardenability. Types L1, L3, L4, and L7 are similar to the production steel 52100 and are used for similar applications.

Because of their relatively low austenitizing temperatures, the L steels are easily heat treated. Recommended heat-treating practices are summarized in Table 16.

Table 16 Recommended heat-treating practices for low-alloy special-purpose tool steels

Steel	**Normalizing temperature**[a]		**Annealing**					Hardening				
			Temperature[b]		**Cooling rate**[c]		**Annealed hardness, HB**	**Austenitizing temperature**[d]		**Holding time, min**	**Quenching medium**	Quenched hardness, HRC[e]
	°C	**°F**	**°C**	**°F**	**°C/h**	**°F/h**		**°C**	**°F**			
L1	900	1650	775-800	1425-1475	22	40	179-207	790-845	1450-1550	10-30	O, W	**64**
L2	870-900	1600-1650	760-790	1400-1450	22	40	163-197	790-845	1450-1550	10-30	W	**63**
L3	900	1650	790-815	1450-1500	22	40	174-201	845-925	1550-1700	10-30	O	**63**
								775-815	1425-1500	10-30	W	**64**
								815-870	1500-1600	10-30	O	**64**
L6	870	1600	760-790	1400-1450	22	40	183-212	790-845	1450-1550	10-30	O	**62**
L7	**900**	**1650**	**790-815**	**1450-1500**	**22**	**40**	**183-212**	**815-870**	**1500-1600**	**10-30**	**O**	64

(a) Holding time, after uniform through heating, varies from about 15 min, for small sections, to about 1 h, for large sections. Work is cooled from temperature in still air.

(b) Lower limit of range should be used for small sections, upper limit for large sections. Holding time varies from about 1 h, for light sections and small furnace charges, to about 4 h, for heavy sections and large charges; for pack annealing, hold for 1 h per inch of pack cross section.

(c) Maximum. Rate is not critical after cooling to below 540 °C (1000 °F).

(d) These steels are seldom preheated.

(e) Typical average values; subject to variations depending on austenitizing temperature and quenching medium

Normalizing should follow forging or any other operation in which the steel has been exposed to temperatures substantially above the transformation range. For the L steels, normalizing consists of through heating to 870 to 900 °C (1600 to 1650 °F) and cooling in still air. The use of a protective atmosphere is recommended.

Annealing must follow normalizing and precede any rehardening operation. Recommended annealing temperatures and cooling rates, as well as expected as-annealed hardness values, are given in Table 16.

Stress relieving prior to hardening may be advantageous for complex tools to minimize distortion during hardening. A common practice for complex tools is to rough machine, heat to 620 to 650 °C (1150 to 1200 °F) for 1 h per inch of cross section, cool in air, and then finish machine prior to hardening.

Austenitizing temperatures recommended for hardening the L steels are listed in Table 16; preheating is seldom employed for steels in this group.

Salt or lead baths and atmosphere furnaces are all satisfactory for austenitizing these steels. A neutral salt, such as No. 3 in Table 1 of the article entitled "Processes and Furnace Equipment for Heat Treating of Tool Steels," is recommended. This salt may be deoxidized, for control of decarburization, by the method indicated in the section on rectification of salt baths in the article "Processes and Furnace Equipment for Heat Treating of Tool Steels" in this Volume.

Quenching. Oil is the quenching medium most commonly used for the L steels. Water or brine may be used for simple shapes, or for large sections that do not attain full hardness by oil quenching. Rolling-mill rolls made of L7 are an example of parts for which water or brine quenching is used. These steels respond well to martempering.

Tempering. Tools made of the L steels should be quenched only to a temperature at which they can be handled with bare hands, about 50 °C (125 °F), and should be tempered immediately thereafter; otherwise, cracking is likely to occur.

The tempering characteristics of these steels are plotted in Fig. 21. For most applications, the S steels are used at near-maximum hardness. It is recommended that tools made of any of these low-alloy steels be tempered at a minimum of 120 °C (250 °F), even though maximum hardness is desired. Double tempering also is recommended.

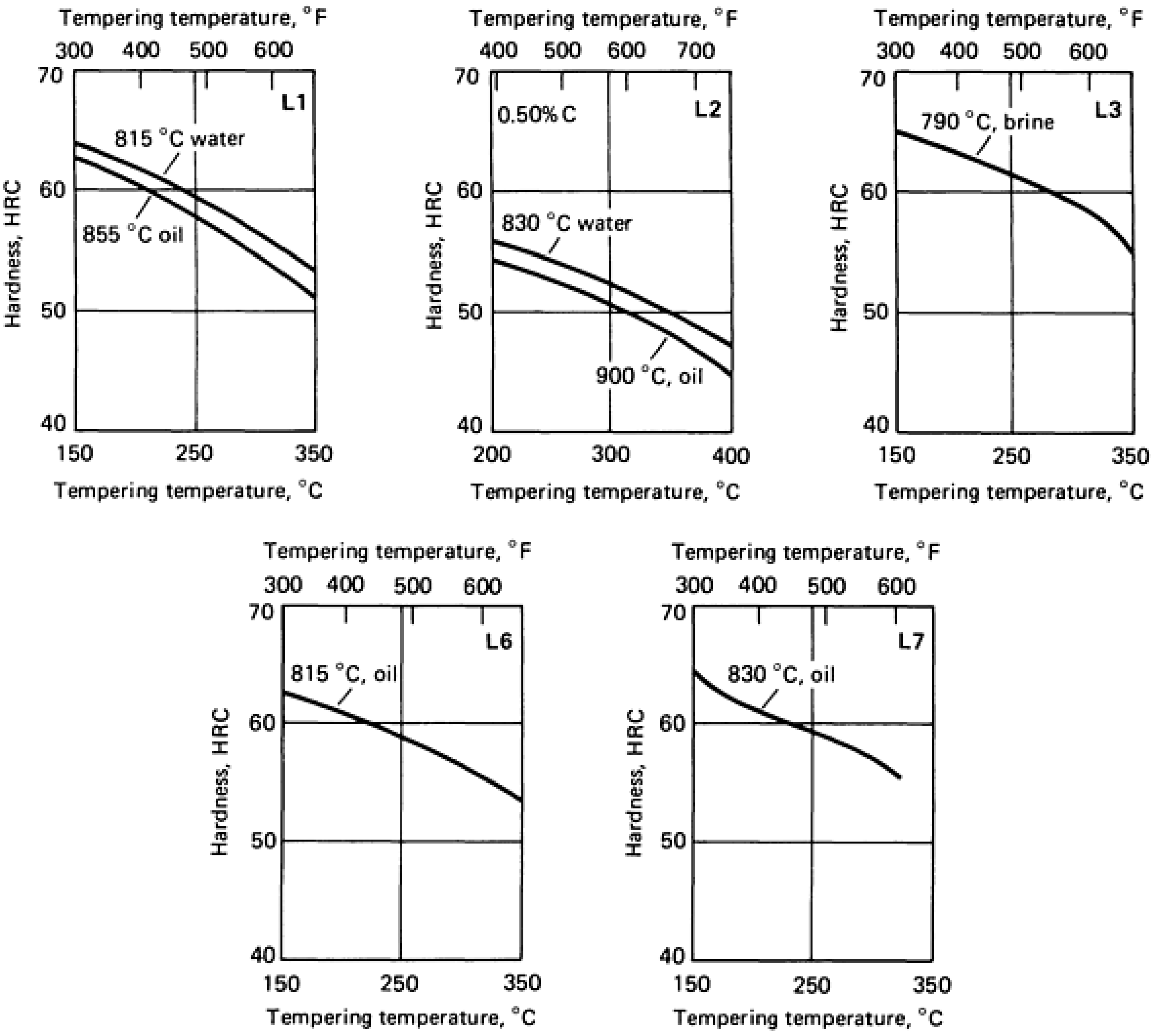


Fig. 21 Hardness of low-alloy special-purpose tool steels after tempering for 2 h

Carbon-Tungsten Special-Purpose Tool Steels

Nominal compositions of carbon-tungsten special-purpose tool steels are given in Table 1 of the article entitled "Introduction to Heat Treating of Tool Steels" in this Volume. Recommended heat-treating practices for these steels are summarized in Table 17.

Table 17 Recommended heat-treating practices for carbon-tungsten special-purpose tool steels

Steel	Normalizing temperature[(a)]		Annealing					Hardening						
								Temperature				Holding time, min	Quenching medium	Quenching hardness, HRC[(d)]
			Temperature[(b)]		Cooling rate[(c)]		Annealed hardness, HB	Preheat		Austenitizing				
	°C	°F	°C	°F	°C/h	°F/h		°C	°F	°C	°F			

F1	900	1650	760-800	1400-1475	22	40	183-207	650	1200	790-870	1450-1600	15	W, B	**64**
F2	900	1650	790-815	1450-1500	22	40	207-235	650	1200	790-870	1450-1600	15	W, B	**66**
F3	**900**	**1650**	**790-815**	**1450-1500**	**22**	**40**	**212-248**	**650**	**1200**	**790-870**	**1450-1600**	**15**	**W, B, O**	**66**

W, water: B, brine; O, oil.

(a) Holding time, after uniform through heating, varies from about 15 min, for small sections, to about 1 h, for large sections. Work is cooled from temperature in still air.

(b) Lower limit of range should be used for small sections, upper limit for large sections. Holding time varies from about 1 h, for light sections and small furnace charges, to about 4 h, for heavy sections and large charges; for pack annealing, hold for 1 h per inch of pack cross section.

(c) Maximum cooling rate. Rate is not critical after steel has been cooled to below 540 °C (1000 °F).

(d) Typical average hardness values; subject to variations depending on austenitizing temperature and quenching medium employed

As a group, these steels are shallow hardening and usually are quenched in water or brine. Steel F3, because of the chromium addition, is the highest in hardenability.

Normalizing and Annealing. These steels should be normalized after they have been forged or otherwise subjected to temperatures above their hardening temperatures. Normalizing and annealing practices are essentially the same as those recommended in the preceding section (see "Low-Alloy Special-Purpose Steels") of this article. Recommendations for normalizing and annealing the F steels are given in Table 17.

Stress relieving as outlined previously for the low-alloy special-purpose steels may be advantageously applied also to the F steels. The same procedure as that described for the L steels would be used.

Austenitizing. Preheating and austenitizing temperatures recommended for the carbon-tungsten special-purpose tool steels are given in Table 17. Equipment and practices are generally the same as those previously described for the low-alloy special-purpose steels.

Quenching. Water or brine quenching causes high distortion in parts made of the F steels. This is often used to advantage in the rehardening of worn dies that have been used for cold drawing of bars and tubes. Such dies are flush quenched--that is, a spout of water is directed into the bore, thus causing shrinkage and allowing further use of dies for the same product size.

Tempering. Because tools made of the F steels (cold drawing dies, for example) are used mainly for applications requiring wear resistance, they are usually placed in service at or near their maximum hardness. Therefore, tempering temperatures higher than 205 °C (400 °F) are seldom used. The effect of tempering temperature on hardness for the F steels is shown in Fig. 22.

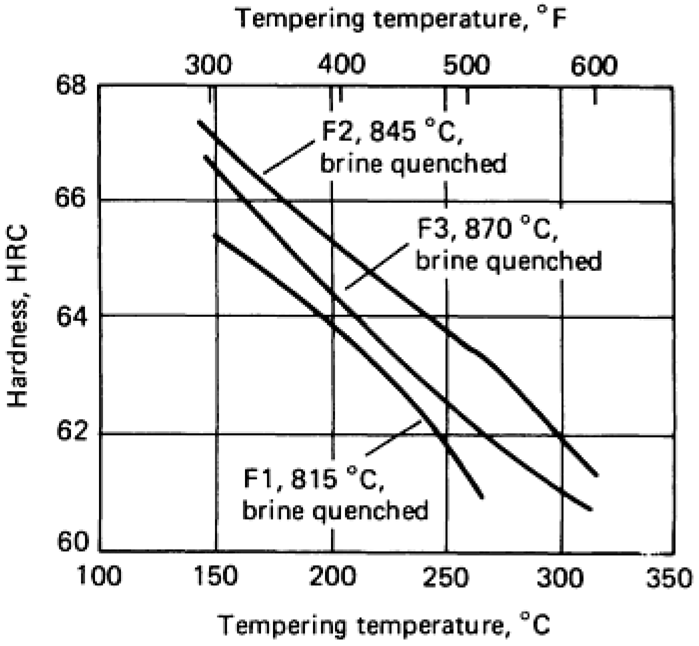


Fig. 22 Tempering characteristics of carbon-tungsten special-purpose tool steels tempered 2 h after being brine quenched

Mold Steels

The principal use of these type P steels is for plastic molds. However, some steels, such as P4, P20, and P21, are used also for die-casting dies. The several types vary widely in composition (see Table 1 of the article "Introduction to Heat Treating of Tool Steels"), from the unalloyed hubbing iron P1, to P4, P6, and P21, which contain over 5% total alloying elements.

The wide variations in composition, method of forming the mold cavity, molding method, and material to be molded are major influences on choice of mold material as well as method of heat treating. The two most common methods of heat treating the mold steels are (1) preharden the steel (or partially machined mold or die) to about 30 to 36 HRC, finish machine, and use at this hardness level and (2) case harden by carburizing. Nitrided molds have proved successful in some instances, but nitriding is not used extensively.

When molds are carburized or nitrided, the same procedures are used as for production steels.

Heat-treating practices for the mold steels are summarized in Table 18. P21 is a special type of mold steel that is heat treated by the manufacturer and delivered ready for the user to machine and place in operation without further treatment. As noted in Table 18, this steel is hardened by solution treating and aging.

Table 18 Recommended heat-treating practices for mold steels

Steel	Normalizing temperature[(a)],		Annealing					Carburizing temperature		Hardening (after carburizing)				
			Temperature[(b)]		Cooling rate[(c)]		Annealed hardness, HB			Austenizing temperature		Holding time, min	Quenching medium	Quenched hardness, HRC
	°C	°F	°C	°F	°C/h	°F/h		°C	°F	°C	°F			
P1	Not req		730-900	1350-1650	22	40	81-101	900-925	1650-1700	790-800	1450-1470	15	W, B	**62-64**
P2	Not req		730-815	1350-1500	22	40	103-123	900-925	1650-1700	830-845	1530-1550	15	O	**62-65**
P3	Not req		730-815	1350-1500	22	40	109-137	900-925	1650-1700	800-830	1470-1530	15	O	**62-64**
P4	Not req		870-900	1600-1650	14	25	116-128	970-995	1780-1820	970-995	1780-1820	15	A	**62-65**
P5	Not req		845-870	1550-1600	22	40	105-116	900-925	1650-1700	845-870	1550-1600	15	O, W	**62-65**
P6	Not req		845	1550	8	15	183-217	900-925	1650-1700	790-8815	1450-1500	15	A, O	**60-62**
P20	900	1650	760-790	1400-1450	22	40	149-179	870-900[(d)]	1600-1650[(d)]	815-870	1500-1600	15	O	**58-64**
P21	**900**	**1650**	**Not rec**		**Hardened by solution treating and aging[(e)]**									

W, water; B, brine; O, oil; A, air; Not rec, not recommended; Not req, not required;

(a) Holding time, after uniform through heating, varies from about 15 min, for small sections, to about 1 h, for large sections. Work is cooled from temperature in still air.

(b) Lower limit of range should be used for small sections, upper limit for large sections. Holding time varies from about 1 h, for light sections and small furnace charges, to about 4 h, for heavy sections and

large charges; for pack annealing, hold for 1 h per inch of pack cross section.

(c) Maximum. Rate is not critical after cooling to below 540 °C (1000 °F).

(d) When applicable.

(e) Solution treatment: Hold at 705 to 730 °C (1300 to 1350 °F) for 1 to 3 h, quench in air or oil; approximate solution treated hardness, 24 to 28 HRC. Aging treatment: Reheat to 510 to 550 °C (950 to 1025 °F); approximate aged hardness, 40 to 30 HRC

Annealing temperatures and expected resulting hardness values are indicated in Table 18. For some types, such as P1, the annealing temperature is not critical. A more important factor is surface protection, especially if the mold cavities will be formed by hubbing. If surfaces are allowed to carburize, even slightly, during annealing, subsequent rubbing will be impaired.

Usually, parts are packed in an inert material such as spent pitch coke and are held at annealing temperature only long enough to become heated through; they are then cooled in the pack to below 540 °C (1000 °F), after which they may be removed from the pack. If rubbing is to follow, it is usually preferable to use the lower side of the annealing temperature range to minimize the danger of carburizing, even though annealing at the higher side of the range will result in slightly lower hardness. Atmosphere-controlled furnaces that can be programmed for slow cooling can also be used for annealing. For hubbing deep cavities, two or more in-process anneals are sometimes required.

When cavities will be formed entirely by machining (sometimes a combination of hubbing and machining is used), annealing usually is neither necessary nor desirable, because slightly harder structures can be machined more easily. Steels as received from the manufacturer are usually suitable for machining. If hardened molds require reworking, they can be annealed as recommended in Table 18.

Additional Heat Treatments. Variations in heat treatment, as necessitated by differences in composition, properties, and intended use, are discussed in the following sections for steels P1 to P20.

P1 steel, although shown in Table 1 of the article entitled "Introduction to Heat Treating of Tool Steels" as containing no alloying elements, may contain about 0.10% V, which promotes a finer grain after carburizing, with no apparent sacrifice in hubbability. This steel usually is used only for hubbed molds for injection molding of general-purpose plastics.

P1 steel can be carburized by any of the regular practices. Whether the steel is reheated to the austenitizing temperature or quenched from a programmed furnace depends on equipment used. Full hardness (Table 18) can be achieved only by water or brine quenching. Practice varies as to working hardness range.

A minimum tempering temperature of 175 °C (350 °F) is recommended. This will retain a finished surface hardness of 60 HRC or slightly higher. However, a more commonly desired hardness range is 54 to 58 HRC, which is obtained by tempering at 260 to 315 °C (500 to 600 °F). If the distortion encountered from water quenching cannot be tolerated for a particular mold design, a type of mold steel that can be hardened by oil quenching must be used instead of P1.

P2 steel also is a hubbing steel, although it is less easily hubbed than P1. Carburizing and hardening practice and the working hardness range are the same as for P1, except that the alloy content of P2 increases hardenability so that full hardness can usually be obtained by oil quenching, thus minimizing distortion.

P3 steel is also hubbed, but it is less easily hubbed than P1 or P2. Except that P3 is usually oil quenched, the carburizing and hardening practice for it is essentially the same as that outlined above for P1. The operating hardness range may vary from 54 to 64 HRC, but common practice is to temper at about 315 °C (600 °F) to achieve a final hardness of 54 to 58 HRC.

P4 steel is sometimes used hubbed, but because of its resistance to cold deformation it is more often used for machined molds or dies. Of all the steels in this group, P4 is the most resistant to wear and to softening by tempering. Because of these properties, it is commonly used for injection molding of plastics that require high curing temperatures and for dies used for die casting low-melting alloys. For the latter application, a common practice is to carburize P4 in cast iron chips to obtain a slight increase in carbon content at the surface. The effect of carburizing practice, as well as case and core hardness values after tempering, is shown in Fig. 23.

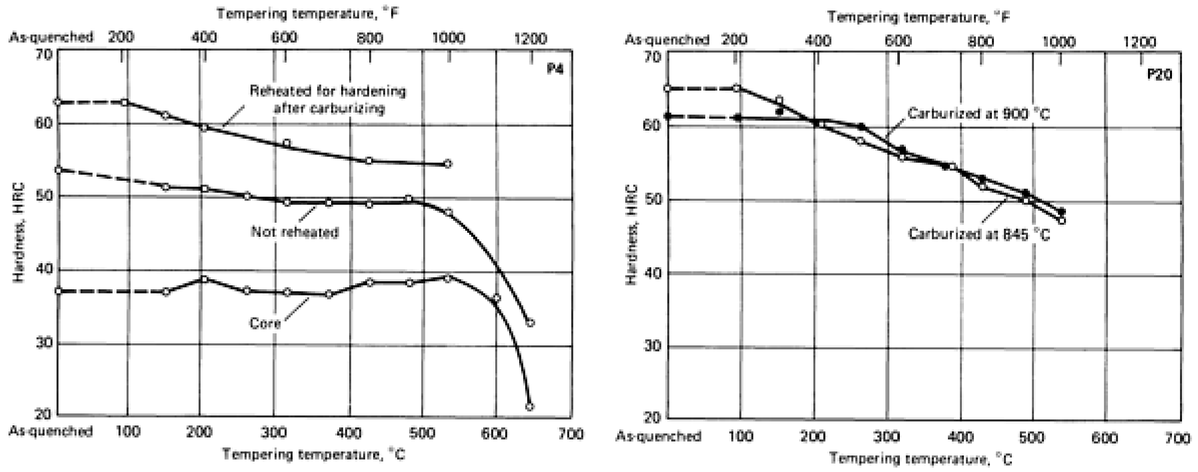


Fig. 23 Tempering characteristics of carburized mold steels. (a) Upper curve represents steel carburized in hardwood charcoal 915 to 925 °C (1675 to 1700 °F) for 8 h, air cooled in pack, reheated at 940 to 955 °C (1725 to 1750 °F), cooled in air and tempered. Middle curve represents steel carburized in cast iron chips at 940 to 955 °C (1725 to 1750 °F), removed from pack, cooled in air and tempered. (b) Surface hardness after heating at temperature for 2 h in carburizing compound, oil quenching, and tempering

Because of its high alloy content, P4 steel can be hardened by air cooling. However, it is sometimes quenched in oil to minimize scaling during cooling. For use in plastic molds, the most common working range is 56 to 60 HRC, which may be obtained by tempering the carburized and hardened molds at 205 to 315 °C (400 to 600 °F) (see Fig. 23).

P5 steel, in which chromium is the major alloying element, approaches P1 in ease of hubbing and has a core strength equivalent to that of P3. After carburizing, a surface hardness of 65 HRC can be achieved by water quenching, or slightly lower values by oil quenching. Choice of quenching medium depends on mold configuration, allowable distortion, and required hardness. A common working range is 54 to 58 HRC; this can be obtained by tempering at about 260 °C (500 °F).

P6 steel, because it can seldom be annealed to a hardness of less than 183 HB (Table 18), is difficult to hub, and hence it is usually used for machine-cut cavities. It can be carburized by conventional practice. Because of its hardenability, heavy sections of P6 can be oil quenched to full hardness from 790 to 815 °C (1450 to 1500 °F). The as-quenched surface hardness is not quite so high as for some other types, because the high nickel content of P6 promotes retention of austenite. Some of this retained austenite is transformed in tempering, with the result that after tempering up to about 260 °C (500 °F) the hardness will be little or no lower than that obtained after quenching. By tempering at 315 °C (600 °F), the most common working hardness range (54 to 58 HRC) is obtained. In some plants, a working hardness range of 58 to 61 HRC, obtained by tempering at 260 °C (500 °F), is considered preferable.

P20 steel is a popular mold material for either injection or compression molding, and also for die casting low-melting alloys.

For injection molding of the general-purpose plastics or die casting of low-melting alloys, P20 is usually used in the prehardened condition. It is available at hardness levels of about 300 HB or slightly higher. In this condition, cavities are machined and the dies or molds placed in service without further heat treatment. Annealed molds or dies can be austenitized at 845 to 870 °C (1550 to 1600 °F), oil quenched, and tempered at 540 °C (1000 °F), to obtain a hardness of about 300 HB.

Type P20 is often carburized for molds used in compression molding, particularly for molding the more abrasive plastics. Carburizing temperatures no higher than 900 °C (1650 °F) are recommended for this steel, because higher temperatures may impair polishability; otherwise, conventional carburizing practice is used, and molds may be quenched in oil directly from the carburizing temperature. A common working range is 54 to 58 HRC.

Tempering characteristics for P20 carburized at two different temperatures are given in Fig. 23.

This steel is sometimes nitrided for special applications. Conventional nitriding practice is employed. Before being nitrided, P20 should first be quenched and tempered to about 300 HB as outlined above, and cavities should be machined; following this sequence will ensure freedom from carburization or decarburization.

Control of Distortion in Tool Steels

Revised by Bruce A. Becherer, Teledyne Vasco; and Larry Ryan, Lindberg Heat Treating Company

Introduction

DIMENSIONAL CHANGES in tool steel caused by heat treatment are particularly important to the manufacture, proper design, and use of tooling. Although no simple solution to the problem of distortion exists, an understanding of the complex factors involved will lead to procedures for minimizing the amount of change in dimensions. This article deals primarily with irreversible changes that affect the actual net dimensional change or distortion of a part. The reversible effects of thermal expansion and contraction--when a part is heated from room temperature to austenitizing temperature and cooled to room temperature--tend to cancel each other out. Reversible changes cause stressing in the elastic range. Under such conditions, the initial dimensional values can be restored by a return to the original state of stress or temperature.

The upper limit of reversible dimensional change in a tool steel is determined by the stress required to initiate deformation (that is, the elastic limit corresponding to a preselected value of plastic strain), the elastic deformation per unit stress (modulus of elasticity), the effect of temperature on these properties, the coefficient of thermal expansion, and the temperature-time combinations at which stress relief and phase changes occur.

For practical purposes, the modulus of elasticity of all tool steels, regardless of composition or heat treatment, is 210 GPa (30×10^6 psi) at room temperature. Therefore, if a tool steel part deforms excessively under service loading but returns to its original dimensions when the load is removed, a change in grade or type of tool steel or in heat treatment will not be useful. To counteract excessive elastic distortion it is necessary to reduce the applied stress by increasing the section size, or to use a tool material with a higher modulus of elasticity (such as cemented tungsten carbide).

Irreversible changes in size or shape of tool steel parts are those caused by stresses that exceed the elastic limit or by changes in metallurgical structure (most notably, phase changes). Such irreversible changes sometimes can be corrected by thermal processing (annealing, tempering, or cold treating) or by mechanical processing to remove excess material or to redistribute residual stresses.

Nature and Causes of Distortion

Distortion is a general term encompassing all irreversible dimensional changes. There are two main types: size distortion, which involves expansion or contraction in volume or linear dimensions without changes in geometrical form; and shape distortion, which entails changes in curvature or angular relations, as in twisting, bending, and/or nonsymmetrical changes in dimensions. Frequently, both size and shape distortion (shown in Fig. 1) occur during a heat-treating operation.

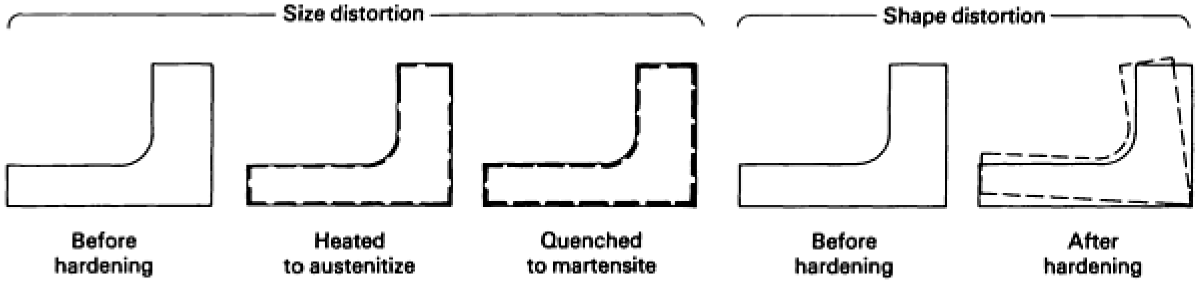


Fig. 1 Size and shape distortion in hardening

Size distortion is the result of a change in volume produced by a change in metallurgical structure during heat treatment. Shape distortion results from either residual or applied stresses. Residual stresses developed during heat treatment are caused by thermal gradients within the metal (producing differing amounts of expansion or contraction), by nonuniform changes in metallurgical structure, and by nonuniformity in the composition of the metal itself, such as that caused by segregation.

Changes in metallurgical structure during heat treatment of tool steels are produced by the three steps described below.

The first step involves heating an annealed structure (usually consisting of ferrite and spheroidal carbides, commonly called spheroidite) to about 800 °C (1450 °F) or higher to change the ferrite to austenite and to dissolve all or most of the spheroidal carbides to the austenite. For plain carbon or low-alloy tool steels, austenitizing results in a contraction in volume. The extent of volumetric contraction decreases with increasing amounts of carbon present in the composition. This can be approximated as follows:

$$V_{SA} = -4.64 + 2.21\ (\%\ C) \qquad \textbf{(Eq 1)}$$

where V_{SA} is the volume change in percent that occurs when spheroidite transforms to austenite. By use of this equation, it can be estimated that, if heated to a temperature high enough to dissolve all of the carbon in the austenite, a 0.50% carbon tool steel would exhibit a volume change of -3.53%, a common type containing 1% carbon would exhibit a change of -2.43%, and a very high-carbon type containing 1.5% carbon would exhibit a change of -1.33%. However, tool steels having carbon contents higher than that of the eutectoid composition are normally austenitized at temperatures only high enough to dissolve the eutectoid amount of carbon. Under these circumstances, 1% carbon and 1.5% carbon tool steels would exhibit changes in volume of -2.77 and -2.53%, respectively, after austenitizing. These percentages are less than that calculated directly from Eq 1 because an allowance must be made for the volume occupied by undissolved carbides, which is about 3.5% for the 1.0% carbon steel and about 12% for the 1.5% carbon steel.

The second step involves cooling quickly enough to cause the austenite to transform to martensite. The steel expands on transformation, the amount of expansion being in inverse proportion to the amount of carbon in solution in the austenite:

$$V_{AM} = 4.64 - 0.53\ (\%\ C) \qquad \textbf{(Eq 2)}$$

where V_{AM} is the percent volume change that occurs when austenite transforms to martensite. By use of Eq 2, it can be estimated that a 0.5% carbon tool steel would exhibit a volume increase for this transformation of 4.37%, and that 1.0 and 1.5% carbon steels would exhibit increases of 4.07% and 3.71%, respectively, if austenitized at the normal austenitizing temperature (only 0.8% carbon, the eutectoid amount, in solution, and again allowing for the volume occupied by undissolved carbides).

Equations 1 and 2 can be used to calculate the net change in dimensions in a tool steel when it is heat treated to transform it from an annealed to a fully hardened (martensitic) state. For the examples referred to above, normal heat treatment would produce net volume increases of -3.53 + 4.37 = 0.84% in the 0.5% carbon tool steel, -2.77 + 4.07 = 1.30% in the 1.0% carbon steel, and -2.53 + 3.71 = 1.18% in the 1.5% carbon steel. Net changes in linear dimensions would be about one-third of the corresponding net changes in volume.

The third step involves reheating the freshly formed martensite to relatively low temperatures (tempering) to increase toughness and reduce lattice stress. Tempering produces various changes in metallurgical structure, depending on temperature and time at temperature.

After very long times at room temperature or shorter times at temperatures up to 200 °C (400 °F), the high-carbon martensite in plain carbon and low-alloy tool steels decomposes into low-carbon martensite (about 0.25% carbon) plus epsilon carbide, with an accompanying contraction in volume. At higher tempering temperatures, 200 to 430 °C (400 to 800 °F), the martensite decomposes into ferrite plus cementite.

Transformation of the maximum amount of austenite to martensite on quenching usually requires continuous cooling to below the martensite-finish temperature (M_f), which for a eutectoid tool steel is about -50 °C (-60 °F). To prevent cracking of very large or very intricate pieces, it is common practice to remove the tool from the quenching medium and to begin tempering it while it is still slightly too warm to hold comfortably in the bare hands (about 60 °C, or 140 °F). Under these conditions, a substantial proportion of the structure (10% or more) may still be austenite. Most alloying

elements lower the M_f temperature. Consequently, more austenite is retained at room temperature in the more highly alloyed tool steels. On tempering at increasing temperatures in the range of 120 to 260 °C (250 to 500 °F), increasing amounts of this retained austenite transform to bainite for some tool steel compositions, with an accompanying expansion in volume.

Depending on the alloy content of the tool steel, all, some, or none of the retained austenite will transform during tempering. In some highly alloyed tool steel compositions, cementite redissolves at tempering temperature of 540 to 595 °C (1000 to 1100 °F) to form alloy carbides, which induces an additional expansion in volume. The formation of alloy carbides during tempering is characteristic of tool steels containing large amounts of carbide-forming elements such as chromium, molybdenum, and tungsten, which are found in high-speed tool steels.

Size Distortion in Tool Steels

Typical volume percentages of martensite, retained austenite, and undissolved carbides are given in Table 1 for four different tool steels quenched from their recommended austenitizing temperatures.

Table 1 Microconstituents in various tool steels after hardening

Steel	**Hardening treatment**	**As-quenched hardness, HRC**	**Martensite, vol%**	**Retained austenite, vol%**	Undissolved carbides, vol%
W1	790 °C (1450 °F), 30 min; WQ	67.0	88.5	9	**2.5**
L3	845 °C (1550 °F), 30 min; OQ	66.5	90	7	**3.0**
M2	1225 °C (2235 °F), 6 min; OQ	64	71.5	20	**8.5**
D2	**1040 °C (1900 °F), 30 min; AC**	**62**	**45**	**40**	**15**

Note: WQ, water quench; OQ, oil quench; AC, air cool

Typical changes in linear dimensions for several tool steels are given in Table 2. As shown in this table, some tool steels such as A10 show very little size change when hardened and tempered over the entire range from 150 to 600 °C (300 to 1100 °F).

Table 2 Typical dimensional changes in hardening and tempering

Hardening treatment				**Total change in linear dimensions, % after quenching**	Total change in linear dimensions, %, after tempering at											
Tool steel	**Temperature**		**Quenching medium**													
	°C	**°F**			**°C °F**	**150 300**	**205 400**	**260 500**	**315 600**	**370 700**	**425 800**	**480 900**	**510 950**	**540 1000**	**565 1050**	595 1100
O1	815	1500	Oil	0.22		0.17	0.16	0.18	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
O1	790	1450	Oil	0.18		0.09	0.12	0.13	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**

O6	790	1450	Oil	0.12		0.07	0.10	0.14	0.10	0.00	-0.05	-0.06	. . .	-0.07	. . .	**. . .**
A2	955	1750	Air	0.09		0.06	0.06	0.08	0.07	. . .	0.05	0.04	. . .	0.06	. . .	**. . .**
A10	790	1450	Air	0.04		0.00	0.00	0.08	0.08	0.01	0.01	0.02	. . .	0.01	. . .	**0.02**
D2	1010	1850	Air	0.06		0.03	0.03	0.02	0.00	. . .	-0.01	-0.02	. . .	0.06	. . .	**. . .**
D3	955	1750	Oil	0.07		0.04	0.02	0.01	-0.02	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
D4	1040	1900	Air	0.07		0.03	0.01	-0.01	-0.03	. . .	-0.4	-0.03	. . .	0.05	. . .	**. . .**
D5	1010	1850	Air	0.07		0.03	0.02	0.01	0.00	. . .	0.3	0.03	. . .	0.05	. . .	**. . .**
H11	1010	1850	Air	0.11		0.06	0.07	0.08	0.08	. . .	0.3	0.01	. . .	0.12	. . .	**. . .**
H13	1010	1850	Air	-0.01		. . .	. . .	. . .	. . .	. . .	. . .	0.00	. . .	0.06	. . .	**. . .**
M2	1210	2210	Oil	-0.02		. . .	. . .	. . .	. . .	. . .	. . .	. . .	-0.06	0.10	0.14	**0.16**
M41	**1210**	**2210**	**Oil**	**-0.16**		**. . .**	**. . .**	**. . .**	**. . .**	**. . .**	**. . .**	**. . .**	**-0.17**	**0.08**	**0.21**	**0.23**

Other types, such as the M2 and M41 high-speed steels, expand about 0.2% (2 mm/m, or 0.002 in./in.) when hardened and tempered in the temperature range of 540 to 595 °C (1000 to 1100 °F) to develop full secondary hardness. Although the information in Table 2 is useful in comparing size distortion in several tool steels, the factor of shape distortion makes it impossible to use these data alone to predict dimensional changes of a particular tool made from any of these steels. Densities and thermal expansion characteristics for several classes of tool steels are presented in Table 3.

Table 3 Density and thermal expansion of selected tool steels

Type	**Density**		Thermal expansion									
			μm/m · K from 20 °C to					μin./in. °F from 68 °F to				
	Mg/m^3	**lb/in.^{3}**	**100 °C**	**205 °C**	**425 °C**	**540 °C**	**650 °C**	**200 °F**	**400 °F**	**800 °F**	**1000 °F**	1200 °F
W1	7.84	0.283	10.4	11.0	13.1	13.8[(a)]	14.2[(b)]	5.76	6.13	7.28	7.64[(a)]	**7.90[(b)]**
W2	7.85	0.283	. . .	. . .	14.4	14.8	14.9	. . .	. . .	8.0	8.2	**8.3**

S1	7.88	0.255	12.4	12.6	13.5	13.9	14.2	6.9	7.0	7.5	7.7	**7.9**
S2	7.79	0.281	10.9	11.9	13.5	14.0	14.2	6.0	6.6	7.5	7.8	**7.9**
S5	7.76	0.280	. . .	. . .	12.6	13.3	13.7	. . .	. . .	7.0	7.4	**7.6**
S6	7.75	0.280	. . .	. . .	12.6	13.3	. . .	. . .	. . .	7.0	7.4	**. . .**
S7	7.76	0.280	. . .	12.6	13.3	13.7[a]	13.3	. . .	7.0	7.4	7.6[a]	**7.4**
O1	7.85	0.283	. . .	10.6[c]	12.8	14.0[d]	14.4[d]	. . .	5.9[c]	7.1	7.8[d]	**8.0[d]**
O2	7.66	0.277	11.2	12.6	13.9	14.6	15.1	6.2	7.0	7.7	8.1	**8.4**
O7	7.8	0.283	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
A2	7.86	0.284	10.7	10.6[c]	12.9	14.0	14.2	5.96	5.91[c]	7.2	7.8	**7.9**
A6	7.84	0.283	11.5	12.4	13.5	13.9	14.2	6.4	6.9	7.5	7.7	**7.9**
A7	7.66	0.277	. . .	. . .	12.4	12.9	13.5	. . .	. . .	6.9	7.2	**7.5**
A8	7.87	0.284	. . .	. . .	12.0	12.4	12.6	. . .	. . .	6.7	6.9	**7.0**
A9	7.78	0.281	. . .	. . .	12.0	12.4	12.6	. . .	. . .	6.7	6.9	**7.0**
D2	7.70	0.278	10.4	10.3	11.9	12.2	12.2	5.8	5.7	6.6	6.8	**6.8**
D3	7.70	0.278	12.0	11.7	12.9	13.1	13.5	6.7	6.5	7.2	7.3	**7.5**
D4	7.70	0.278	. . .	. . .	12.4	. . .	. . .	. . .	. . .	6.9	. . .	**. . .**
D5	. . .	. . .	. . .	. . .	. . .	12.0	. . .	. . .	. . .	. . .	6.7	**. . .**
H10	7.81	0.281	. . .	. . .	12.2	13.3	13.7	. . .	. . .	6.8	7.4	**7.6**
H11	7.75	0.280	11.9	12.4	12.8	12.9	13.3	6.6	6.9	7.1	7.2	**7.4**
H13	7.76	0.280	10.4	11.5	12.2	12.4	13.1	5.8	6.4	6.8	6.9	**7.3**
H14	7.89	0.285	11.0	. . .	. . .	. . .	. . .	6.1	. . .	. . .	. . .	**. . .**

H19	7.98	0.288	11.0	11.0	12.0	12.4	12.9	6.1	6.1	6.7	6.9	**7.2**
H21	8.28	0.299	12.4	12.6	12.9	13.5	13.9	6.9	7.0	7.2	7.5	**7.7**
H22	8.36	0.302	11.0	. . .	11.5	12.0	12.4	6.1	. . .	6.4	6.7	**6.9**
H26	8.67	0.313	. . .	. . .	. . .	12.4	. . .	. . .	. . .	. . .	6.9	**. . .**
H42	8.15	0.295	. . .	. . .	. . .	11.9	. . .	. . .	. . .	. . .	6.6	**. . .**
T1	8.67	0.313	. . .	9.7	11.2	11.7	11.9	. . .	5.4	6.2	6.5	**6.6**
T2	8.67	0.313	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
T4	8.68	0.313	. . .	. . .	. . .	11.9	. . .	. . .	. . .	. . .	6.6	**. . .**
T5	8.75	0.316	11.2	. . .	. . .	11.5	. . .	6.2	. . .	. . .	6.4	**. . .**
T6	8.89	0.321	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
T8	8.43	0.305	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
T15	8.19	0.296	. . .	9.9	11.0	11.5	. . .	. . .	5.5[c]	6.1	6.4	**. . .**
M1	7.89	0.285	. . .	10.6[c]	11.3	12.0	12.4	. . .	5.9[c]	6.3	6.7	**6.9**
M2	8.16	0.295	10.1	9.4[c]	11.2	11.9	12.2	5.6	5.2[c]	6.2	6.6	**6.8**
M3, class 1	8.15	0.295	. . .	. . .	11.5	12.0	12.2	. . .	. . .	6.4	6.7	**6.8**
M3, class 2	8.16	0.295	. . .	. . .	11.5	12.0	12.8	. . .	. . .	6.4	6.7	**7.1**
M4	7.97	0.288	. . .	9.5[c]	11.2	12.0	12.2	. . .	5.3[c]	6.2	6.7	**6.8**
M7	7.95	0.287	. . .	9.5[c]	11.5	12.2	12.4	. . .	5.3[c]	6.4	6.8	**6.9**
M10	7.88	0.255	. . .	. . .	11.0	11.9	12.4	. . .	. . .	6.1	6.6	**6.9**
M30	8.01	0.289	. . .	. . .	11.2	11.7	12.2	. . .	. . .	6.2	6.5	**6.8**
M33	8.03	0.290	. . .	. . .	11.0	11.7	12.0	. . .	. . .	6.1	6.5	**6.7**

M36	8.18	0.296	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
M41	8.17	0.295	. . .	9.7	10.4	11.2	. . .	. . .	5.4	5.8	6.2	**. . .**
M42	7.98	0.288	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
M46	7.83	0.283	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
M47	7.96	0.288	10.6	11.0	11.9	. . .	12.6	5.9	6.1	6.6	. . .	**7.0**
L2	7.86	0.284	. . .	. . .	14.4	14.6	14.8	. . .	. . .	8.0	8.1	**8.2**
L6	7.86	0.284	11.3	12.6	12.6	13.5	13.7	6.3	7.0	7.0	7.5	**7.6**
P2	7.86	0.284	. . .	. . .	13.7	. . .	. . .	. . .	. . .	7.6	. . .	**. . .**
P5	7.80	0.282	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
P6	7.85	0.283	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
P20	**7.85**	**0.283**	**. . .**	**. . .**	**12.8**	**13.7**	**14.2**	**. . .**	**. . .**	**7.1**	**7.6**	**7.9**

(a) From 20 to 500 °C (68 to 930 °F).

(b) From 20 to 600 °C (68 to 1110 °F).

(c) From 20 to 260 °C (68 to 500 °F).

(d) From 38 °C (100 °F)

Shape Distortion in Tool Steels

The strength of any tool steel decreases rapidly above about 600 °C (1100 °F). At the austenitizing temperature, the yield strength is so low that plastic deformation often occurs simply from the stresses induced in the part by gravity. Therefore, long parts, large parts, and parts of complex shape must be properly supported at critical locations to prevent sagging at the hardening temperature.

Rapid heating increases shape distortion, especially in large tools and in complex tools containing both light and heavy sections. If the rate of heating is high, light sections will increase in temperature much faster than heavy sections. Likewise, the outer surfaces in heavy sections will increase in temperature much faster than the interior. Differences in thermal expansion due to the differences in temperature between light and heavy sections or between surface and interior in heavy sections will be enough to set up large stresses in the material. Under these stresses, the hotter regions will deform plastically to relieve the thermally induced stress.

Eventually, the hotter portions will reach the furnace temperature, whereas the cooler portions will continue to increase in temperature. At this point, a decrease in thermal differential begins, which will cause a partial reversal in thermal stress that produced plastic deformation when the temperature differential was high. This may cause the part to undergo further plastic deformation, but to a lesser extent than the deformation caused by the initial high-temperature differential. Such deformation will occur in a different direction.

Slow heating minimizes distortion by keeping temperature differentials low and thermal stresses within the elastic range of the material throughout the heating cycle. Ideally, all heat treatment of tool steel parts should start from a cold furnace to provide the greatest freedom from shape distortion during heating. Starting from a cold furnace is neither very practical nor energy efficient unless heat treating is being done in a vacuum furnace. When heat treating in fused salt or an atmosphere furnace, preheating the parts at one or more intermediate temperatures prior to heating them to the austenitizing temperature provides the best compromise.

During quenching, large temperature differences between surface and interior, and between light and heavy sections can cause severe shape distortion, because of thermal stress and mechanical stress produced by a martensitic transformation. This problem is most severe if the hardenability of the steel is so low that a fast cooling rate is required to obtain full hardness. In such a situation, especially when making a large or complex part, it may be best to substitute a high-hardenability, air-hardening tool steel, which requires only a slow cooling rate to fully harden. It is worth noting that water quenched steels will generally show large dimensional changes after quenching. However, because plain carbon tool steels such as W1 and W2 are shallow hardening, the amount of movement in large cross sections may be less than comparable tools made from higher-hardenability grades.

However, if lower-hardenability steels requiring liquid quenching are used, fixturing and pressure die quenching can help minimize distortion. Long symmetrical parts should be fixtured and should be quenched in the vertical position with vertical agitation of the quench mediums.

Special Techniques for Controlling Shape Distortion

Special quenching procedures such as martempering and austempering may also be useful for controlling distortion in parts that have an appropriate configuration and have been made of material of appropriate hardenability. In martempering, parts are quenched in hot molten salt fast enough to avoid transformation to high-temperature transformation products such as ferrite or pearlite. The parts are held at a bath temperature in the range from slightly above to slightly below the M_s just long enough to equalize the interior and surface temperatures. The parts are then removed from the bath and allowed to air cool to room temperature. Slow cooling through the martensitic transformation range reduces distortion as compared with rapid quenching. Martempered tools must be given the usual tempering treatment.

Austempering can be used to reduce distortion if a hardness no higher than 57 HRC is acceptable for the application. In austempering, parts are also quenched in hot molten salt but by temperature selection are forced to transform into bainite rather than martensite. Bainite forms at temperatures above those at which martensite forms. The parts must be held long enough at a temperature above M_s (usually about 230 °C, or 450 °F) to permit the austenite to transform to lower bainite. When air cooled to room temperature, austempered tools exhibit less shape distortion and generally require no subsequent tempering.

Besides being reduced through control of rates of heating and cooling, shape distortion can be reduced by employing a localized method of heating and quenching such as flame hardening, induction hardening, electron beam or laser hardening to treat only that portion of the tool that must be hardened.

Controlling out-of-roundness is important for certain precision applications, such as class C and D cutting hobs made of high-speed steels. Class C and D hobs must be held close to size limits because they are not ground to size after heat treatment, but rather are used in the unground condition.

Normal size distortion in hardening and tempering can be accommodated by making the tool slightly oversize or slightly undersize, as required, before heat treating. High-speed steel bars, however, have been observed to go out-of-round as much as 0.05 mm (0.002 in.) during heat treatment. The pattern of size distortion shown in Fig. 2(a) can occur. It appears to be related to the initial shape of the cast ingot and to the specific primary-mill processing used to reduce the ingot into bars. By changing steel-making, forgings, and rolling procedures, out-of-roundness has been reduced to the smaller differential pattern shown in Fig. 2(b), where the difference between high and low points is only 0.005 mm (0.0002 in.).

High-speed steel bars made this way are marketed by a few tool steel producers as "close tolerance hob stock." An even better method of combating out-of-roundness is to use high-speed tool steel bars made from hot isostatically pressed powders, which maintain the best possible symmetry during conventional heat treatment (see the discussion of powder metallurgy steels later in this article).

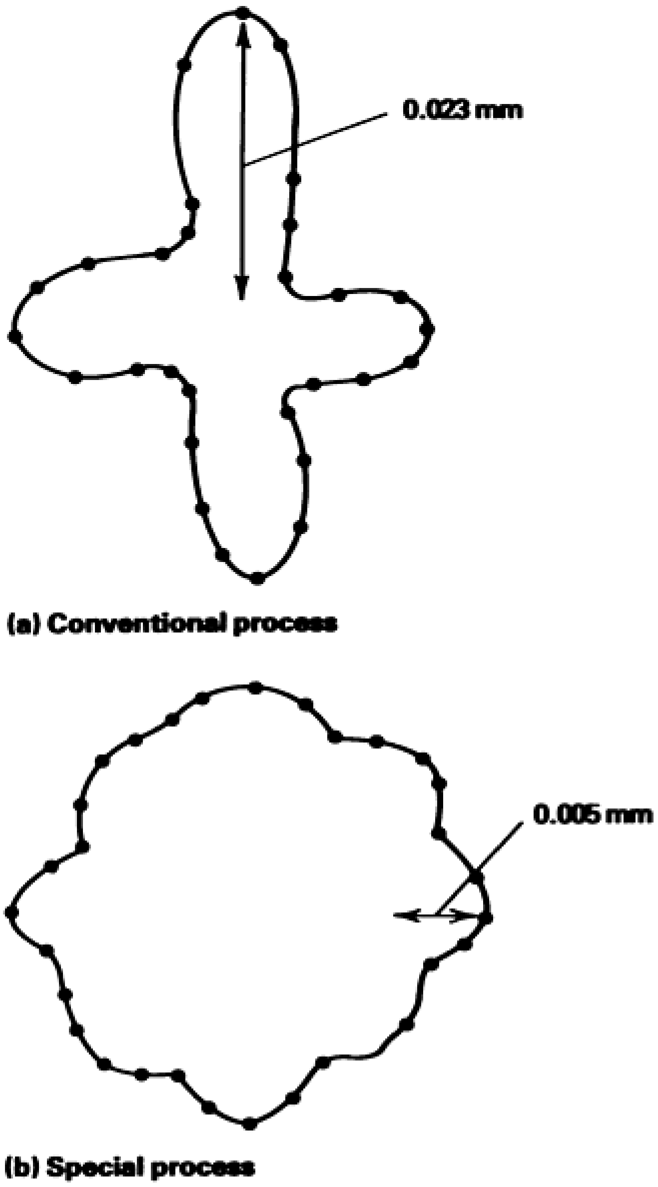


Fig. 2 Typical diameter changes during heat treatment for high-speed steel bars. Drawings produced by calculation from precision measurements of diameter. Charts are plots on polar coordinates depicting variations in diameter after heat treatment for a bar that was round within ±1.25 μm (±0.00005 in.) before heat treatment.

Stabilization involves reducing the amount of retained austenite in heat-treated material. Retained austenite can slowly transform and produce distortion if the material is later heated or subjected to stress. Stabilization also reduces internal (residual) stress, making distortion in service less likely to occur. Stabilization is most important for tools that must retain their exact size and shape over long periods (that is, gages and blocks).

If the tool steel chosen provides the required hardness after tempering at a relatively high temperature, it is possible to reduce the amount of retained austenite and the internal stress by multiple tempering. Initial tempering reduces internal stress and conditions the retained austenite so that it can transform to martensite on cooling from the tempering

temperature. A second or third retempering is usually necessary to reduce the internal stress set up by the transformation of retained austenite.

Single or repeated cold treatment to a temperature below M_f will cause most of the retained austenite to transform to martensite in plain carbon or low-alloy tool steels that must be tempered at low temperatures to achieve the hardness required. Cold treatment may be applied either before or after the first temper. If, however, the tools tend to crack because of the additional stress induced by dimensional expansion during cold treatment, it is generally prudent to apply cold treatment after first tempering of the tools. When cold treatment is applied after the first temper, the amount of retained austenite that transforms during the cold treatment may be considerably less than desired because some of the austenite may have been stabilized by tempering prior to cold treating. Cold treatment is usually done in a commercial refrigeration unit capable of attaining -70 to -95 °C (-100 to -140 °F). Tools must be retempered promptly after return to room temperature following cold treatment to reduce internal stress and to increase the toughness of the newly formed martensite.

For some tools, a small percentage of retained austenite is desirable for improving toughness and providing a favorable internal stress pattern that will help the tool to withstand service stresses. For these tools, a full stabilizing treatment may actually result in tools that are unfit to perform their required functions.

Temper Straightening of Martempered Tool Steels. Temper straightening is used for correcting distortion caused by heat treatment. The workpiece first is tempered to a hardness somewhat higher than required, and then clamped in a straightening fixture and tempered to the required hardness. The greater the hardness difference between the first and the corrective tempering operations, the more accurate the dimensions will be. Temper straightening is most successful at hardness levels of 55 HRC and lower.

Deep-hardening alloy and tool steels that are being martempered to minimize distortion should be held straight during the cooling period after austenitizing and until the completion of martempering. If straightness is not maintained throughout martempering, the workpiece will warp as martensite continues to form. Straightening should be done below 480 °C (900 °F). Cold bars or chills contacting the high side will more rapidly extract the heat from the workpiece and aid in straightening.

Other Considerations. One of the most common instances of dimensional change in steel articles is the warpage that occurs during the heating operation and that is often mistaken for a dimensional change occurring in the quench. It will be noted that on heating, a relatively large expansion takes place, and that at the transformation temperature, a slight contraction occurs. Because this contraction occurs when the steel is hot and very plastic, it is not likely to lead to cracking. However, the continuous expansion on heating will cause heavy objects or long slim objects to warp if not properly supported, if the rate of heating is too great or if nonuniform heating occurs. It is necessary to emphasize the importance of proper support for any article to be heated to a high temperature, because at this temperature the lack of strength will often allow the steel to bend under its own weight. Warpage and dimensional changes can also arise on heating from machining stresses and from unbalanced design. Slow rates of heating offer less danger of either occurring than fast rates of heating because at any one time the temperature gradients throughout the steels are less.

Excessively high austenitizing temperatures in tool steels will lead to excessive grain growth and a more stabilized austenite. This overheated condition along with the larger thermal gradients experienced during heating and quenching will result in irregular dimensional changes.

Another factor that will influence shape distortion is surface chemistry variation. For example, when lower or higher carbon concentrations exist, as in decarburization or carburization, the surface transformation temperature will be changed. The difference between the surface and the subsurface transformation will set up compressive or tensile stresses that can cause distortion and/or cracking. Elimination of surface mill decarburization or carburization by machining or grinding prior to heat treatment are recommended to eliminate such effects.

Shape change caused by mechanical thermal stresses prior to heat treatment can be addressed by stress relieving. Mechanical sources such as forming, grinding, or machining can set up nonuniform residual stresses. Brazing, welding, and torch heating can cause thermal residual stresses. These residual stresses remain in the component until thermally relieved. As the component is heated, the steel will yield plastically at the point where the hot yield strength and residual stress level coincide. The creep deformation occurs simultaneously with any stress relaxation. Localized mechanical stresses such as stamped identification marks, machining marks, sharp corners, and changes in section size will have a

significant influence on the degree and location of the shape distortion. A separate stress-relieving cycle by heating to approximately 650 °C (1200 °F) and air cooling allows the control of mechanically or thermally induced residual stress.

Upon cooling from the stress relief, the part may be distorted, but can be easily corrected in the annealed condition with an additional operation of straightening, machining, or grinding. In many situations where extensive machining is required, a good practice is to rough machine, stress relieve, and then finish machine or grind using light passes. Annealing in place of stress relieving is acceptable and preferred if considerable welding has been performed.

Preheating as the initial phase of hardening will provide a stress-relieving effect. However, distortion will manifest itself and if allowed to exist through the hardening operation, the effect of stress relieving will be lost because straightening of a hardened part is very difficult to accomplish.

Fundamentals such as the technique of placing the tools in a high heat furnace as well as racking and handling methods must be considered as potential causes of shape distortion. Uniform support of pans in a furnace is important to prevent sagging, particularly at high heat temperatures for long, slender sections. Large parts must be raised off the hearth plate to ensure satisfactory heat circulation and more even heating and cooling. Because tool steel is austenitic when it is removed from the high heat furnace, care must be exercised in transferring the load. Preferably, the parts should be placed on trays that can be grasped to remove the load. If the individual part must be handled with tongs, avoid holding it at the thinner sections, which will lose heat rapidly and might bend more easily.

Powder Metallurgy Steels

In recent years, tool steels with improved properties have been produced by the powder metallurgy (P/M) process.

The basic production routes now in commercial use for P/M tool steels are summarized in Fig. 3. All these processes use gas-or water-atomized powders and either hot isostatic pressing (HIP), mechanical compaction (extrusion, forging, and so on), or vacuum sintering for densification. The basic difference among these processes is that the use of gas atomization will yield spherical particles, while water atomization will produce angular particles of significantly higher oxygen content. The angular particles can be cold pressed to provide a compact that has sufficient mechanical strength to be handled and processed directly, while the spherical gas-atomized powder must be encapsulated prior to densification. The most widely used of the aforementioned production practices utilize gas atomization and HIP.

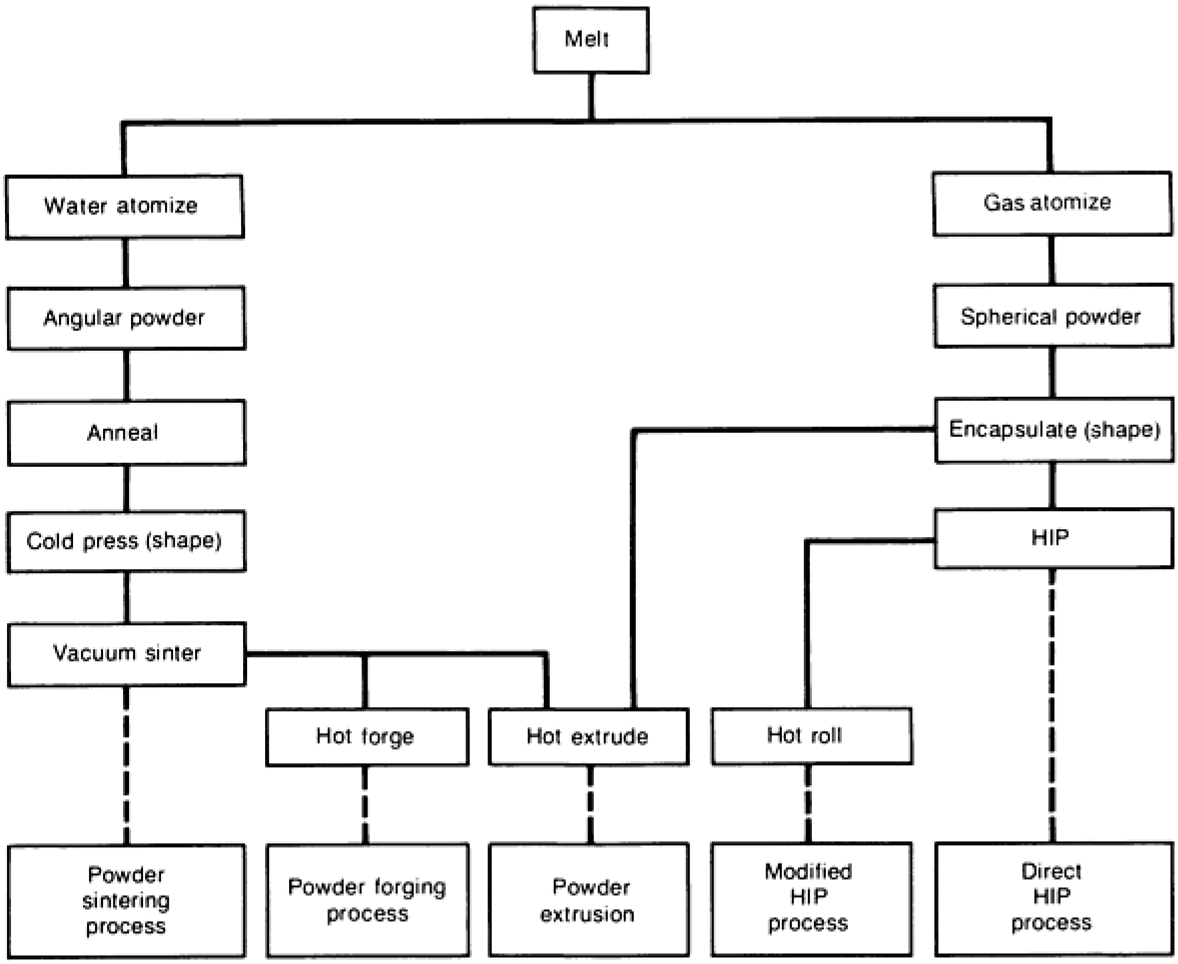


Fig. 3 Current manufacturing processes for P/M tool steels. Source: *ASM Handbook*, Volume 1, formerly 10th Edition *Metals Handbook*

P/M tool steels have two major advantages: complete freedom from macrosegregation and porosity, and uniform distribution of extremely fine carbides. These characteristics provide deeper hardening and faster response to hardening conditions (see Fig. 4). The latter is important, particularly for molybdenum high-speed steels, which tend to decarburize rapidly at austenitizing temperatures. P/M products also show less out-of-roundness distortion in large-diameter bars (see Table 4).

Table 4 Out-of-roundness distortion in large-diameter bars of M2S tool steel

Bar diameter		**Production method**	Typical out-of-roundness[(a)]	
mm	**in.**		**mm**	in.
75	3	P/M	0.008	**0.0003**
		Conventional	0.020	**0.0008**
125	5	P/M	0.013	**0.0005**

		Conventional	0.033	**0.0013**
190	7.5	P/M	0.015	**0.0006**
		Conventional	**0.051**	**0.0020**

(a) Maximum diameter minus minimum diameter after normal hardening treatment

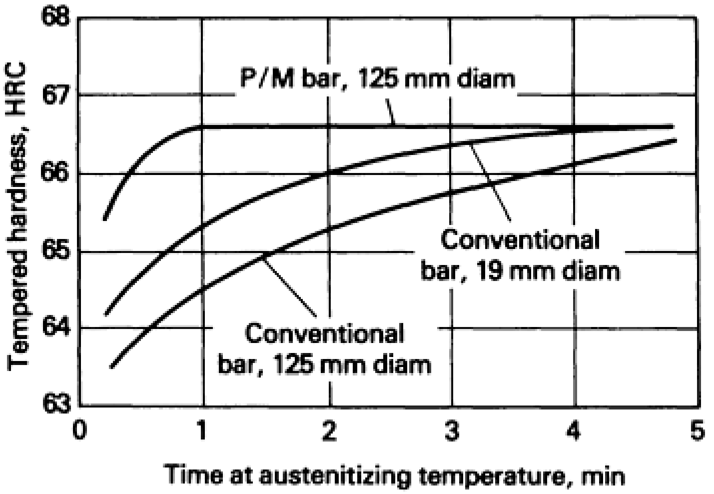


Fig. 4 Comparison of response to hardening for P/M and conventionally produced bars of M25 (HC) tool steel. Hardness at midradius was evaluated for bars oil quenched from 1200 °C (2200 °F) and tempered 2 + 2 + 2 h at 550 °C (1025 °F).

When sulfur is added to P/M tool steels, they exhibit a very fine homogeneous distribution of sulfides. This uniform sulfide distribution promotes better machinability. After heat treating, the refined, hardened, and tempered P/M tool steels exhibit better grindability and greater toughness than conventionally processed (cast and wrought) tool steels. As of 1990, more than 30 different P/M tool steel compositions were commercially available. Many of these correspond directly to AISI wrought counterparts. More detailed information on processing and properties of P/M tool steels can be found in the article "P/M Tool Steels" in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.*

Maraging Steels

A group of alloys known as 18% Ni maraging steels are commonly used for tooling. These maraging steels are chosen for a variety of reasons, not the least of which is their freedom from distortion associated with the austenite to martensite transformation. Maraging steels are supplied by producers in a soft martensitic condition, approximately 28 to 35 HRC, referred to as the solution treated or solution annealed condition. In this solution treated condition, the alloy can be formed, machined, and conventionally fabricated. The full hardness of the alloy is achieved by a simple aging treatment, usually 3 to 6 h at approximately 480 °C (900 °F) followed by air cooling. This aging or precipitation hardening treatment is not accompanied by an austenite/martensite phase change and therefore is not prone to the distortion prominent with other tool steels. A uniform predictable shrinkage does occur in the amount of approximately 0.025 mm/25 mm (0.001 in./in.). Because the development of hardness is essentially independent of the cooling rate from the aging temperature, full through hardness can be achieved even in massive sections with only minimal shrinkage and essentially no distortion.

Decarburization, another cause of stress and distortion in conventional tool steels, is not a factor with 18Ni maraging steels because they contain only low residual carbon levels (less than 0.025%).

Several maraging steels are available and provide a wide variety of hardness or strength levels (Table 5). The 18Ni maraging steels are alloyed to obtain a specific hardness level and are given a standard aging treatment. Choice of a specific grade will dictate that hardness. It is typically not recommended to under- or overage the alloy because some degradation of properties can occur. The system for identification of the various maraging grades incorporates a three digit number and a letter (C or T) designating the approximate tensile strength (in ksi) and the principal alloy strengthener (cobalt or titanium), respectively. For example, 18Ni C (250) is an 18% Ni maraging steel alloyed with cobalt that has a tensile strength of ~250 ksi (~1720 MPa). More detailed information on these alloys can be found in the article "Heat Treating of Maraging Steels" in this Volume.

Table 5 Typical hardening (aging) treatments and resultant hardnesses for maraging steels

Grade	**Aging treatment**[(a)]		Nominal hardness, HRC
	°C	**°F**	
18Ni C (200)	480	(900)[(b)]	**44**
18Ni T (200)	480	(900)[(b)]	**44**
18Ni C (250)	480	(900)[(b)]	**50**
18Ni T (250)	480	(900)[(b)]	**50**
18Ni C (300)	480	(900)[(b)]	**53**
18Ni T (300)	480	(900)[(b)]	**53**

(a) 3 to 6 h + 1 h per additional in. (25 mm) of cross section.

(b) Aging treatment of 530 °C (990 °F) is recommended for aluminum die casting dies which result in hardness values slightly lower (~2 HRC) than indicated.

Heat Treating of Stainless Steels

Revised by Joseph Douthett, Armco Research and Technology

Introduction

HEAT TREATING of stainless steel serves to produce changes in physical condition, mechanical properties, and residual stress level, and to restore maximum corrosion resistance when that property has been adversely affected by previous fabrication or heating. Frequently, a combination of satisfactory corrosion resistance and optimum mechanical properties is obtained in the same heat treatment.

Heat Treating of Stainless Steels

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Austenitic Stainless Steels

In furnace loading, the high thermal expansion of austenitic stainless steels (about 50% higher than that of a mild carbon steel) should be considered. The spacing between parts should be adequate to accommodate this expansion. Stacking, when necessary, should be employed judiciously to avoid deformation of parts at elevated temperatures.

Susceptibility to Intergranular Attack

The austenitic stainless steels may be divided into five groups:

- Conventional austenitics, such as types 301, 302, 303, 304, 305, 308, 309, 310, 316, and 317
- Stabilized compositions, primarily types 321, 347, and 348
- Low-carbon grades, such as types 304L, 316L, and 317L
- High-nitrogen grades, such as AISI types 201, 202, 304N, 316N, and the Nitronic series of alloys
- Highly alloyed austenitics, such as 317LM, 317LX, JS700, JS777, 904L, AL-4X, 2RK65, Carpenter 20Cb-3, Sanicro 28, AL-6X, AL-6XN, and 254 SMO

The compositions of standard and nonstandard austenitic stainless steels are listed in Tables 1 and 2.

Table 1 Compositions of standard wrought stainless steels

Type	UNS designation	Composition[(a)], %							
		C	Mn	Si	Cr	Ni	P	S	Other
Austenitic									
201	S20100	0.15	5.5-7.5	1.00	16.0-18.0	3.5-5.5	0.06	0.03	0.25 N
202	S20200	0.15	7.5-	1.00	17.0-	4.0-6.0	0.06	0.03	0.25 N

Type	UNS designation	Composition[a], %							
		C	Mn	Si	Cr	Ni	P	S	Other
			10.0		19.0				
205	S20500	0.12-0.25	14.0-15.5	1.00	16.5-18.0	1.0-1.75	0.06	0.03	0.32-0.40 N
301	S30100	0.15	2.00	1.00	16.0-18.0	6.0-8.0	0.045	0.03	. . .
302	S30200	0.15	2.00	1.00	17.0-19.0	8.0-10.0	0.045	0.03	. . .
302B	S30215	0.15	2.00	2.0-3.0	17.0-19.0	8.0-10.0	0.045	0.03	. . .
303	S30300	0.15	2.00	1.00	17.0-19.0	8.0-10.0	0.20	0.15 min	0.6 Mo[b]
303Se	S30323	0.15	2.00	1.00	17.0-19.0	8.0-10.0	0.20	0.06	0.15 min Se
304	S30400	0.08	2.00	1.00	18.0-20.0	8.0-10.5	0.045	0.03	. . .
304H	S30409	0.04-0.10	2.00	1.00	18.0-20.0	8.0-10.5	0.045	0.03	. . .
304L	S30403	0.03	2.00	1.00	18.0-20.0	8.0-12.0	0.045	0.03	. . .
304LN	S30453	0.03	2.00	1.00	18.0-20.0	8.0-12.0	0.045	0.03	0.10-0.16 N
302Cu	S30430	0.08	2.00	1.00	17.0-19.0	8.0-10.0	0.045	0.03	3.0-4.0 Cu
304N	S30451	0.08	2.00	1.00	18.0-20.0	8.0-10.5	0.045	0.03	0.10-0.16 N
305	S30500	0.12	2.00	1.00	17.0-19.0	10.5-13.0	0.045	0.03	. . .
308	S30800	0.08	2.00	1.00	19.0-21.0	10.0-12.0	0.045	0.03	. . .

Type	UNS designation	Composition[(a)], %							
		C	Mn	Si	Cr	Ni	P	S	Other
309	S30900	0.20	2.00	1.00	22.0-24.0	12.0-15.0	0.045	0.03	. . .
309S	S30908	0.08	2.00	1.00	22.0-24.0	12.0-15.0	0.045	0.03	. . .
310	S31000	0.25	2.00	1.50	24.0-26.0	19.0-22.0	0.045	0.03	. . .
310S	S31008	0.08	2.00	1.50	24.0-26.0	19.0-22.0	0.045	0.03	. . .
314	S31400	0.25	2.00	1.5-3.0	23.0-26.0	19.0-22.0	0.045	0.03	. . .
316	S31600	0.08	2.00	1.00	16.0-18.0	10.0-14.0	0.045	0.03	2.0-3.0 Mn
316F	S31620	0.08	2.00	1.00	16.0-18.0	10.0-14.0	0.20	0.10 min	1.75-2.5 Mo
316H	S31609	0.04-0.10	2.00	1.00	16.0-18.0	10.0-14.0	0.045	0.03	2.0-3.0 Mo
316L	S31603	0.03	2.00	1.00	16.0-18.0	10.0-14.0	0.045	0.03	2.0-3.0 Mo
316LN	S31653	0.03	2.00	1.00	16.0-18.0	10.0-14.0	0.045	0.03	2.0-3.0 Mo; 0.10-0.16 N
316N	S31651	0.08	2.00	1.00	16.0-18.0	10.0-14.0	0.045	0.03	2.0-3.0 Mo; 0.10-0.16 N
317	S31700	0.08	2.00	1.00	18.0-20.0	11.0-15.0	0.045	0.03	3.0-4.0 Mo
317L	S31703	0.03	2.00	1.00	18.0-20.0	11.0-15.0	0.045	0.03	3.0-4.0 Mo
321	S32100	0.08	2.00	1.00	17.0-19.0	9.0-12.0	0.045	0.03	5 × %C min Ti

Type	UNS designation	Composition[a], %							
		C	Mn	Si	Cr	Ni	P	S	Other
321H	S32109	0.04-0.10	2.00	1.00	17.0-19.0	9.0-12.0	0.045	0.03	5 × %C min Ti
330	N08330	0.08	2.00	0.75-1.5	17.0-20.0	34.0-37.0	0.04	0.03	. . .
347	S34700	0.08	2.00	1.00	17.0-19.0	9.0-13.0	0.045	0.03	10 × %C min Nb
347H	S34709	0.04-0.10	2.00	1.00	17.0-19.0	9.0-13.0	0.045	0.03	8 × %C min - 1.0 max Nb
348	S34800	0.08	2.00	1.00	17.0-19.0	9.0-13.0	0.045	0.03	0.2 Co; 10 × %C min Nb; 0.10 Ta
348H	S34809	0.04-0.10	2.00	1.00	17.0-19.0	9.0-13.0	0.045	0.03	0.2 Co; 8 × %C min - 1.0 max Nb; 0.10 Ta
384	S38400	0.08	2.00	1.00	15.0-17.0	17.0-19.0	0.045	0.03	. . .
Ferritic									
405	S40500	0.08	1.00	1.00	11.5-14.5	. . .	0.04	0.03	0.10-0.30 Al
409	S40900	0.08	1.00	1.00	10.5-11.75	0.50	0.045	0.045	6 × %C min - 0.75 max Ti
429	S42900	0.12	1.00	1.00	14.0-16.0	. . .	0.04	0.03	. . .
430	S43000	0.12	1.00	1.00	16.0-18.0	. . .	0.04	0.03	. . .
430F	S43020	0.12	1.25	1.00	16.0-18.0	. . .	0.06	0.15 min	0.6 Mo[b]
430FSe	S43023	0.12	1.25	1.00	16.0-18.0	. . .	0.06	0.06	0.15 min Se
434	S43400	0.12	1.00	1.00	16.0-	. . .	0.04	0.03	0.75-1.25 Mo

Type	UNS designation	Composition[a], %							
		C	Mn	Si	Cr	Ni	P	S	Other
					18.0				
436	S43600	0.12	1.00	1.00	16.0-18.0	. . .	0.04	0.03	0.75-1.25 Mo; 5 × %C min - 0.70 max Nb
439	S43035	0.07	1.00	1.00	17.0-19.0	0.50	0.04	0.03	0.15 Al; 12 × %C min - 1.10 Ti
442	S44200	0.20	1.00	1.00	18.0-23.0	. . .	0.04	0.03	. . .
444	S44400	0.025	1.00	1.00	17.5-19.5	1.0	0.04	0.03	1.75-2.50 Mo; 0.035 max N; (Ti + Nb) 0.20 + 4 (C + N) min; 0.80 max
446	S44600	0.20	1.50	1.00	23.0-27.0	. . .	0.04	0.03	0.25 N
Duplex (ferritic-austenitic)									
329	S32900	0.20	1.00	0.75	23.0-28.0	2.50-5.00	0.040	0.030	1.00-2.00 Mo
Martensitic									
403	S40300	0.15	1.00	0.50	11.5-13.0	. . .	0.04	0.03	. . .
410	S41000	0.15	1.00	1.00	11.5-13.5	. . .	0.04	0.03	. . .
414	S41400	0.15	1.00	1.00	11.5-13.5	1.25-2.50	0.04	0.03	. . .
416	S41600	0.15	1.25	1.00	12.0-14.0	. . .	0.06	0.15 min	0.6 Mo[b]
416Se	S41623	0.15	1.25	1.00	12.0-14.0	. . .	0.06	0.06	0.15 min Se
420	S42000	0.15 min	1.00	1.00	12.0-14.0	. . .	0.04	0.03	. . .

Type	UNS designation	Composition[a], %							
		C	Mn	Si	Cr	Ni	P	S	Other
420F	S42020	0.15 min	1.25	1.00	12.0-14.0	. . .	0.06	0.15 min	0.6 Mo[b]
422	S42200	0.20-0.25	1.00	0.75	11.5-13.5	0.5-1.0	0.04	0.03	0.75-1.25 Mo; 0.75-1.25 W; 0.15-0.3 V
431	S43100	0.20	1.00	1.00	15.0-17.0	1.25-2.50	0.04	0.03	. . .
440A	S44002	0.60-0.75	1.00	1.00	16.0-18.0	. . .	0.04	0.03	0.75 Mo
440B	S44003	0.75-0.95	1.00	1.00	16.0-18.0	. . .	0.04	0.03	0.75 Mo
440C	S44004	0.95-1.20	1.00	1.00	16.0-18.0	. . .	0.04	0.03	0.75 Mo
Precipitation hardening									
PH 13-8Mo	S13800	0.05	0.20	0.10	12.25-13.25	7.5-8.5	0.01	0.008	2.0-2.5 Mo; 0.90-1.35 Al; 0.01 N
15-5 PH	S15500	0.07	1.00	1.00	14.0-15.5	3.5-5.5	0.04	0.03	2.5-4.5 Cu; 0.15-0.45 Nb
17-4 PH	S17400	0.07	1.00	1.00	15.0-17.5	3.0-5.0	0.04	0.03	3.0-5.0 Cu; 0.15-0.45 Nb
17-7 PH	S17700	0.09	1.00	1.00	16.0-18.0	6.5-7.75	0.04	0.04	0.75-1.5 Al

(a) Single values are maximum values unless otherwise indicated.

(b) Optional

Table 2 Compositions of nonstandard wrought stainless steels

Designation[a]	**UNS designation**	Composition[b], %							
		C	**Mn**	**Si**	**Cr**	**Ni**	**P**	**S**	Other
Austenitic stainless steels									
Gall-Tough	S20161	0.15	4.00-6.00	3.00-4.00	15.00-18.00	4.00-6.00	0.040	0.040	**0.08-0.20 N**
203 EZ (XM-1)	S20300	0.08	5.0-6.5	1.00	16.0-18.0	5.0-6.5	0.040	0.18-0.35	**0.5 Mo; 1.75-2.25 Cu**
Nitronic 50 (XM-19)	S20910	0.06	4.0-6.0	1.00	20.5-23.5	11.5-13.5	0.040	0.030	**1.5-3.0 Mo; 0.2-0.4 N; 0.1-0.3 Nb; 0.1-0.3 V**
Tenelon (XM-31)	S21400	0.12	14.5-16.0	0.3-1.0	17.0-18.5	0.75	0.045	0.030	**0.35 N**
Cryogenic Tenelon (XM-14)	S21460	0.12	14.0-16.0	1.00	17.0-19.0	5.0-6.0	0.060	0.030	**0.35-0.50 N**
Esshete 1250	S21500	0.15	5.5-7.0	1.20	14.0-16.0	9.0-11.0	0.040	0.030	**0.003-0.009 B; 0.75-1.25 Nb; 0.15-0.40 V**
Type 216 (XM-17)	S21600	0.08	7.5-9.0	1.00	17.5-22.0	5.0-7.0	0.045	0.030	**2.0-3.0 Mo; 0.25-0.50 N**
Type 216 L (XM-18)	S21603	0.03	7.5-9.0	1.00	17.5-22.0	7.5-9.0	0.045	0.030	**2.0-3.0 Mo; 0.25-0.50 N**
Nitronic 60	S21800	0.10	7.0-9.0	3.5-4.5	16.0-18.0	8.0-9.0	0.040	0.030	**0.08-0.18 N**
Nitronic 40 (XM-10)	S21900	0.08	8.0-10.0	1.00	19.0-21.5	5.5-7.5	0.060	0.030	**0.15-0.40 N**
21-6-9 LC	S21904	0.04	8.00-10.00	1.00	19.00-21.50	5.50-7.50	0.060	0.030	**0.15-0.40 N**
Nitronic 33 (18-3-Mn)	S24000	0.08	11.50-14.50	1.00	17.00-19.00	2.50-3.75	0.060	0.030	**0.20-0.40 N**
Nitronic 32 (18-2-Mn)	S24100	0.15	11.00-14.00	1.00	16.50-19.50	0.50-2.50	0.060	0.030	**0.20-0.45 N**

Designation[a]	**UNS designation**	Composition[b], %							
		C	**Mn**	**Si**	**Cr**	**Ni**	**P**	**S**	Other
18-18 Plus	S28200	0.15	17.0-19.0	1.00	17.5-19.5	. . .	0.045	0.030	**0.5-1.5 Mo; 0.5-1.5 Cu; 0.4-0.6 N**
303 Plus X (XM-5)	S30310	0.15	2.5-4.5	1.00	17.0-19.0	7.0-10.0	0.020	0.25 min	**0.6 Mo**
MVMA[c]	S30415	0.05	0.60	1.30	18.5	9.50	. . .	. . .	**0.15 N; 0.04 Ce**
304B4	S30424	0.08	2.00	0.75	18.00-20.00	12.00-15.00	0.045	0.030	**0.10 N; 1.00-1.25 B**
304 HN (XM-21)	S30452	0.04-0.10	2.00	1.00	18.0-20.0	8.0-10.5	0.045	0.030	**0.16-0.30 N**
Cronifer 1815 LCSi	S30600	0.018	2.00	3.7-4.3	17.0-18.5	14.0-15.5	0.020	0.020	**0.2 Mo**
RA 85 H[c]	S30615	0.20	0.80	3.50	18.5	14.50	. . .	. . .	**1.0 Al**
253 MA	S30815	0.05-0.10	0.80	1.4-2.0	20.0-22.0	10.0-12.0	0.040	0.030	**0.14-0.20 N; 0.03-0.08 Ce; 1.0 Al**
Type 309 S Cb	S30940	0.08	2.00	1.00	22.0-24.0	12.0-15.0	0.045	0.030	**10 × %C min to 1.10 max Nb**
Type 310 Cb	S31040	0.08	2.00	1.50	24.0-26.0	19.0-22.0	0.045	0.030	**10 × %C min to 1.10 max Nb + Ta**
254 SMO	S31254	0.020	1.00	0.80	19.50-20.50	17.50-18.50	0.030	0.010	**6.00-6.50 Mo; 0.50-1.00 Cu; 0.180-0.220 N**
Type 316 Ti	S31635	0.08	2.00	1.00	16.0-18.0	10.0-14.0	0.045	0.030	**5 × %(C + N) min to 0.70 max Ti; 2.0-3.0 Mo; 0.10 N**
Type 316 Cb	S31640	0.08	2.00	1.00	16.0-18.0	10.0-14.0	0.045	0.030	**10 × %C min to 1.10 max Nb + Ta; 2.0-3.0 Mo; 0.10 N**
Type 316 HQ	. . .	0.030	2.00	1.00	16.00-18.25	10.00-14.00	0.030	0.015	**3.00-4.00 Cu; 2.00-3.00 Mo**
Type 317 LM	S31725	0.03	2.00	1.00	18.0-20.0	13.5-17.5	0.045	0.030	**4.0-5.0 Mo; 0.10 N**

Designation[a]	**UNS designation**	Composition[b], %							
		C	**Mn**	**Si**	**Cr**	**Ni**	**P**	**S**	Other
17-14-4 LN	S31726	0.03	2.00	0.75	17.0-20.0	13.5-17.5	0.045	0.030	**4.0-5.0 Mo; 0.10-0.20 N**
Type 317 LN	S31753	0.03	2.00	1.00	18.0-20.0	11.0-15.0	0.030	0.030	**0.10-0.22 N**
Type 370	S37000	0.03-0.05	1.65-2.35	0.5-1.0	12.5-14.5	14.5-16.5	0.040	0.010	**1.5-2.5 Mo; 0.1-0.4 Ti; 0.005 N; 0.05 Co**
18-18-2 (XM-15)	S38100	0.08	2.00	1.5-2.5	17.0-19.0	17.5-18.5	0.030	0.030	**. . .**
19-9 DL	S63198	0.28-0.35	0.75-1.50	0.03-0.8	18.0-21.0	8.0-11.0	0.040	0.030	**1.0-1.75 Mo; 0.1-0.35 Ti; 1.0-1.75 W; 0.25-0.60 Nb**
20Cb-3	N08020	0.07	2.00	1.00	19.0-21.0	32.0-38.0	0.045	0.035	**2.0-3.0 Mo; 3.0-4.0 Ca; 8 × %C min to 1.00 max Nb**
20Mo-4	N08024	0.03	1.00	0.50	22.5-25.0	35.0-40.0	0.035	0.035	**3.50-5.00 Mo; 0.50-1.50 Cu; 0.15-0.35 Nb**
20Mo-6	N08026	0.03	1.00	0.50	22.00-26.00	33.00-37.20	0.03	0.03	**5.00-6.70 Mo; 2.00-4.00 Cu**
Sanicro 28	N08028	0.02	2.00	1.00	26.0-28.0	29.5-32.5	0.020	0.015	**3.0-4.0 Mo; 0.6-1.4 Cu**
AL-6X	N08366	0.035	2.00	1.00	20.0-22.0	23.5-25.5	0.030	0.030	**6.0-7.0 Mo**
AL-6XN	N08367	0.030	2.00	1.00	20.0-22.0	23.50-25.50	0.040	0.030	**6.00-7.00 Mo; 0.18-0.25 N**
JS-700	N08700	0.04	2.00	1.00	19.0-23.0	24.0-26.0	0.040	0.030	**4.3-5.0 Mo; 8 × %C min to 0.5 max Nb; 0.5 Cu; 0.005 Pb; 0.035 S**
JS-777[d]	. . .	0.04	2.00	1.00	19.3-23.0	24.0-26.0	0.045	0.035	**4.0-5.0 Mo; 1.9-2.5 Cu**
Type 332	N08800	0.01	1.50	1.00	19.0-23.0	30.0-35.0	0.045	0.015	**0.15-0.60 Ti; 0.15-0.60 Al**

Designation[(a)]	**UNS designation**	Composition[(b)], %							
		C	**Mn**	**Si**	**Cr**	**Ni**	**P**	**S**	Other
904L	N08904	0.02	2.00	1.00	19.0-23.0	23.0-28.0	0.045	0.035	**4.0-5.0 Mo; 1.0-2.0 Cu**
Cronifer 1925 hMo	N08925	0.02	1.00	0.50	24.0-26.0	19.0-21.0	0.045	0.030	**6.0-7.0 Mo; 0.8-1.5 Cu; 0.10-0.20 N**
Cronifer 2328	. . .	0.04	0.75	0.75	22.0-24.0	26.0-28.0	0.030	0.015	**2.5-3.5 Cu; 0.4-0.7 Ti; 2.5-3.0 Mo**
2RK65	. . .	0.02	1.8	. . .	19.5	25.0	. . .	. . .	**4.5 Mo; 1.5 Cu**
Ferritic stainless steels									
18-2 FM (XM-34)	S18200	0.08	1.25-2.50	1.00	17.5-19.5	. . .	0.040	0.15 min	**1.5-2.5 Mo**
Type 430 Ti	S43036	0.10	1.00	1.00	16.0-19.5	0.75	0.040	0.030	**5 × %C min to 0.75 max Ti**
Type 441	S44100	0.03	1.00	1.00	17.5-19.5	1.00	0.040	0.040	**0.3 + 9 × (%C) min to 0.90 max Nb: 0.1-0.5 Ti; 0.03 N**
E-Brite 26-1	S44627	0.01	0.40	0.40	25.0-27.0	0.50	0.020	0.020	**0.75-1.5 Mo; 0.05-0.2 Nb; 0.015 N; 0.2 Cu**
MONIT (25-4-4)	S44635	0.025	1.00	0.75	24.5-26.0	3.5-4.5	0.040	0.030	**3.5-4.5 Mo; 0.2 +4 (%C + %N) min to 0.8 max (Ti + Nb); 0.035 N**
Sea-Cure (SC-1)	S44660	0.025	1.00	1.00	25.0-27.0	1.5-3.5	0.040	0.030	**2.5-3.5 Mo; 0.2 + 4 (%C + %N) min to 0.8 max (Ti + Nb); 0.035 N**
AL 29-4C	S44735	0.030	1.00	1.00	28.0-30.0	1.00	0.040	0.030	**3.60-4.20 Mo; 0.20-1.00 Ti + Nb and 6 (%C + %N) min Ti + Nb; 0.045 N**
AL 29-4-2	S44800	0.01	0.30	0.20	28.0-30.0	2.0-2.5	0.025	0.020	**3.5-4.2 Mo; 0.15 Cu; 0.02 N; 0.025 max (%C + %N)**
18 SR[(c)]	. . .	0.04	0.30	1.00	18.0	. . .	. . .	. . .	**2.0 Al; 0.4 Ti**

Designation[a]	UNS designation	Composition[b], %							
		C	Mn	Si	Cr	Ni	P	S	Other
12 SR[c]	. . .	0.02	. . .	0.50	12.0	. . .	. . .	. . .	**1.2 Al; 0.3 Ti**
406	. . .	0.06	1.00	0.50	12.0-14.0	0.50	0.040	0.030	**2.75-4.25 Al; 0.6 Ti**
408 Cb	. . .	0.03	0.2-0.5	0.2-0.5	11.75-12.25	0.45	0.030	0.020	**0.75-1.25 Al; 0.65-0.75 Nb; 0.3-0.5 Ti; 0.03 N**
ALFA IV	. . .	0.03	0.50	0.60	19.0-21.0	0.45	0.035	0.005	**4.75-5.25 Al; 0.005-0.035 Ce; 0.03 N**
Sealmet 1	. . .	0.08	0.5-0.8	0.3-0.6	28.0-29.0	0.40	0.030	0.015	**0.04 N**
Duplex stainless steels									
44LN	S31200	0.030	2.00	1.00	24.0-26.0	5.50-6.50	0.045	0.030	**1.20-2.00 Mo; 0.14-0.20 N**
DP-3	S31260	0.030	1.00	0.75	24.0-26.0	5.50-7.50	0.030	0.030	**2.50-3.50 Mo; 0.20-0.80 Cu; 0.10-0.30 N; 0.10-0.50 W**
3RE60	S31500	0.030	1.20-2.00	1.40-2.00	18.00-19.00	4.25-5.25	0.030	0.030	**2.50-3.00 Mo**
2205	S31803	0.030	2.00	1.00	21.0-23.0	4.50-6.50	0.030	0.020	**2.50-3.50 Mo; 0.08-0.20 N**
2304	S32304	0.030	2.50	1.0	21.5-24.5	3.0-5.5	0.040	0.040	**0.05-0.60 Mo; 0.05-0.60 Cu; 0.05-0.20 N**
Uranus 50	S32404	0.04	2.00	1.0	20.5-22.5	5.5-8.5	0.030	0.010	**2.0-3.0 Mo; 1.0-2.0 Cu; 0.20 N**
Ferralium 255	S32550	0.04	1.50	1.00	24.0-27.0	4.50-6.50	0.04	0.03	**2.00-4.00 Mo; 1.50-2.50 Cu; 0.10-0.25 N**
7-Mo Plus	S32950	0.03	2.00	0.60	26.0-29.0	3.50-5.20	0.035	0.010	**1.00-2.50 Mo; 0.15-0.35 N**
AF 22	. . .	0.03	2.0	1.0	21-23	4.5-6.5	. . .	. . .	**2.5-3.5 Mo**

Designation[a]	**UNS designation**	Composition[b], %							
		C	**Mn**	**Si**	**Cr**	**Ni**	**P**	**S**	Other
Martensitic stainless steels									
Type 410S	S41008	0.08	1.00	1.00	11.5-13.5	0.60	0.040	0.030	**. . .**
Type 410 Cb (XM-30)	S41040	0.15	1.00	1.00	11.5-13.5	. . .	0.040	0.030	**0.05-0.20 Nb**
E4	S41050	0.04	1.00	1.00	10.5-12.5	0.60-1.1	0.045	0.030	**0.10 N**
CA6NM	S41500	0.05	0.5-1.0	0.60	11.5-14.0	3.5-5.5	0.030	0.030	**0.5-1.0 Mo**
416 Plus X (XM-6)	S41610	0.15	1.5-2.5	1.00	12.0-14.0	. . .	0.060	0.15 min	**0.6 Mo**
Type 418 (Greek Ascolloy)	S41800	0.15-0.20	0.50	0.50	12.0-14.0	1.8-2.2	0.040	0.030	**2.5-3.5 W**
TrimRite	S42010	0.15-0.30	1.00	1.00	13.5-15.0	0.25-1.00	0.040	0.030	**0.40-1.00 Mo**
Type 420 F Se	S42023	0.3-0.4	1.25	1.00	12.0-14.0	. . .	0.060	0.060	**0.15 min Se; 0.6 Zr; 0.6 Cu**
Lapelloy	S42300	0.27-0.32	0.95-1.35	0.50	11.0-12.0	0.50	0.025	0.025	**2.5-3.0 Mo; 0.2-0.3 V**
Type 440 F	S44020	0.95-1.20	1.25	1.00	16.0-18.0	0.75	0.040	0.10-0.35	**0.08 N**
Type 440 F Se	S44023	0.95-1.20	1.25	1.00	16.0-18.0	0.75	0.040	0.030	**0.15 min Se; 0.60 Mo**
Precipitation-hardening stainless steels									
PH 15-7 Mo (Type 632)	S15700	0.09	1.00	1.00	14.0-16.0	6.5-7.75	0.040	0.030	**2.0-3.0 Mo; 0.75-1.5 Al**
AM-350 (Type 633)	S35000	0.07-0.11	0.5-1.25	0.50	16.0-17.0	4.0-5.0	0.040	0.030	**2.5-3.25 Mo; 0.07-0.13 N**

Designation[a]	**UNS designation**	Composition[b], %							
		C	**Mn**	**Si**	**Cr**	**Ni**	**P**	**S**	Other
AM-355 (Type 634)	S35500	0.10-0.15	0.5-1.25	0.50	15.0-16.0	4.0-5.0	0.040	0.030	**2.5-3.25 Mo; 0.07-0.13 N**
Custom 450 (XM-25)	S45000	0.05	1.00	1.00	14.0-16.0	5.0-7.0	0.030	0.030	**1.25-1.75 Cu; 0.5-1.0 Mo; 8 × %C min Nb**
Custom 455 (XM-16)	**S45500**	**0.05**	**0.50**	**0.50**	**11.0-12.5**	**7.5-9.5**	**0.040**	**0.030**	**1.5-2.5 Cu; 0.8-1.4 Ti; 0.1-0.5 Nb; 0.5 Mo**

(a) XM designations in this column are ASTM designations for the listed alloy.

(b) Single values are maximum values unless otherwise indicated.

(c) Nominal compositions.

(d) Ref 1

Conventional austenitics cannot be hardened by heat treatment but will harden as a result of cold working. These steels are usually purchased in an annealed or cold-worked state. Following welding or thermal processing, a subsequent reanneal may be required for optimum corrosion resistance, softness, and ductility. During annealing, chromium carbides, which markedly decrease resistance to intergranular corrosion, are dissolved. Annealing temperatures, which vary somewhat with the composition of the steel, are given in Table 3 for wrought alloys and in Table 4 for the corresponding cast alloys. Table 5 includes compositions and typical microstructures for selected austenitic corrosion-resistant cast steels listed in Table 4.

Table 3 Recommended annealing temperatures for austenitic stainless steels

UNS No.	**Designation**	Temperature[a]	
		°C	°F
Conventional grades			
S30100	301	1010-1120	**1850-2050**
S30200	302	1010-1120	**1850-2050**
S30215	302B	1010-1120	**1850-2050**

S30300	303	1010-1120	**1850-2050**
S30323	303Se	1010-1120	**1850-2050**
S30400	304	1010-1120	**1850-2050**
S30500	305	1010-1120	**1850-2050**
S30800	308	1010-1120	**1850-2050**
S30900	309	1040-1120	**1900-2050**
S30908	309S	1040-1120	**1900-2050**
30100	310	1040-1065	**1900-1950**
S31008	310S	1040-1065	**1900-1950**
S31600	316	1040-1120	**1900-2050**
S31700	317	1065-1120	**1950-2050**
Stabilized grades			
S32100	321	955-1065	**1750-1950**
S34700	347	980-1065	**1800-1950**
S34800	348	980-1065	**1800-1950**
N08020	20Cb-3	925-955	**1700-1750**
Low-carbon grades			
S30403	304L	1010-1120	**1850-2050**
S30453	304LN	1010-1120	**1850-2050**
S31603	316L	1040-1110	**1900-2025**
S31653	316LN	1040-1110	**1900-2025**

S31703	317L	1040-1110	**1900-2025**
High-nitrogen grades			
S20100	201	1010-1120	**1850-2050**
S20200	202	1010-1120	**1850-2050**
S30451	304N	1010-1120	**1850-2050**
S31651	316N	1010-1120	**1850-2050**
S24100	Nitronic 32, 18Cr-2Ni-12Mn	1010-1065	**1850-1950**
S24000	Nitronic 33	1040-1095	**1900-2000**
S21904	Nitronic 40, 21Cr-6Ni-9Mn	980-1175	**1800-2150**
S20910	Nitronic 50, 22Cr-13Ni-5Mn	1065-1120	**1950-2050**
S21800	Nitronic 60	1040-1095	**1900-2000**
S28200	18-18 Plus	1040-1095	**1900-2000**
Highly alloyed grades			
S31725	317LM	1120-1150	**2050-2100**
. . .	317LX	1120-1150	**2050-2100**
. . .	317L Plus	1120-1150	**2050-2100**
. . .	317LMO	1120-1150	**2050-2100**
. . .	7L4	1120-1150	**2050-2100**
. . .	JS700	1065-1150	**1950-2100**
. . .	JS777	1065-1150	**1950-2100**
N08904	904L	1075-1125	**1965-2055**

. . .	AL-4X	1075-1125	**1965-2055**
. . .	2RK65	1075-1125	**1965-2055**
N08028	Sanicro 28	. . .	**. . .**
N08366	AL-6X	1205-1230	**2200-2250**
S31254	**254SMO**	**1150-1205**	**2100-2200**

(a) Temperatures given are for annealing a composite structure. Time at temperature and method of cooling depend on thickness. Light sections may be held at temperature for 3 to 5 min per 2.5 mm (0.10 in.) of thickness, followed by rapid air cooling. Thicker sections are water quenched. For many of these grades, a postweld heat treatment is not necessary. For proprietary alloys, alloy producers may be consulted for details. Although cooling from the annealing temperature must be rapid, it must also be consistent with limitations of distortion.

Table 4 Annealing of ferritic and austenitic stainless steel castings

Type	**Minimum temperature**		**Quench**[(a)]	Typical ultimate tensile strength[(b)]	
	°C	**°F**		**MPa**	ksi
For full softness					
CB-30	790	1450	FC + A[(c)]	660	**95**
CC-50	790	1450	A	670	**97**
For maximum corrosion resistance					
CE-30	1095	2000	W, O, A	670	**97**
CF-3	1040	1900	W, O, A	530	**77**
CF-3M	1040	1900	W, O, A	530	**77**
CF8	1040	1900	W, O, A	530	**77**
CF-8C[(d)]	1040	1900	W, O, A	530	**77**
CF-8M	1040	1900	W, O, A	550	**80**
CF-12M[(e)]	1040	1900	W, O, A	550	**80**

CF-16F	1040	1900	W, O, A	530	**77**
CF-20	1040	1900	W, O, A	530	**77**
CH-20	1095	2000	W, O, A	610	**88**
CK-20	1095	2000	W, O, A	520	**76**
CN-7M	**1120**	**2050**	**W, O, A**	**480**	**69**

(a) FC, furnace cool; W, water; O, oil; A, air.

(b) Approximate.

(c) Furnace cool to 540 °C (1000 °F) and then air cool.

(d) CF-8C may be reheated to 870 to 925 °C (1600 to 1700 °F) and then air cooled for precipitation of niobium carbides.

(e) CF-12M should be quenched from a temperature above 1095 °C (2000 °F).

Table 5 Compositions and typical microstructures of Alloy Casting Institute (ACI) corrosion-resistant cast steels

ACI type	UNS No.	Wrought alloy type[a]	ASTM specifications	Most common end-use microstructure	Composition[b], %					
					C	**Mn**	**Si**	**Cr**	**Ni**	Others[c]
Chromium steels										
CA-15	J91150	410	A 743, A 217, A 487	Martensite	0.15	1.00	1.50	11.5-14.0	1.0	**0.50 Mo[d]**
CA-15M	J91151	. . .	A 743	Martensite	0.15	1.00	0.65	11.5-14.0	1.0	**0.15-1.00 Mo**
CA-40	J91153	420	A 743	Martensite	0.40	1.00	1.50	11.5-14.0	1.0	**0.5 Mo[d]**
CA-40F	. . .	. . .	A 743	Martensite	0.2-0.4	1.00	1.50	11.5-14.0	1.0	**. . .**

ACI type	UNS No.	Wrought alloy type[a]	ASTM specifications	Most common end-use microstructure	Composition[b], %					
					C	**Mn**	**Si**	**Cr**	**Ni**	Others[c]
CB-30	J91803	431, 442	A 743	Ferrite and carbides	0.30	1.00	1.50	18.0-22.0	2.0	**. . .**
CC-50	J92615	446	A 743	Ferrite and carbides	0.30	1.00	1.50	26.0-30.0	4.0	**. . .**
Chromium-nickel steels										
CA-6N	J91650	. . .	A 743	Martensite	0.06	0.50	1.00	10.5-12.5	6.0-8.0	**. . .**
CA-6NM	J91540	. . .	A 743, A 487	Martensite	0.06	1.00	1.00	11.5-14.0	3.5-4.5	**0.4-1.0 Mo**
CA-28MWV	. . .	. . .	A 743	Martensite	0.20-0.28	0.50-1.00	1.00	11.0-12.5	0.50-1.00	**0.9-1.25 Mo; 0.9-1.25 W; 0.2-0.3 V**
CB-7Cu-1	J92180	. . .	A 747	Martensite, age hardenable	0.07	0.70	1.00	15.5-17.7	3.6-4.6	**2.5-3.2 Cu; 0.20-0.35 Nb; 0.05 N max**
CB-7Cu-2	J92110	. . .	A 747	Martensite, age hardenable	0.07	0.70	1.00	14.0-15.5	4.5-5.5	**2.5-3.2 Cu; 0.20-0.35 Nb; 0.05 N max**
CD-4MCu	J93370	. . .	A 351, A 743, A 744, A 890	Austenite in ferrite, age hardenable	0.04	1.00	1.00	25.0-26.5	4.75-6.0	**1.75-2.25 Mo; 2.75-3.25 Cu**
CE-30	J93423	312	A 743	Ferrite in austenite	0.30	1.50	2.00	26.0-30.0	8.0-11.0	**. . .**
CF-3[e]	J92700	304L	A 351, A 743, A 744	Ferrite in austenite	0.03	1.50	2.00	17.0-21.0	8.0-12.0	**. . .**
CF-3M[e]	J92800	316L	A 351, A 743, A 744	Ferrite in austenite	0.03	1.50	2.00	17.0-21.0	8.0-12.0	**2.0-3.0 Mo**
CF-3MN	. . .	. . .	A 743	Ferrite in austenite	0.03	1.50	1.50	17.0-21.0	9.0-13.0	**2.0-3.0 Mo; 0.10-0.20 N**
CF-8[e]	J92600	304	A 351, A 743, A 744	Ferrite in austenite	0.08	1.50	2.00	18.0-21.0	8.0-11.0	**. . .**

ACI type	UNS No.	Wrought alloy type[a]	ASTM specifications	Most common end-use microstructure	Composition[b], %					
					C	**Mn**	**Si**	**Cr**	**Ni**	Others[c]
CF-8C	J92710	347	A 351, A 743, A 744	Ferrite in austenite	0.08	1.50	2.00	18.0-21.0	9.0-12.0	**Nb[f]**
CF-8M	J92900	316	A 351, A 743, A 744	Ferrite in austenite	0.08	1.50	2.00	18.0-21.0	9.0-12.0	**2.0-3.0 Mo**
CF-10	J93401	. . .	A 351	Ferrite in austenite	0.04-0.10	1.50	2.00	18.0-21.0	8.0-11.0	**. . .**
CF-10M	. . .	. . .	A 351	Ferrite in austenite	0.04-0.10	1.50	1.50	18.0-21.0	9.0-12.0	**2.0-3.0 Mo**
CF-10MC	J92971	. . .	A 351	Ferrite in austenite	0.10	1.50	1.50	15.0-18.0	13.0-16.0	**1.75-2.25 Mo**
CF-10SMnN	. . .	. . .	A 351, A 743	Ferrite in austenite	0.10	7.00-9.00	3.50-4.50	16.0-18.0	8.0-9.0	**0.08-0.18 N**
CF-12M	. . .	316	. . .	Ferrite in austenite or austenite	0.12	1.50	2.00	18.0-21.0	9.0-12.0	**2.0-3.0 Mo**
CF-16F	J92701	303	A 743	Austenite	0.16	1.50	2.00	18.0-21.0	9.0-12.0	**1.50 Mo max; 0.20-0.35 Se**
CF-20	J92602	302	A 743	Austenite	0.20	1.50	2.00	18.0-21.0	8.0-11.0	**. . .**
CG-6MMN	J93799	. . .	A 351, A 743	Ferrite in austenite	0.06	4.00-6.00	1.00	20.5-23.5	11.5-13.5	**1.50-3.00 Mo; 0.10-0.30 Nb; 0.10-30 V; 0.20-0.40 N**
CG-8M	J93000	317	A 351, A 743, A 744	Ferrite in austenite	0.08	1.50	1.50	18.0-21.0	9,0-13.0	**3.0-4.0 Mo**
CG-12	J93001	. . .	A 743	Ferrite in austenite	0.12	1.50	2.00	20.0-23.0	10.0-13.0	**. . .**
CH-8	J93400	. . .	A 351	Ferrite in austenite	0.08	1.50	1.50	22.0-26.0	12.0-15.0	**. . .**
CH-10	J93401	. . .	A 351	Ferrite in austenite	0.04-0.10	1.50	2.00	22.0-26.0	12.0-15.0	**. . .**

ACI type	**UNS No.**	**Wrought alloy type**[(a)]	**ASTM specifications**	**Most common end-use microstructure**	Composition[(b)], %					
					C	**Mn**	**Si**	**Cr**	**Ni**	Others[(c)]
CH-20	J93402	309	A 351, A 743	Austenite	0.20	1.50	2.00	22.0-26.0	12.0-15.0	**. . .**
CK-3MCuN	. . .	. . .	A 351, A 743, A 744	Ferrite in austenite	0.025	1.20	1.00	19.5-20.5	17.5-19.5	**6.0-7.0V; 0.18-0.24 N; 0.50-1.00 Cu**
CK-20	J94202	310	A 743	Austenite	0.20	2.00	2.00	23.0-27.0	19.0-22.0	**. . .**
Nickel-chromium steel										
CN-3M	. . .	. . .	A 743	Austenite	0.03	2.00	1.00	20.0-22.0	23.0-27.0	**4.5-5.5 Mo**
CN-7M	N08007	. . .	A351, A 743, A 744	Austenite	0.07	1.50	1.50	19.0-22.0	27.5-30.5	**2.0-3.0Mo; 3.0-4.0 Cu**
CN-7MS	J94650	. . .	A 743, A 744	Austenite	0.07	1.50	3.50[(g)]	18.0-20.0	22.0-25.0	**2.5-3.0Mo; 1.5-2.0 Cu**
CT-15C	**. . .**	**. . .**	**A 351**	**Austenite**	**0.05-0.15**	**0.15-1.50**	**0.50-1.50**	**19.0-21.0**	**31.0-34.0**	**0.5-1.5V**

(a) Type numbers of wrought alloys are listed only for nominal identification of corresponding wrought and cast grades. Composition ranges of cast alloys are not the same as for corresponding wrought alloys; cast alloy designations should be used for castings only.

(b) Maximum unless a range is given. The balance of all compositions is iron.

(c) Sulfur content is 0.04% in all grades except: CG-6MMN, 0.030% S (max); CF-10SMnN, 0.03% S (max); CT-15C, 0.03% S (max); CK-3MCuN, 0.010% S (max); CN-3M, 0.030% S (max); CA-6N, 0.020% S (max); CA-28MWV, 0.030% S (max); CA-40F, 0.20-0.40% S; CB-7Cu-1 and -2, 0.03% S (max). Phosphorus content is 0.04% (max) in all grades except: CF-16F, 0.17% P (max); CF-10SMnN, 0.060% P (max); CT-15C, 0.030% P (max); CK-3MCuN, 0.045% P (max); CN-3M, 0.030% P (max); CA-6N, 0.020% P (max); CA-28MWV, 0.030% P (max); CB-7Cu-1 and -2, 0.035% P (max).

(d) Molybdenum not intentionally added.

(e) CF-3A, CF-3MA, and CF-8A have the same composition ranges as CF-3, CF-3M, and CF-8, respectively, but have balanced compositions so that ferrite contents are at levels that permit higher mechanical property specifications than those for related grades. They are covered by ASTM A 351.

(f) Nb, 8 × %C min (1.0% max); or Nb + Ta × %C (1.1% max).

(g) For CN-7MS, silicon ranges from 2.50 to 3.50%.

Because carbide precipitation can occur at temperatures between 425 and 900 °C (800 and 1650 °F), it obviously is desirable that the annealing temperature should be safely above this limit. Moreover, because all carbides should be in solution before cooling begins, and because the chromium carbide dissolves slowly, the highest practical temperature consistent with limited grain growth is selected. This temperature is in the vicinity of 1095 °C (2000 °F).

Cooling from the annealing temperature must be rapid, but it must also be consistent with limitations of distortion. Whenever considerations of distortion permit, water quenching is used, thus ensuring that dissolved carbides remain in solution. Because it precipitates carbides more rapidly, type 310 invariably requires water quenching. Where practical considerations of distortion rule out such a fast cooling rate, cooling in an air blast is used. With some thin-section parts, even this intermediate rate of cooling produces excessive distortion, and parts must be cooled in still air. If cooling in still air does not provide a rate sufficient to prevent carbide precipitation, maximum corrosion resistance will not be obtained. A solution to this dilemma is the use of a stabilized grade or the low-carbon alloys.

Stabilized austenitic alloys, namely types 321, 347, 348, and Carpenter 20Cb-3, contain controlled amounts of titanium or of niobium, which render the steel nearly immune to intergranular precipitation of chromium carbide and its adverse effects on corrosion resistance. Nevertheless, these alloys may require annealing to relieve stresses, to increase softness and ductility, or to provide additional stabilization.

To obtain maximum softness and ductility, the stabilized grades are annealed at the temperatures shown in Table 3. Unlike the unstabilized grades, these steels do not require water quenching or other acceleration of cooling from the annealing temperature to prevent subsequent intergranular corrosion; air cooling is generally adequate.

When maximum corrosion resistance of the stabilized austenitic grades is required, it may be necessary to employ a heat treatment known as a stabilizing anneal. The treatment consists of holding at 845 to 900 °C (1550 to 1650 °F) for up to 5 h, depending on section thickness. It may be applied either prior to, or in the course of, fabrication, and it may be followed by short-time stress relieving at 705 °C (1300 °F) without danger of harmful carbide precipitation (see the section "Stress Relieving of Austenitic Stainless Steels" in this article).

Carpenter 20Cb-3 stainless steel is unlike the conventional stabilized austenitics (types 321, 347, and 348) because of its higher alloy content and improved corrosion resistance. This alloy normally is stabilized and annealed at 925 to 955 °C (1700 to 1750 °F). For special applications, the alloy can be annealed at higher temperatures (up to 1150 °C, or 2100 °F), but this is permissible only if the alloy will not be subject to welding or heating temperatures over 540 °C (1000 °F).

Certain restrictions on furnace atmosphere are mandatory. Furnace combustion must be carefully controlled to eliminate carburizing or excessively oxidizing conditions. Because the properties of the stabilized steels are based on their original carbon content, carbon absorption cannot be tolerated. Excessively oxidizing conditions cause the formation of a scale that is difficult to remove in subsequent descaling operations. Direct impingement of flame on the work must be prevented. The sulfur content of the furnace atmosphere, particularly in oil-fired furnaces, must be kept low; natural gas, not producer gas, should be used.

Low-carbon austenitics are intermediate in tendency to precipitate chromium carbides to the stabilized and unstabilized grades. Carbon content (0.03% max) is low enough to reduce precipitation of intergranular carbides. This characteristic of limited sensitization is of particular value in welding, flame cutting, and other hot-working operations. They do not require the quenching treatment that unstabilized grades require to retain carbon in solid solution. Nevertheless, the low-carbon alloys are not satisfactory for long-time service in the sensitizing temperature range of 540 to 760 °C (1000 to 1400 °F) because they are not completely immune to the formation of carbides deleterious to corrosion resistance. Recommended annealing temperatures for the low-carbon alloys are given in Table 3.

The effects of sensitization and susceptibility to general corrosion vary among the low-carbon alloys, depending on their chemical composition. Because they contain molybdenum, types 316L and 317L are susceptible to σ-phase formation as a result of long-time exposure at 650 to 870 °C (1200 to 1600 °F). However, the corrosion resistance of these grades can be

improved by employing a stabilizing treatment (ASTM A 262C), consisting of holding at 885 °C (1625 °F) for 2 h, prior to stress relieving at 675 °C (1250 °F). After receiving the stabilizing heat treatment, these alloys pass the copper-copper sulfate 16% sulfuric acid test (ASTM A 262, Practice E) for freedom from intergranular carbide precipitation.

Magnetic Permeability. The low-carbon alloys are frequently used in the production of articles requiring low magnetic permeability. These materials are nonmagnetic in the fully annealed condition, with permeabilities below 1.02 max at 0.02 T (200 G) but may develop ferromagnetic qualities as a result of cold working during fabrication. Cold working may generate some low-carbon martensite, which is strongly magnetic. Fusion welding with a low-nickel filler rod is another possible cause of magnetism. Magnetism due to any of these causes can be eliminated by a full anneal to restore the alloy to its fully austenitic condition.

High-nitrogen austenitic stainless steels are heat treated in the same manner and are subject to the same problems (carbide precipitation and distortion) as conventional austenitics. They cannot be hardened by heat treatment but will harden by cold working. High-nitrogen austenitics are annealed to ensure maximum corrosion resistance, softness, and ductility. Rapid cooling is preferred. Annealing temperature ranges are listed in Table 3.

Highly alloyed austenitic stainless steels contain large amounts of molybdenum to provide very good resistance to chloride corrosion. They usually are produced with low carbon to avoid sensitization and may contain copper for increased acid resistance. These alloys are austenitic in the mill-annealed condition but may form σor δ ferrite phases under certain conditions of heat treatment or service. Those phases may be detrimental to corrosion resistance and mechanical properties. Annealing temperatures are confined to a narrow range to avoid σ-phase formation at lower temperature, or δ ferrite at higher temperature. Recommended annealing temperatures are given in Table 1. Rapid cooling following annealing is usually advisable, especially in heavy sections. Stress-relief treatments may be used below the annealing temperature range, but holding times should be held to a minimum to avoid ω phase and sensitization problems.

Magnetic Permeability. The more highly alloyed austenitic grades, along with the high-nitrogen grades such as 316N, the Nitronic family, and Carpenter 18-18 Plus, will not develop low-carbon martensite with cold work and thereby do not require a full anneal to reduce magnetic permeability. The permeability of these alloys will remain below 1.02 even with significant amounts of cold work.

Bright Annealing of Austenitic Stainless Steels

All grades of austenitic stainless steel can be bright annealed in either pure hydrogen or dissociated ammonia, provided the dew point of the atmosphere is less than -50 °C (-60 °F) and the workpieces, upon entering the furnace, are dry and scrupulously clean. The furnaces used in bright annealing must be clean, moisture-free, and tight if low dew points are to be maintained. If a low dew point is not maintained, a thin greenish oxide will form on the work. This oxide is very difficult to remove in subsequent descaling operations.

To maintain close control of dew point, atmosphere samples should be withdrawn from the furnace at frequent intervals and tested or continuously monitored, as in most commercial operations. Traces of oxygen in hydrogen gas can be removed before the gas enters the furnace by passing the gas through a catalytic tower that causes excess oxygen to combine with the hydrogen to form water vapor. The gas is then passed through activated alumina to remove moisture.

In using dissociated ammonia, it is important that maximum dissociation be obtained before the gas enters the furnace. The presence of any undissociated ammonia will result in objectionable nitriding action. Because the undissociated gas is entirely soluble in water, its removal can be easily accomplished. However, the remaining fully dissociated product must be processed through drying towers to restore the required low dew point.

Stress Relieving of Austenitic Stainless Steels

Austenitic stainless steels have good creep resistance; consequently, these steels must be heated to about 900 °C (1650 °F) to attain adequate stress relief. In some instances, heating to the annealing temperature may be desirable. Holding at a temperature lower than about 870 °C (1600 °F) results in only partial stress relief. The most effective stress-relieving results are achieved by slow cooling. Quenching or other rapid cooling, as is normal in the annealing of austenitic stainless steel, will usually reintroduce residual stresses. Stress relieving is only necessary when austenitic stainless parts are subjected to corrosive conditions conducive to stress corrosion or intergranular corrosion failures.

Selection of Treatment. Selection of an optimum stress-relieving treatment is difficult because heat treatments that provide adequate stress relief can impair the corrosion resistance of stainless steel, and heat treatments that are not harmful to corrosion resistance may not provide adequate stress relief. To avoid specifying a heat treatment that might prove harmful, ASME Code neither requires nor prohibits stress relief of austenitic stainless steel.

Metallurgical characteristics of austenitic stainless steels that may affect the selection of a stress-relieving treatment are discussed below:

- *Heating in the range from 480 to 815 °C (900 to 1500 °F):* Chromium carbides will precipitate in the grain boundaries of wholly austenitic unstabilized grades. In partially ferritic cast grades, the carbides will precipitate initially in the discontinuous ferrite pools rather than in a continuous grain-boundary network. After prolonged heating such as is necessary for heavy sections, however, grain-boundary carbide precipitation will occur. For cold-worked stainless, carbide precipitation may occur as low as 425 °C (800 °F); for types 309 and 310, the upper limit for carbide precipitation may be as high as 900 °C (1650 °F). In this condition, the steel is susceptible to intergranular corrosion. By using stabilized or extra-low-carbon grades, these intergranular precipitates of chromium carbide can be avoided
- *Heating in the range from 540 to 925 °C (1000 to 1700 °F):* The formation of hard, brittle σ phase may result, which can decrease both corrosion resistance and ductility. During the times necessary for stress relief, σ will not form in fully austenitic wrought, cast, or welded stainless. However, if the stainless is partly ferritic, the ferrite may transform to σ during stress relief. This is generally not a problem in wrought stainless steels because they are fully austenitic; however, some wrought grades--particularly types 309, 309Cb, 312, and 329--may contain some ferrite. Furthermore, the composition of most austenitic stainless welds and castings is intentionally adjusted so that ferrite is present as a deterrent to cracking. The niobium- (columbium)-containing cast grade CF-8C normally contains 5 to 20% ferrite, which is more likely to transform to σ than the niobium-free ferrite in the unstabilized CF-8 grade
- *Slow cooling an unstabilized grade (other than an extra-low-carbon grade):* Through either of the above temperature ranges, slow cooling may allow sufficient time for these detrimental effects to take place
- *Heating at 815 to 925 °C (1500 to 1700 °F):* The coalescence of chromium carbide precipitates or σ phase will occur, resulting in a form less harmful to corrosion resistance or mechanical properties
- *Heating at 955 to 1120 °C (1750 to 2050 °F):* This annealing treatment causes all grain-boundary chromium carbide precipitates to redissolve and transforms σ back to ferrite, as well as fully softening the steel. Long heating times (>1 h) may even dissolve some of the ferrite present and further reduce the probability of σ reforming upon slow cooling
- *Stress relieving to improve the notch toughness:* Unlike carbon and alloy steels, austenitic steels are not notch sensitive. Consequently, stress relieving to improve notch toughness would be of no benefit. Notch-impact strength may actually be decreased if the steel is stress relieved at a temperature at which chromium carbide is precipitated or σ phase forms

Although stabilized alloys do not require high-temperature annealing to avoid intergranular corrosion, the stress-relieving temperature exerts an influence on the general corrosion resistance of these alloys. Figure 1 shows the effect of stress relieving for 2 h at various temperatures on the corrosion rate of type 347 stainless steel in boiling 65% nitric acid. The corrosion resistance of type 347 in boiling nitric acid is better when the material is treated at 815 to 870 °C (1500 to 1600 °F) than when treated at 650 to 705 °C (1200 to 1300 °F). The 650 to 705 °C (1200 to 1300 °F) stress relief may be promoting the formation of a small quantity of chromium carbides as a result of free carbon not previously tied up as niobium carbides.

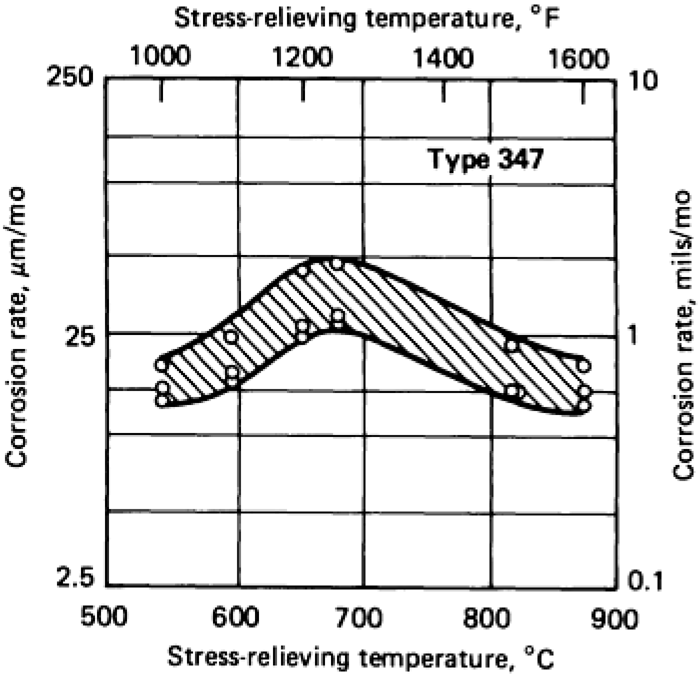


Fig. 1 Effect of stress relieving on corrosion rate of type 347 stainless steel in boiling 65% HNO_3. All stress-relief treatments lasted 2 h.

Figure 2 shows how the percentage of stress relief increases with an increase in stress-relieving temperature for type 347 stainless steel. These data also demonstrate the relative unimportance of holding time.

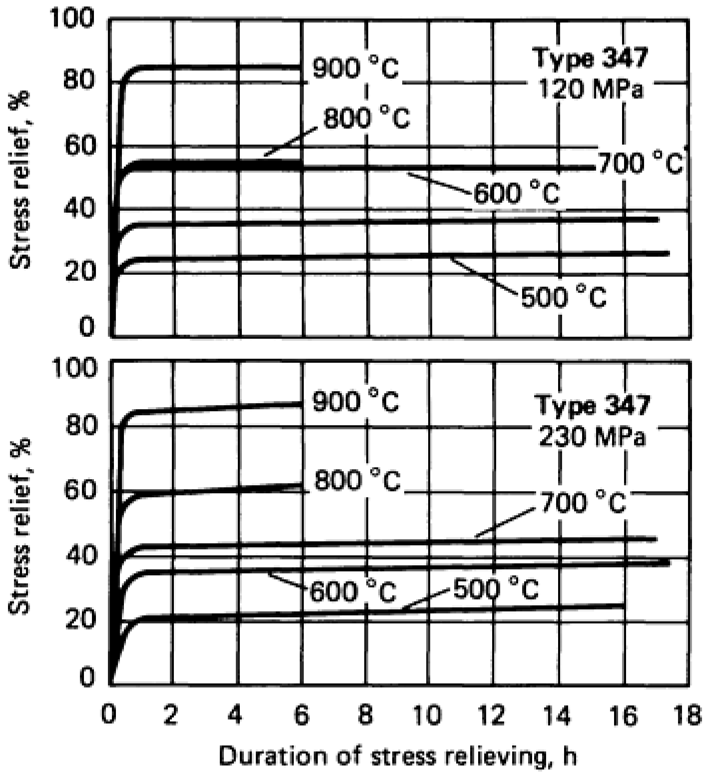


Fig. 2 Stress relief obtained in type 347 stainless steel, as a function of temperature, initial stress, and time at

temperature

General Recommendations. In the selection of the proper stress-relieving treatment, consideration must be given also to the specific material used, fabrication procedures involved, and to the design and operating conditions of the equipment. Stress relieving generally is not advisable unless the service environment is known or suspected to cause stress corrosion. If stress relieving seems warranted, due regard should be given the metallurgical factors and their effect on the steel in the intended service. The use of stabilized or extra-low-carbon grades is an advantage in view of the greater latitude allowed in stress relieving.

Table 6 gives suggested stress-relieving treatments for service applications and environments. Because of the varying degrees of stress relief that may be required, number of different grades of stainless in use, many fabricating procedures that may be employed, and the multitude of service requirements, many alternative treatments are indicated in Table 6 to allow selection of the stress-relieving treatment best suited to particular circumstances.

Table 6 Stress-relieving treatments for austenitic stainless steels

Application or desired characteristics	**Extra-low-carbon grades, such as 304L and 316L**	Suggested thermal treatment[a]	
		Stabilized grades, such as 318, 321, and 347	Unstabilized grades, such as 304 and 316
Severe stress corrosion	A, B	B, A	[b]
Moderate stress corrosion	A, B, C	B, A, C	**C**[b]
Mild stress corrosion	A, B, C, E, F	B, A, C, E, F	**C, F**
Remove peak stresses only	F	F	**F**
No stress corrosion	None required	None required	**None required**
Intergranular corrosion	A, C[c]	A, C, B[c]	**C**
Stress relief after severe forming	A, C	A, C	**C**
Relief between forming operations	A, B, C	B, A, C	**C**[d]
Structural soundness[e]	A, C, B	A, C, B	**C**

(a) Thermal treatments are listed in order of decreasing preference. A: Anneal at 1065 to 1120 °C (1950 to 2050 °F) and then slow cool. B: Stress relieve at 900 °C (1650 °F) and then slow cool. C: Anneal at 1065 to 1120 °C (1950 to 2050 °F) and then quench or cool rapidly. D: Stress relieve at 900 °C (1650 °F) and then quench or cool rapidly. E: Stress relieve at 480 to 650 °C (900 to 1200 °F) and then slow cool. F: Stress relieve at below 480 °C (900 °F) and then slow cool. G: Stress relieve at 205 to 480 °C (400 to 900 °F) and then slow cool (usual time, 4 h per inch of section).

(b) To allow the optimum stress-relieving treatment, the use of stabilized or extra-low-carbon grades is recommended.

(c) In most instances, no heat treatment is required, but where fabrication procedures may have sensitized the stainless steel the heat treatments noted may be employed.

(d) Treatment A B, or D also may be used, if followed by treatment C when forming is completed.

(e) Where severe fabricating stresses coupled with high service loading may cause cracking. Also, after welding heavy sections

Results Obtained by Various Treatments. Austenitic stainless steels have in many instances been stress relieved at temperatures normally used for carbon steels (540 to 650 °C, or 1000 to 1200 °F). Although at these temperatures virtually all residual stress is relieved in carbon steel, only 30 to 40% of the residual stress is relieved in austenitic stainless (Fig. 2). Because the treatment does not provide adequate stress relief, stainless stress relieved in this temperature range is often susceptible to stress corrosion. Table 7 shows the residual stresses remaining in solid austenitic stainless steels after being stress relieved for various times at temperatures ranging from 595 to 1010 °C (1100 to 1850 °F).

Table 7 Residual stresses in welded austenitic stainless steel before and after various treatments

Treatment			Residual stress	
Temperature		**Time, h**		
°C	**°F**		**MPa**	ksi
After welding 235 mm (9.25 in.) OD, 165 mm (6.5 in.) ID pipe				
As-welded			207-177	**30.0-25.7**
595	1100	16	138	**20.0**
595	1100	48	138	**20.0**
595	1100	72	159	**23.0**
650	1200	4	148-166	**21.5-24.0**
After welding 127 mm (5 in.) OD, 102 mm (4 in.) ID pipe				
As-welded			128-101	**18.5-14.7**
650	1200	4	94-105	**13.7-15.3**

650	1200	12	110	**16.0**
650	1200	36	108	**15.6**
900	1650	2	nil	**nil**
1010	**1850**	**1**	**nil**	**nil**

Annealing and Water Quenching. Numerous instances have been reported in which satisfactory service was obtained for vessels and parts that were stress relieved by being annealed (at 1065 to 1120 °C, or 1950 to 2050 °F) and water quenched. However, it is unlikely that these products were subjected to service environments conducive to severe stress corrosion (the presence of chlorides is one such hostile environment) because a water quench will almost always reintroduce high residual stresses.

Intergranular Corrosion. In a number of instances, partially stress-relieved stainless steel parts have failed through intergranular corrosion.

For example, partially stress relieved (at 620 to 650 °C, or 1150 to 1200 °F) type 316 stainless steel hardware used in coastal steam stations failed due to intergranular attack in seawater over a span of less than 6 mo.

Another typical case of intergranular corrosion involved a type 304 stainless steel heat exchanger (partially stress relieved at 650 °C, or 1200 °F) for 2 h and furnace cooled) that failed within 7 days.

Prevention of Stress Corrosion by Stress Relieving. A number of instances have been recorded in which beneficial effects were derived from an adequate stress-relief treatment.

Heaters made of type 316L failed after a few weeks of service while in contact with acid organic chloride and ammonium chloride, but those that were stress relieved at 955 °C (1750 °F) were completely free of stress-corrosion cracking (SCC) after 4 years of service under the same conditions.

Typically, when two type 316L stainless steel vessels are used in 85% phosphoric acid service, the vessel not stress relieved underwent extensive stress corrosion, whereas the stress-relieved (540 °C, or 1000 °F) vessel was completely free of any stress corrosion. This illustrates that even though a stainless steel component may not be completely stress relieved, reducing the stress level may totally prevent stress corrosion.

Stress relief of unstabilized grades of stainless at 900 °C (1650 °F) will result in some intergranular carbide precipitation, and in some instances a small amount of intergranular attack is preferable to failure within a few weeks by stress-corrosion cracking. Moreover, the intergranular attack probably could be avoided by using an extra-low-carbon or stabilized grade of austenitic stainless steel.

Reference cited in this section

1. A.K. Sinha, *Ferrous Physical Metallurgy,* Butterworths, 1989, p 335

Ferritic Stainless Steels

The ferritic stainless steels may be divided into two groups:

- Conventional ferritics such as types 405, 409, 430, 434, 439, and 446
- Low-interstitial ferritics such as types 444, E-Brite, Sea-Cure, AL 29-4C, and AL 29-4-2

The ferritic stainless steels are not normally hardened by quenching but rather develop minimum hardness and maximum ductility, toughness, and corrosion resistance in the annealed and quenched condition. Therefore, the only heat treatment applied to the ferritics is annealing. This treatment relieves stresses developed during welding or cold working and provides a more homogeneous structure by dissolving transformation products formed during welding. Postweld heat treatment of the low-interstitial ferritic stainless steels is generally unnecessary and is frequently undesirable. Table 8 summarizes current annealing practices for the ferritic grades.

Table 8 Recommended annealing treatments for ferritic stainless steels

UNS No.	**Designation**	Treatment temperature	
		°C	°F
Conventional ferritic grades			
S40500	405	650-815	**1200-1500**
S40900	409	870-925	**1600-1700**
S43000	430	705-790	**1300-1450**
S43020	430F	705-790	**1300-1450**
S43400	434	705-790	**1300-1450**
S44600	446	760-830	**1400-1525**
S43035	439	870-925	**1600-1700**
Low-interstitial ferritic grades[a]			
. . .	18 SR	870-925	**1600-1700**
S44400	444	955-1010	**1750-1850**
S44626	E-Brite	760-955	**1400-1750**
S44660	Sea-Cure (SC-1)	1010-1065	**1850-1950**
. . .	AL 29-4C	1010-1065	**1850-1950**
S44800	AL 29-4-2	1010-1065	**1850-1950**

(a) Postweld heat treating of the low-interstitial ferritic stainless steels is generally unnecessary and frequently undesirable. Any annealing of these grades should be followed by water quenching or very rapid cooling.

Austenite-Martensite Embrittlement. When grades such as 430 and 434 are cooled rapidly from above 925 °C (1700 °F), they may become brittle from austenite transforming to as much as 30% martensite. This may be corrected by a tempering treatment such as 650 to 790 °C (1200 to 1450 °F), which softens the alloy.

After such a treatment, some carbide formation can occur. After severe cold working, an anneal under 925 °C (1700 °F) is recommended to avoid further sensitization. Stabilized ferritics such as 439 or 444 avoid the austenite-martensite embrittlement concern by removing the strong austenite-forming elements (carbon plus nitrogen) from solution.

475 °C (885 °F) Embrittlement. A potentially harmful form of embrittlement common to the ferritic grades can develop from prolonged exposure to, or slow cooling within, the temperature range from about 370 to 540 °C (700 to 1000 °F), with the maximum rate of embrittlement occurring at about 475 °C (885 °F). The embrittlement is caused by precipitation of the α' phase, and the effects of embrittlement increase rapidly with chromium content. Lower-chromium alloys such as type 409 show little tendency to embrittle with 475 °C (885 °F) exposure. Certain heat treatments must be controlled to avoid embrittlement. The brittle condition can be eliminated by the treatments listed in Table 8, using temperatures clearly above the upper boundary of embrittlement, followed by rapid cooling to prevent a recurrence.

Intermetallic Phase Embrittlement. Intermetallic phases, such as σ, χ, and Laves, may form at elevated temperatures in ferritic stainless steels containing more than about 14% Cr and/or the addition of elements such as niobium or molybdenum. These intermetallic phases increase hardness (sometimes usefully) and decrease ductility, notch toughness, and corrosion resistance. The temperature range over which these phases form is approximately 595 to 1000 °C (1100 to 1830 °F). Generally, such phases are of most concern when affected parts are cooled to room temperature. At elevated temperatures, the phases do not appear to be a major problem from a ductility or toughness standpoint. In the case of Laves nphase, such intermetallics can even improve high-temperature creep strength. Figure 3 compares stress-rupture properties of selected ferritic and austenitic stainless steels.

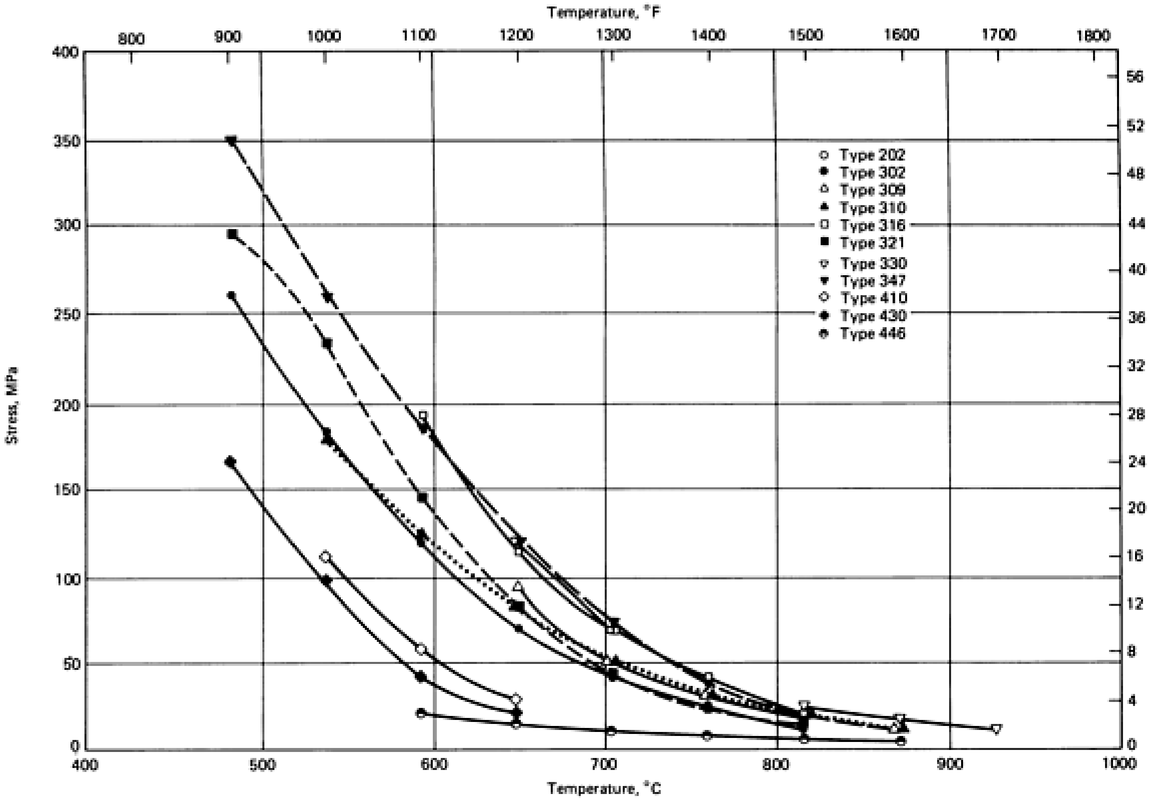


Fig. 3 10 000-h stress-rupture strength of wrought stainless steels. All samples were annealed with the

exception of type 410 (heat treated at 980 °C, or 1800 °F, for $\frac{1}{2}$ h, oil quenched, tempered at 650 °C, or 1200 °F, for 2 h and then air cooled). Extrapolated data were used for all curves.

Intermetallic phase embrittlement is primarily a service problem involving long exposures at elevated temperatures. These phases can be dissolved by heating to above 1000 °C (1830 °F).

Duplex Stainless Steels

Duplex stainless steels consist of a mixed microstructure of austenite and ferrite. Some duplex stainless steels are rich in ferrite, others in austenite, and others are equally balanced. Compared with type 316, the annealed duplex alloys provide improved resistance to chloride stress-corrosion cracking. Although the duplex grades are generally not as resistant to SCC as the low-interstitial ferritics, they are normally available in heavier section thicknesses. Another useful characteristic of the duplex grades is that they typically have yield strengths more than twice that of the conventional austenitic stainless steels. In thicker sections, the duplex alloys are more impact resistant than ferritic alloys.

Duplex stainless steels, such as SAF 2205, AF 22, DP 3, and Ferralium alloy 255, are alloyed with 0.15 to 0.20% N. This minimizes alloy element segregation between the ferrite and austenite, thereby improving the as-welded corrosion resistance compared with the type 329 alloy. The nitrogen addition also increases the precipitation of austenite during casting and welding and prevents high-ferrite content in rapidly cooled welds. Recommended annealing temperatures for duplex stainless steels are listed in Table 9.

Table 9 Recommended annealing temperatures for selected duplex stainless steels

UNS No.	**Designation**	Annealing temperature[(a)] °C (°F)
S32900	329	**925-955 (1700-1750)**
S32950	7 Mo Plus	**995-1025 (1825-1875)**
S31500	3RE60	**975-1025 (1785-1875)**
S31803	SAF 2205	**1020-1100 (1870-2010)**
. . .		**1020-1100 (1870-2010)**
S31260	DP-3	**1065-1175 (1950-2150)**
S32550	**Ferralium 255**	**1065-1175 (1950-2150)**

(a) Cooling from the annealing temperature must be rapid, but it also must be consistent with

limitations of distortion.

Martensitic Stainless Steels

The heat treating of martensitic stainless steel is essentially the same as for plain-carbon or low-alloy steels, in that maximum strength and hardness depend chiefly on carbon content. The principal metallurgical difference is that the high alloy content of the stainless grades causes the transformation to be so sluggish, and the hardenability to be so high, that maximum hardness is produced by air cooling in the center of sections up to approximately 305 mm (12 in.) thick.

Surface hardness ranges for the various heat-treated conditions from fully annealed to fully hardened are given in Fig. 4.

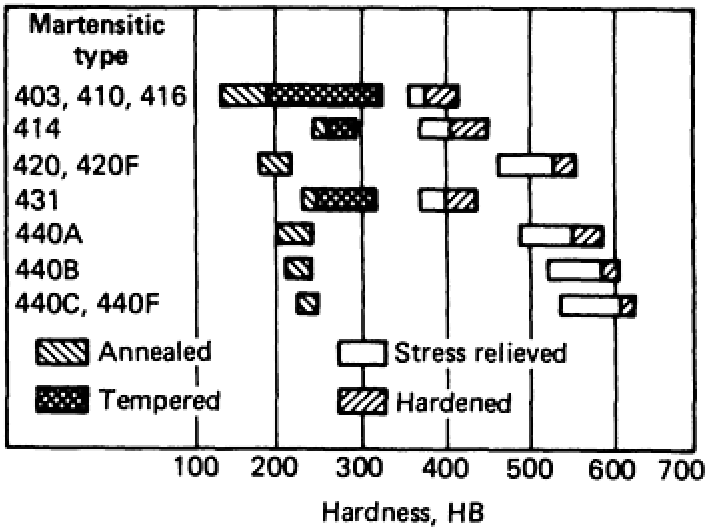


Fig. 4 Effect of heat treatments on the hardness of wrought martensitic stainless steels

The martensitic stainless steels are more sensitive to heat-treating variables than are carbon and low-alloy steels; rejection rates due to faults in heat treating are correspondingly high.

Prior Cleaning. To avoid contamination, all parts and heat-treating fixtures must be cleaned thoroughly before they are placed in the furnace. Proper cleaning is particularly important when the heat treatment is to be performed in a protective atmosphere. Grease, oil, and even location lines made by an ordinary lead pencil can cause carburization. Perspiration stains from fingerprints are a source of chloride contamination and may cause severe scaling in oxidizing atmospheres. Furthermore, a protective atmosphere cannot be effective unless it is permitted to make unobstructed contact with metal surfaces.

Preheating. Martensitic stainless steels normally are hardened by being heated to the austenitizing range of 925 to 1065 °C (1700 to 1950 °F) and then cooled in air or oil.

The thermal conductivity of stainless steels is characteristically lower than that of carbon and alloy steels. Accordingly, high thermal gradients and high stresses during rapid heating may cause warpage and cracking in some parts. To avoid these problems, preheating is usually recommended in the treatment of martensitic stainless steels. In annealing or hardening, the following parts should be preheated:

- Heavy section parts
- Parts with both thin and thick sections
- Parts with sharp corners and reentrant angles
- Heavily ground parts
- Parts machined with heavy deep cuts

- Parts that have been cold formed or straightened
- Previously hardened parts that are being reheat treated

Preheating is normally accomplished at 760 to 790 °C (1400 to 1450 °F), and heating need be continued only long enough to ensure that all portions of each part have reached the preheating temperature. Large heavy parts are sometimes preheated at approximately 540 °C (1000 °F) prior to the 790 °C (1450 °F) preheat. Types 403, 410, and 416 require less preheating than the higher-carbon types 431, 420, and 440 grades.

Austenitizing temperatures, soaking times, and quenching media are summarized in Table 10. When maximum corrosion resistance and strength are desired, the steel should be austenitized at the high end of the temperature range. For alloys that are to be tempered above 565 °C (1050 °F), the low side of the austenitizing range is recommended because it enhances ductility and impact properties.

Table 10 Procedures for hardening and tempering wrought martensitic stainless steels to specific strength and hardness levels

Type	Austenitizing[(a)]			Tempering temperature[(d)]				Tensile strength		Hardness, HRC
	Temperature[(b)]		Quenching medium[(c)]	°C		°F				
	°C	°F		min	max	min	max	MPa	ksi	
403, 410	925-1010	1700-1850	Air or oil	565	605	1050	1125	760-965	110-140	25-31
				205	370	400	700	1105-1515	160-220	38-47
414	925-1050	1700-1925	Air or oil	595	650	1100	1200	760-965	110-140	25-31
				230	370	450	700	1105-1515	160-220	38-49
416, 416Se	925-1010	1700-1850	Oil	565	605	1050	1125	760-965	110-140	25-31
				230	370	450	700	1105-1515	160-220	35-45
420	980-1065	1800-1950	Air or oil[(e)]	205	370	400	700	1550-1930	225-280	48-56
431	980-1065	1800-1950	Air or oil[(e)]	565	605	1050	1125	860-1035	125-150	26-34
				230	370	450	700	1210-1515	175-220	40-47
440A	1010-1065	1850-1950	Air or oil[(e)]	150	370	300	700	. . .	. . .	49-57
440B	1010-1065	1850-1950	Air or oil[(e)]	150	370	300	700	. . .	. . .	53-59

440C, 440F	1010-1065	1850-1950	Air or oil[(c)]	. . .	160	. . .	325	. . .	. . .	60 min
				. . .	190	. . .	375	. . .	. . .	58 min
				. . .	230	. . .	450	. . .	. . .	57 min
				. . .	355	. . .	675	. . .	. . .	52-56

(a) Preheating to a temperature within the process annealing range (see Table 12) is recommended for thin-gage parts, heavy sections, previously hardened parts, parts with extreme variations in section or with sharp reentrant angles, and parts that have been straightened or heavily ground or machined, to avoid cracking and minimize distortion, particularly for types 420, 431, and 440A, B, C, and F.

(b) Usual time at temperature ranges from 30 to 90 min. The low side of the austenitizing range is recommended for all types subsequently tempered to 25 to 31 HRC; generally, however, corrosion resistance is enhanced by quenching from the upper limit of the austenitizing range.

(c) Where air or oil is indicated, oil quenching should be used for parts more than 6.4 mm ($\frac{1}{4}$ in.) thick; martempering baths at 150 to 400 °C (300 to 750 °F) may be substituted for an oil quench.

(d) Generally, the low end of the tempering range of 150 to 370 °C (300 to 700 °F) is recommended for maximum hardness, the middle for maximum toughness, and the high end for maximum yield strength. Tempering in the range of 370 to 565 °C (700 to 1050 °F) is not recommended because it results in low and erratic impact properties and poor resistance to corrosion and stress corrosion.

(e) For minimum retained austenite and maximum dimensional stability, a subzero treatment -75 ± 10 °C (-100 ± 20 °F) is recommended; this should incorporate continuous cooling from the austenitizing temperature to the cold transformation temperature.

The effect of austenitizing temperature on the as-quenched hardness of three martensitic grades is shown in Fig. 5. The hardness increases with increasing austenitizing temperature to about 980 °C (1800 °F), then decreases because of austenite retention and (occasionally) the formation of δ ferrite.

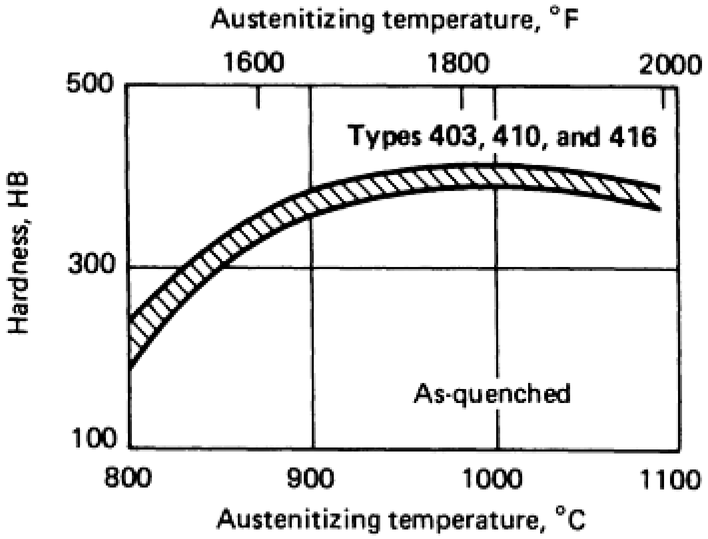


Fig. 5 Effect of austenitizing temperature on asquenched hardness. Specimens were wrought martensitic

stainless steels containing 0.15% max C.

Certain anomalies in these steels that should be considered before specifying a heat-treating procedure are exemplified in the opposing injurious effects of the high and low extremes of austenitizing temperature, depending on the subsequent tempering temperature. Table 11 shows that the Izod impact properties of type 431 are caused by retained austenite.

Table 11 Izod impact energy of wrought martensitic stainless steels using selected heat treatments

Temperature				**Izod impact energy**	
Austenitizing		**Tempering**			
°C	**°F**	**°C**	**°F**	**J**	**ft · lbf**
980	1795	315	600	20.3-33.9	15.0-25.0
1065	1950	315	600	40.7-81.3	30.0-60.0
980	1795	595	1100	74.6-108.5	55.0-80.0

Soaking times employed in the hardening of martensitic stainless steels represent a compromise between achieving maximum solution of chromium-iron carbides for maximum strength and corrosion resistance, and avoiding decarburization, excessive grain growth, retained austenite, brittleness, and quench cracking. For sections 13 mm ($\frac{1}{2}$ in.) thick and under, a soaking time of 30 to 60 min is sometimes recommended. For most parts, adding 30 min for each additional inch of thickness or fraction thereof has proved adequate. However, soaking times should be doubled if parts to be hardened have been fully annealed or isothermally annealed.

The effect of soaking time at austenitizing temperature and other variables, on the impact strength and room-temperature hardness of types 403, 420, and 431 is plotted in Fig. 6, 7, and 8.

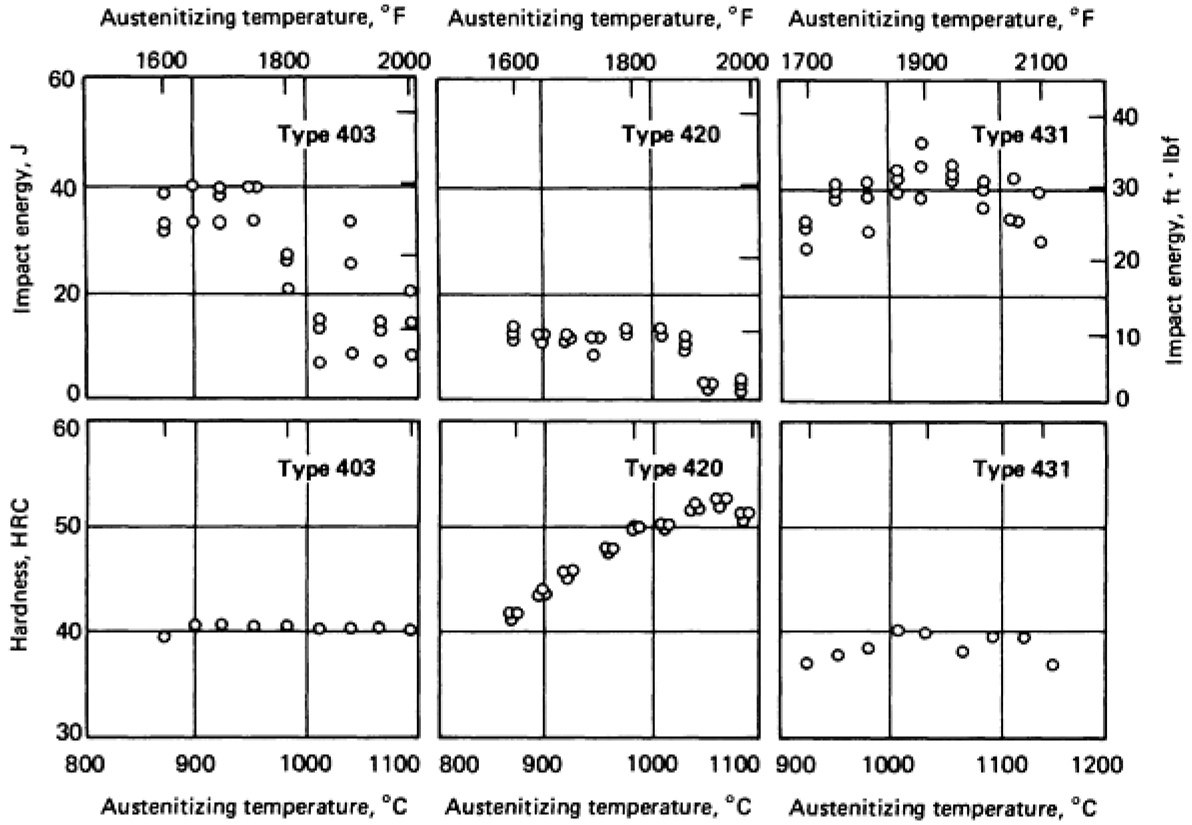


Fig. 6 Effect of variations in austenitizing temperature on hardness and impact strength of wrought martensitic stainless steels. Specimens were tempered at 480 °C (900 °F) for 4 h.

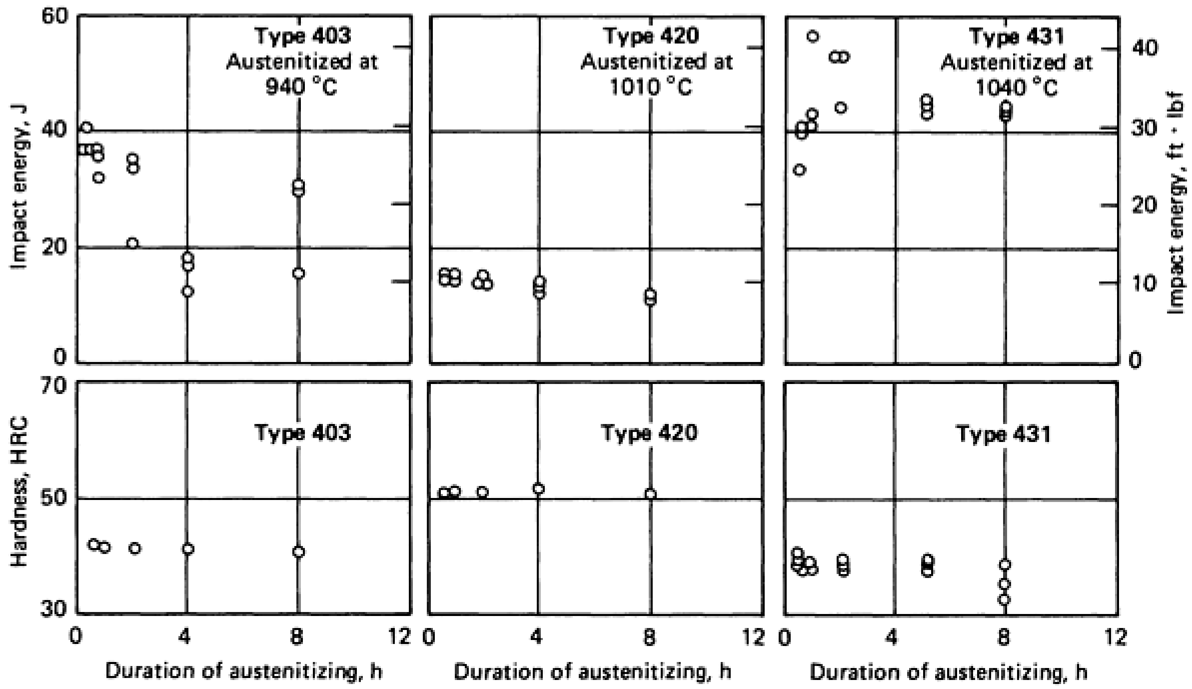


Fig. 7 Effect of variations in austenitizing time on hardness and impact strengths of wrought martensitic stainless steels. Specimens were tempered at 480 °C (900 °F) for 4 h.

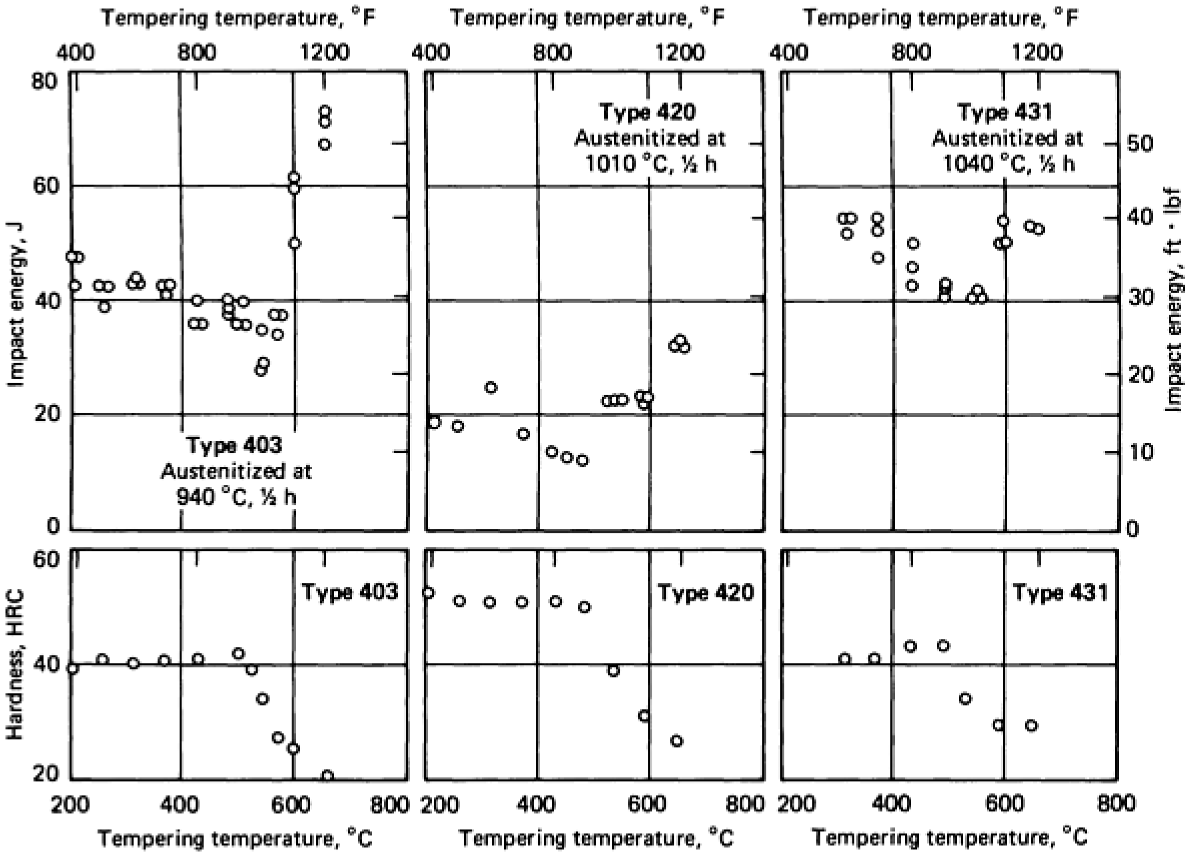


Fig. 8 Effect of variation in tempering temperature on hardness and impact strengths of wrought martensitic stainless steels

Quenching. Because of their high hardenability, martensitic stainless steels can be quenched in either oil or air. Some decrease in corrosion resistance and ductility, resulting from air quenching, may occur in these grades. These steels may precipitate carbides in grain-boundary areas if heavy sections are cooled slowly through the temperature range of about 870 to 540 °C (1600 to 1000 °F). Too slow a cooling rate in bright annealing (see the section "Austenitic Stainless Steels" in this article) these alloys may impair their corrosion resistance. Although oil quenching is preferred, air cooling may be required for large or complex sections to prevent distortion or quench cracking.

Martempering is particularly easy with these steels because of their high hardenability.

Retained Austenite. The higher-carbon martensitic grades, such as 440C, and the higher-nickel type 431, are likely to retain large amounts of untransformed austenite in the as-quenched structure, frequently as much as 30% by volume. Stress relieving at about 150 °C (300 °F) has little effect. Delayed transformation, particularly in type 440C, may occur as a result of temperature fluctuations in service, thus resulting in embrittlement and unacceptable dimensional changes.

Subzero Cooling. A portion of the austenite retained in quenching may be transformed by subzero cooling to about -75 °C (-100 °F) immediately after quenching. To obtain maximum transformation of retained austenite, double tempering may be necessary. Parts should be air cooled to room temperature between the tempering cycles.

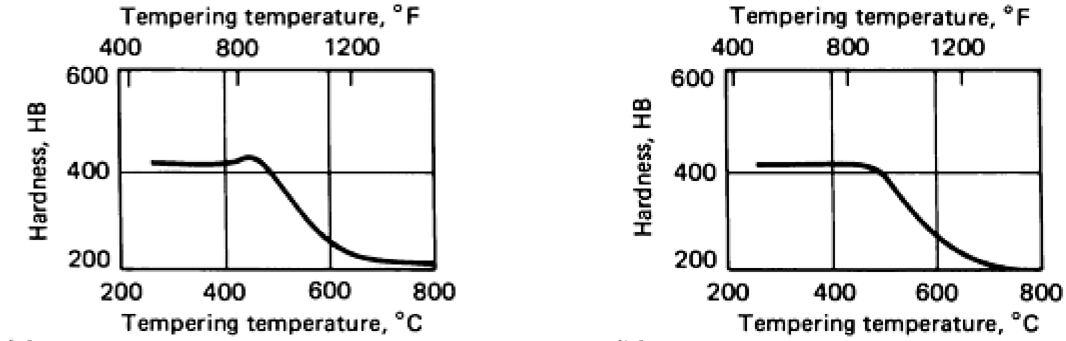
Subzero cooling is frequently included in the hardening treatment of parts such as the slides and sleeves of slide valves, and bearings requiring maximum dimensional stability.

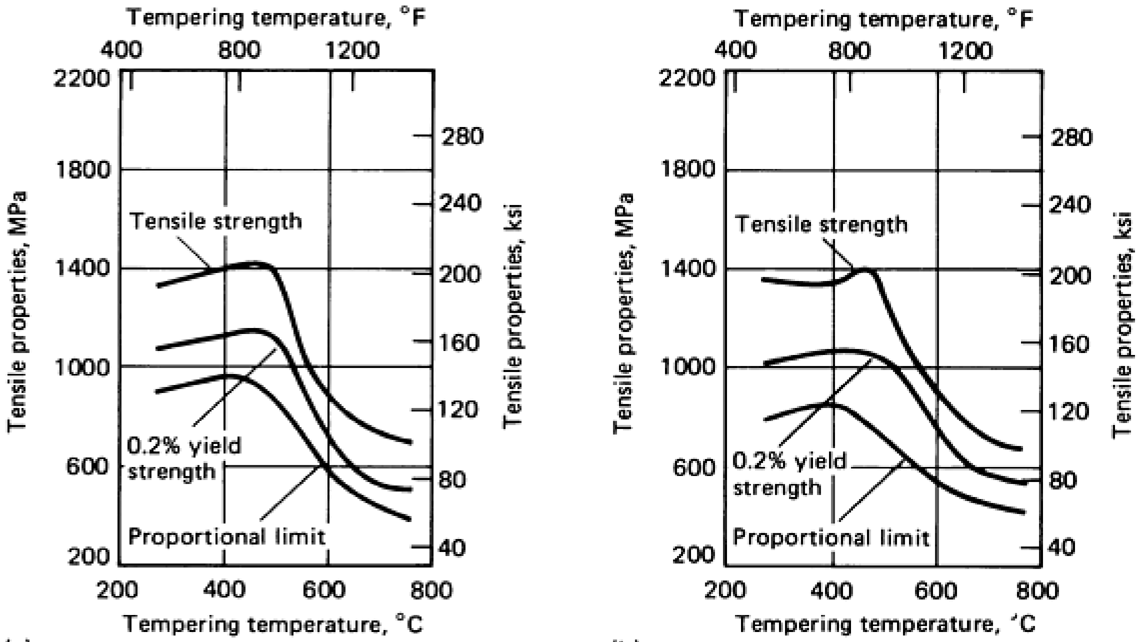
Reheating. For fully hardened steels, increasing degrees of recovery are achieved by:

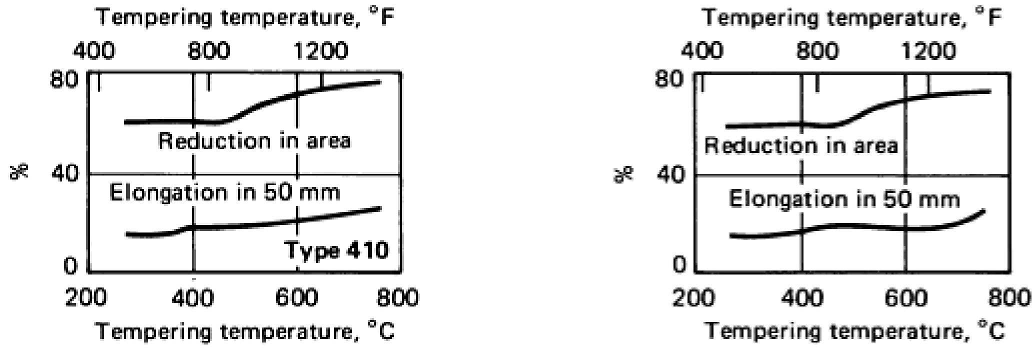
- *Stress relieving* at 150 to 370 °C (300 to 700 °F) after hardening to reduce transformation stresses without significantly affecting microconstituents or mechanical properties

- *Tempering* at intermediate temperatures to modify properties
- *Subcritical annealing* (variously called process, mill, or low annealing) in the upper portion of the ferritic range, just below the lower critical Ac_1 temperature, to achieve maximum softening without the complications of reentering the γ or austenitic field
- *Full annealing* for maximum softening by a return to the austenitic range, followed by slow cooling

Although the strength, elongation, and hardness curves shown in Fig. 9, 10, 11, 12, 13, and 14 appear to have the same general form as those of low-alloy steel, the increase in tensile strength and hardness between 400 and 510 °C (750 and 950 °F) may be associated with a serious decrease in notch toughness, whereas tempering on the high side of the temperature range generally coincides with a decrease in corrosion resistance. The tempering temperatures most frequently employed to achieve desired hardness and other mechanical properties are included in Table 10.


Tempering temperature, °F
400
800
1200
600
400
200
Hardness, HB
200
400
600
800
Tempering temperature, °C
(a) (b)


Tempering temperature, °F
400
800
1200
2200
1800
1400
1000
600
200
Tensile properties, MPa
280
240
200
160
120
80
40
Tensile properties, ksi
Tensile strength
0.2% yield strength
Proportional limit
200
400
600
800
Tempering temperature, °C
(a) (b)


Tempering temperature, °F
400
800
1200
80
40
0
%
Reduction in area
Elongation in 50 mm
Type 410
200
400
600
800
Tempering temperature, °C
(a) (b)

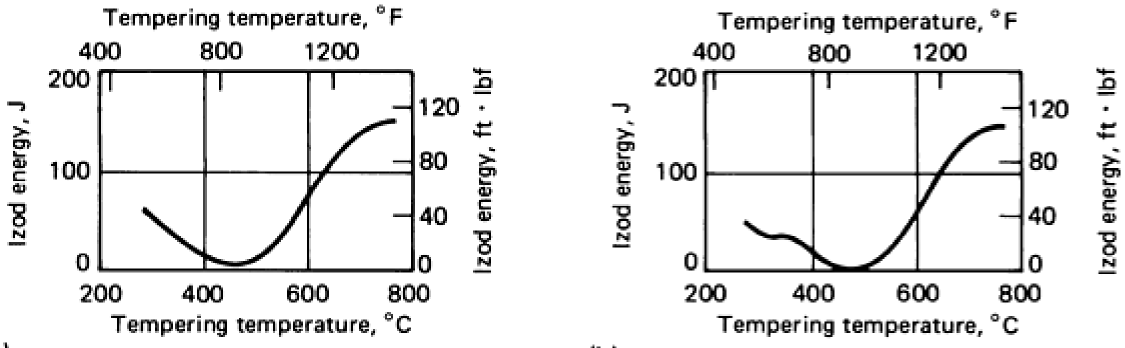
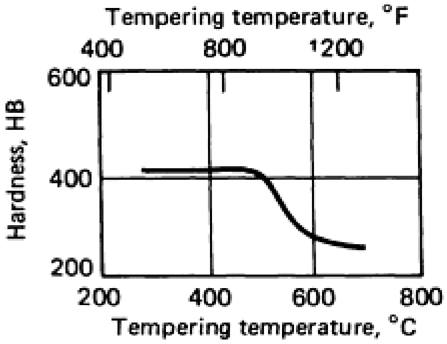
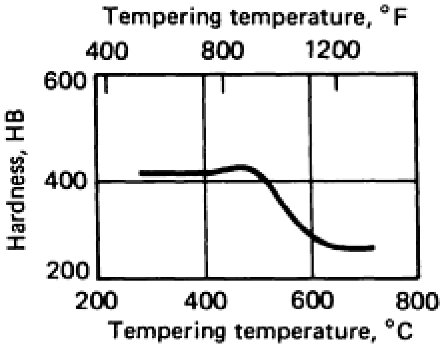

Tempering temperature, °F
400
800
1200
200
100
0
Izod energy, J
120
80
40
0
Izod energy, ft · lbf
200
400
600
800
Tempering temperature, °C
(a) (b)

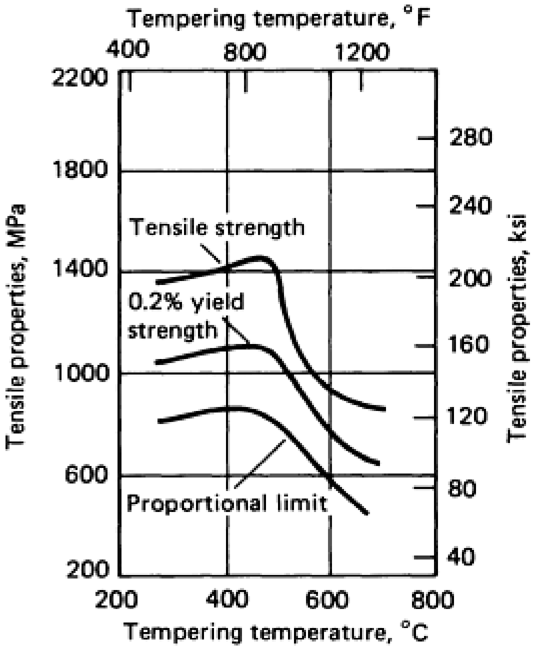
Fig. 9 Effect of austenitizing and tempering temperatures on mechanical properties of type 410 martensitic stainless steel. Austenitized 30 min; oil quenched to 65 to 95 °C (150 to 200 °F); double stress relieved at 175 °C (350 °F) for 15 rain and water quenched; tempered 2 h. (a) Quenched from 925 °C (1700 °F). (b) Quenched from 1010 °C (1050 °F)


Tempering temperature, °F
400
800
1200
600
400
200
Hardness, HB
200
400
600
800
Tempering temperature, °C

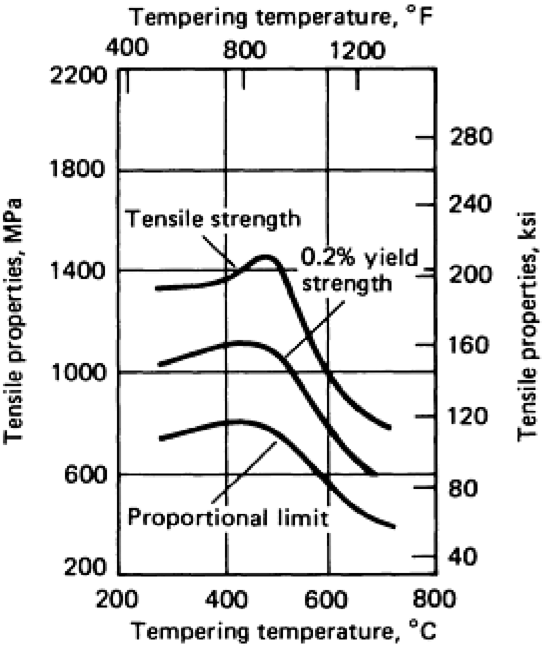
(a)


Tempering temperature, °F
400
800
1200
600
400
200
Hardness, HB
200
400
600
800
Tempering temperature, °C

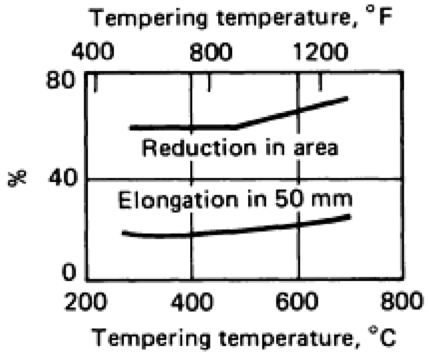
(b)


Tempering temperature, °F
400
800
1200
2200
1800
1400
1000
600
200
Tensile properties, MPa
280
240
200
160
120
80
40
Tensile properties, ksi
Tensile strength
0.2% yield strength
Proportional limit
200
400
600
800
Tempering temperature, °C

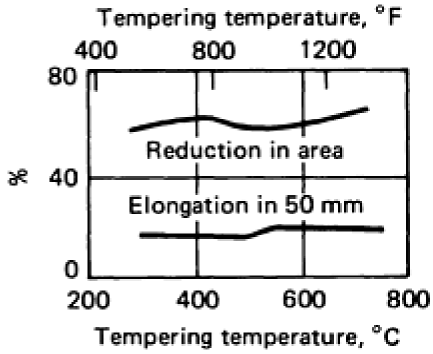
(a)


Tempering temperature, °F
400
800
1200
2200
1800
1400
1000
600
200
Tensile properties, MPa
280
240
200
160
120
80
40
Tensile properties, ksi
Tensile strength
0.2% yield strength
Proportional limit
200
400
600
800
Tempering temperature, °C

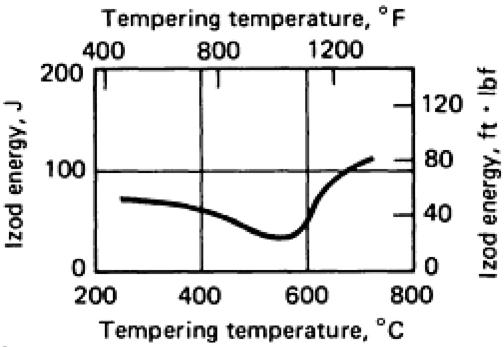
(b)


Tempering temperature, °F
400
800
1200
80
40
0
%
Reduction in area
Elongation in 50 mm
200
400
600
800
Tempering temperature, °C

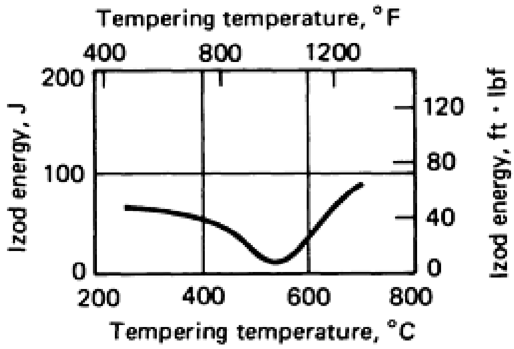
(a)


Tempering temperature, °F
400
800
1200
80
40
0
%
Reduction in area
Elongation in 50 mm
200
400
600
800
Tempering temperature, °C

(b)

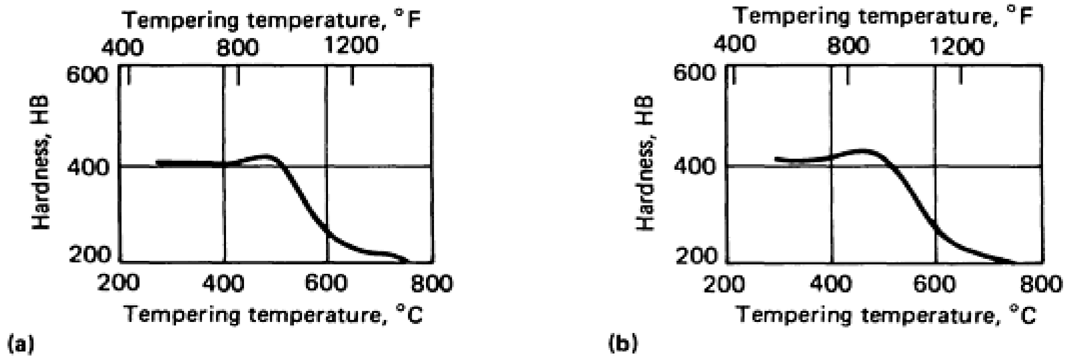

Tempering temperature, °F
400
800
1200
200
100
0
Izod energy, J
120
80
40
0
Izod energy, ft · lbf
200
400
600
800
Tempering temperature, °C

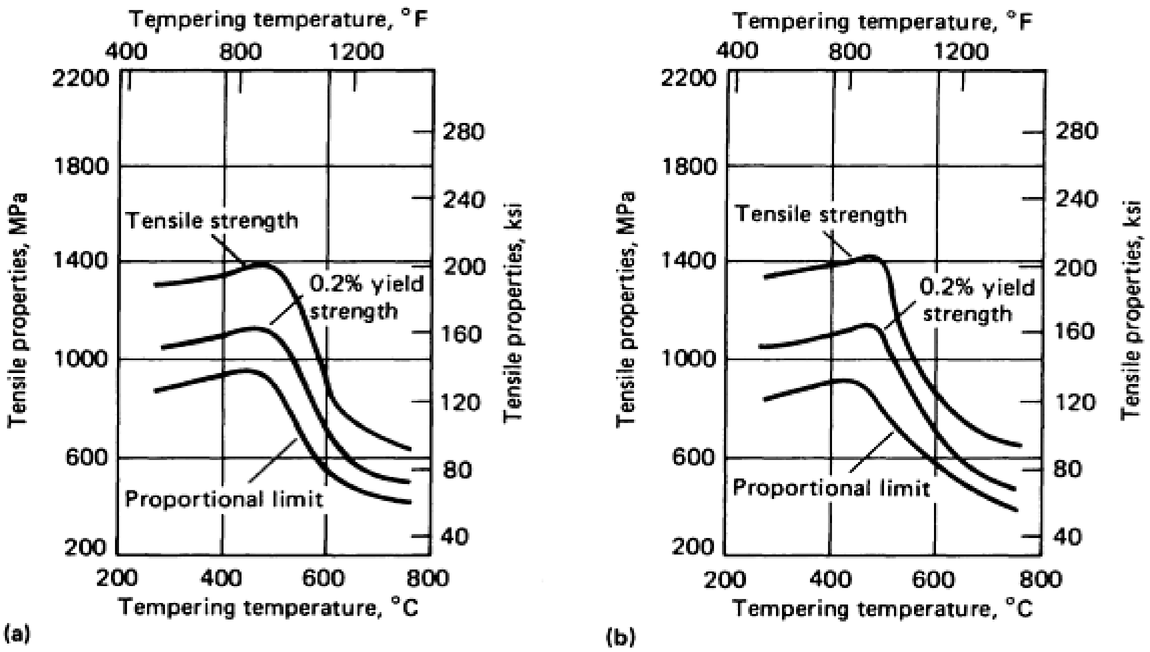
(a)

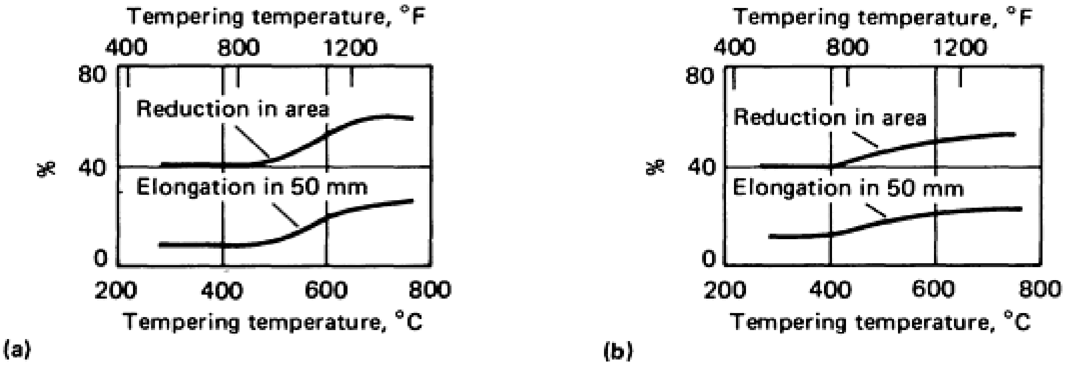

Tempering temperature, °F
400
800
1200
200
100
0
Izod energy, J
120
80
40
0
Izod energy, ft · lbf
200
400
600
800
Tempering temperature, °C

(b)

Fig. 10 Effect of austenitizing and tempering temperatures on typical mechanical properties of type 414 martensitic stainless steel. Austenitized 30 rain; oil quenched to 65 to 95 °C (150 to 200 °F); double stress relieved at 175 °C (350 °F) for 15 min and water quenched; tempered 2 h. (a) Quenched from 925 °C (1700 °F). (b) Quenched from 1040 °C (1900 °F)


Tempering temperature, °F
400
800
1200
600
400
200
Hardness, HB
200
400
600
800
Tempering temperature, °C
(a)
(b)


Tempering temperature, °F
400
800
1200
2200
1800
1400
1000
600
200
Tensile properties, MPa
280
240
200
160
120
80
40
Tensile properties, ksi
Tensile strength
0.2% yield strength
Proportional limit
200
400
600
800
Tempering temperature, °C
(a)
(b)


Tempering temperature, °F
400
800
1200
80
40
0
%
Reduction in area
Elongation in 50 mm
200
400
600
800
Tempering temperature, °C
(a)
(b)

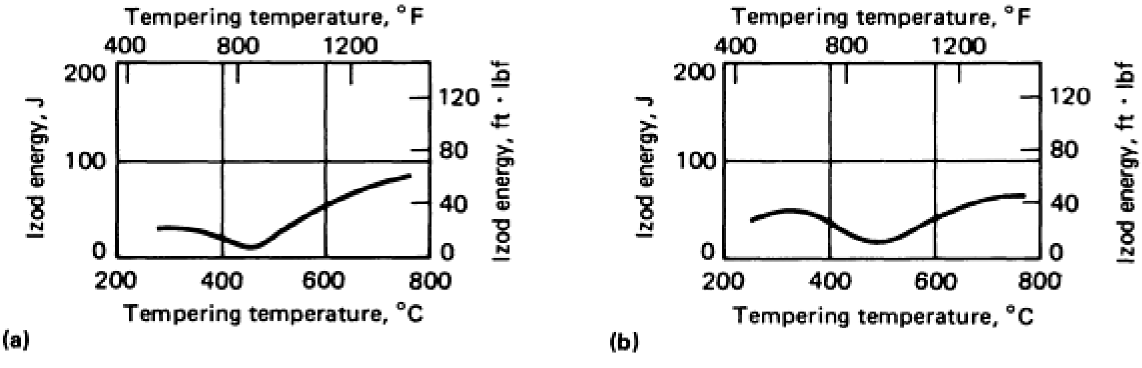
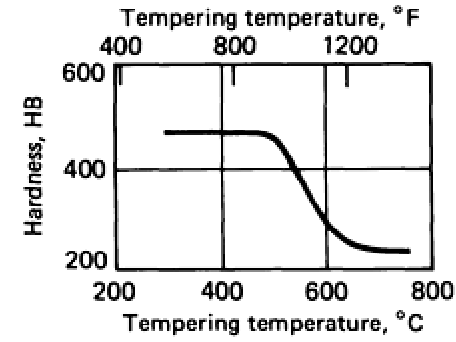
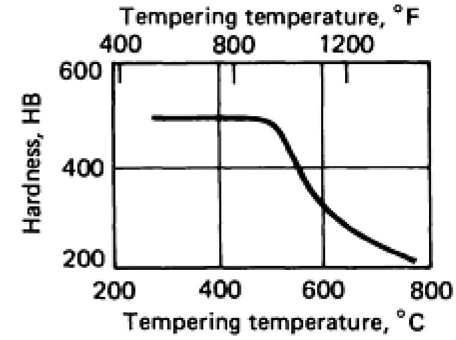

Tempering temperature, °F
400
800
1200
200
100
0
Izod energy, J
120
80
40
0
Izod energy, ft · lbf
200
400
600
800
Tempering temperature, °C
(a)
(b)

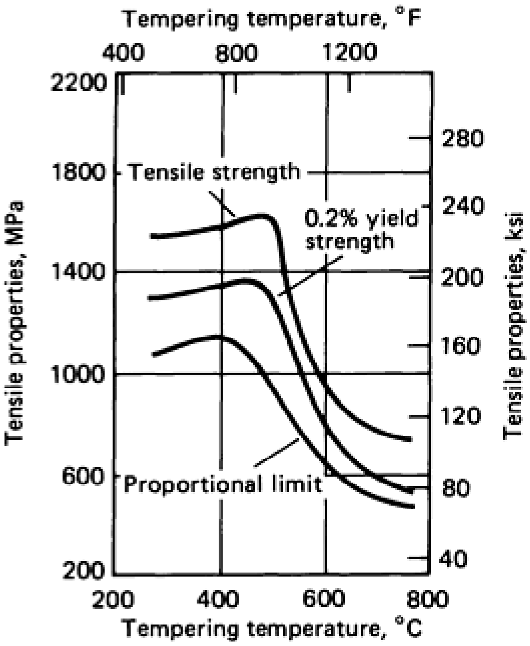
Fig. 11 Effect of austenitizing and tempering temperatures on typical mechanical properties of type 416 martensitic stainless steel. Austenitized 30 min; oil quenched to 65 to 95 °C (150 to 200 °); double stress relieved at 175 °C (350 °F) for 15 min and water quenched; tempered 2 h. (a) Quenched from 925 °C (1700 °F). (b) Quenched from 980 °C (1800 °F)


Tempering temperature, °F
400
800
1200
600
400
200
Hardness, HB
200
400
600
800
Tempering temperature, °C

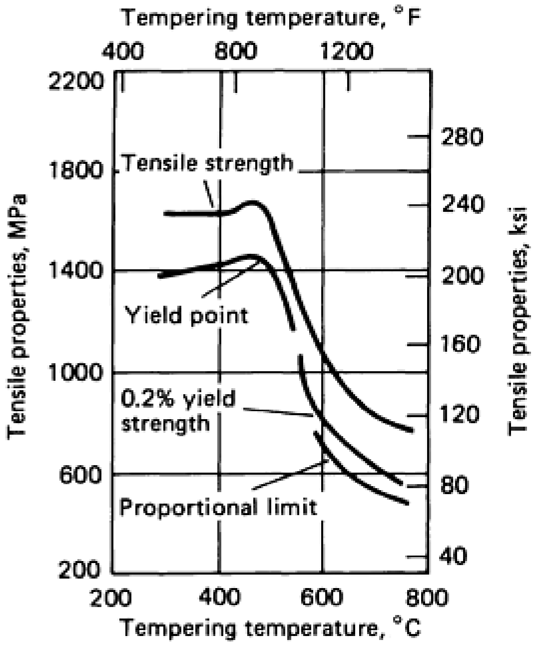
(a)


Tempering temperature, °F
400
800
1200
600
400
200
Hardness, HB
200
400
600
800
Tempering temperature, °C

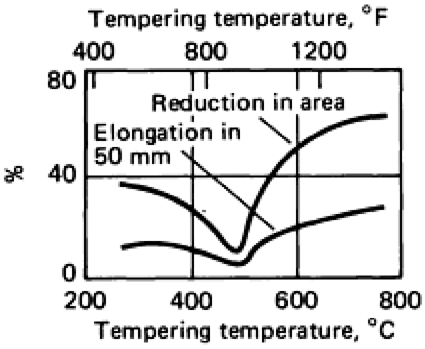
(b)


Tempering temperature, °F
400
800
1200
2200
1800
1400
1000
600
200
Tensile properties, MPa
280
240
200
160
120
80
40
Tensile properties, ksi
Tensile strength
0.2% yield strength
Proportional limit
200
400
600
800
Tempering temperature, °C

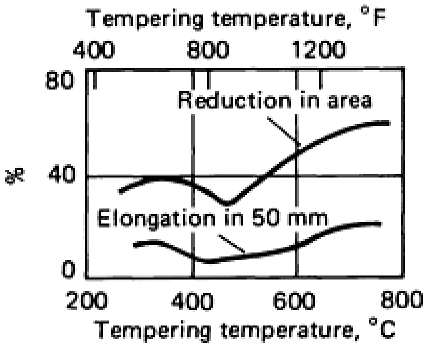
(a)


Tempering temperature, °F
400
800
1200
2200
1800
1400
1000
600
200
Tensile properties, MPa
280
240
200
160
120
80
40
Tensile properties, ksi
Tensile strength
Yield point
0.2% yield strength
Proportional limit
200
400
600
800
Tempering temperature, °C

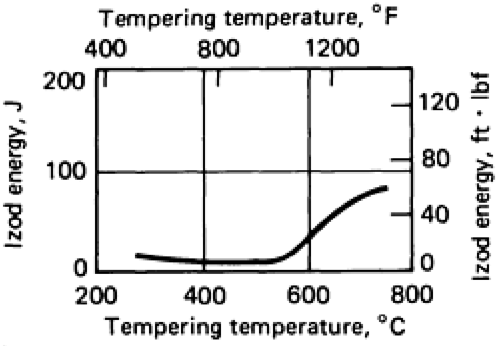
(b)


Tempering temperature, °F
400
800
1200
80
40
0
%
Reduction in area
Elongation in 50 mm
200
400
600
800
Tempering temperature, °C

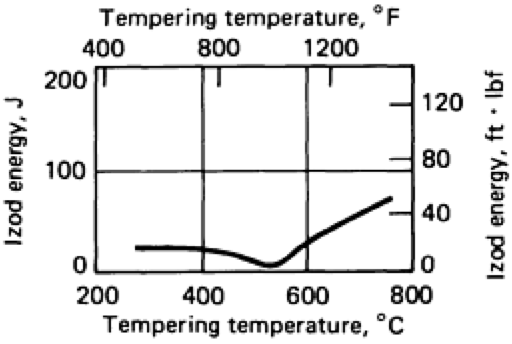
(a)


Tempering temperature, °F
400
800
1200
80
40
0
%
Reduction in area
Elongation in 50 mm
200
400
600
800
Tempering temperature, °C

(b)

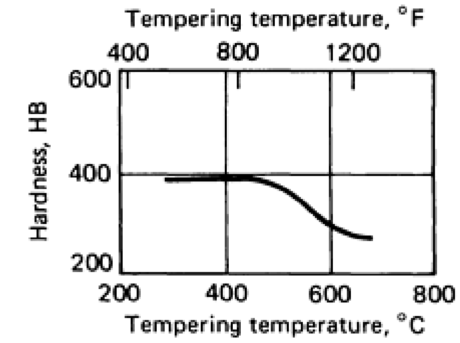

Tempering temperature, °F
400
800
1200
200
100
0
Izod energy, J
120
80
40
0
Izod energy, ft · lbf
200
400
600
800
Tempering temperature, °C

(a)

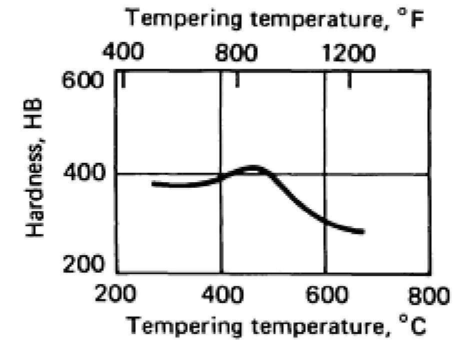

Tempering temperature, °F
400
800
1200
200
100
0
Izod energy, J
120
80
40
0
Izod energy, ft · lbf
200
400
600
800
Tempering temperature, °C

(b)

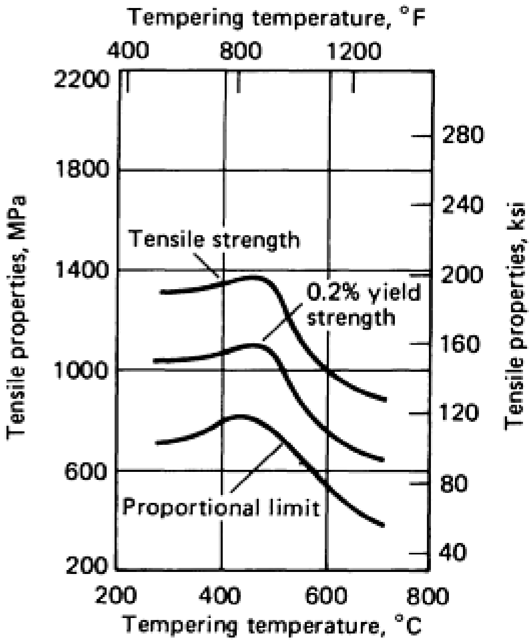
Fig. 12 Effect of austenitizing and tempering temperatures on typical mechanical properties of type 420 martensitic stainless steel. Austenitized 30 min; oil quenched to 65 to 95 °C (150 to 200 °F); double stress relieved at 175 °C (350 °F) for 15 min and water quenched; tempered 2 h. (a) Quenched from 925 °C (1700 °F). (b) Quenched from 1025 °C (1875 °F)


Tempering temperature, °F
400
800
1200
600
400
200
Hardness, HB
200
400
600
800
Tempering temperature, °C

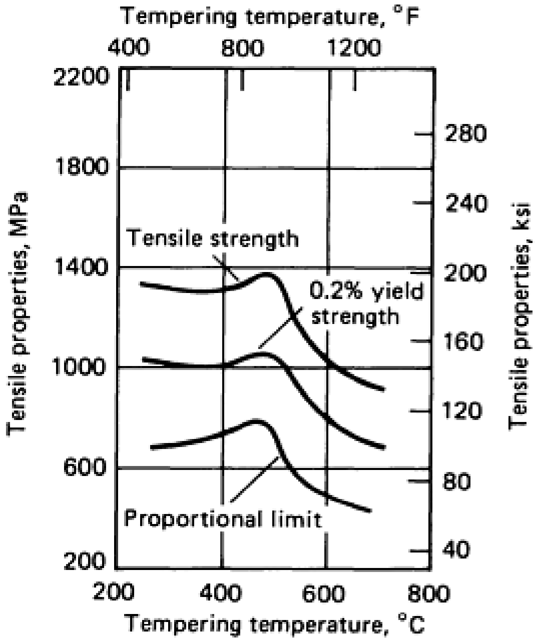
(a)


Tempering temperature, °F
400
800
1200
600
400
200
Hardness, HB
200
400
600
800
Tempering temperature, °C

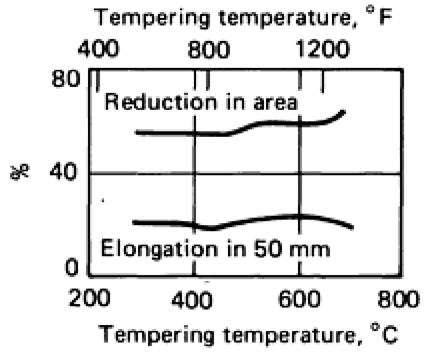
(b)


Tempering temperature, °F
400
800
1200
2200
1800
1400
1000
600
200
Tensile properties, MPa
280
240
200
160
120
80
40
Tensile properties, ksi
Tensile strength
0.2% yield strength
Proportional limit
200
400
600
800
Tempering temperature, °C

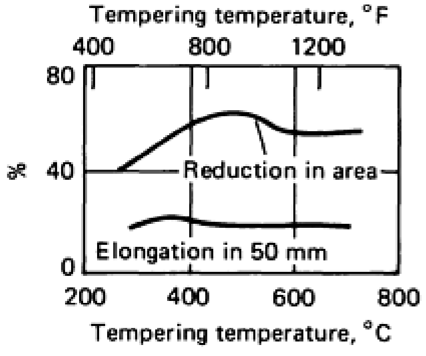
(a)


Tempering temperature, °F
400
800
1200
2200
1800
1400
1000
600
200
Tensile properties, MPa
280
240
200
160
120
80
40
Tensile properties, ksi
Tensile strength
0.2% yield strength
Proportional limit
200
400
600
800
Tempering temperature, °C

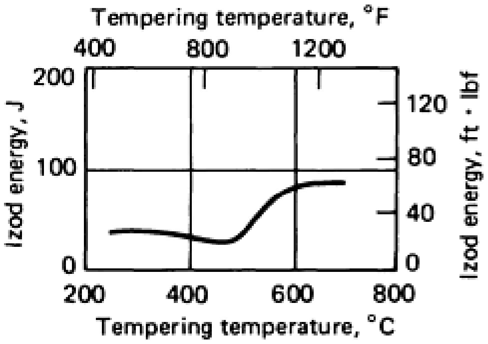
(b)


Tempering temperature, °F
400
800
1200
80
40
0
%
Reduction in area
Elongation in 50 mm
200
400
600
800
Tempering temperature, °C

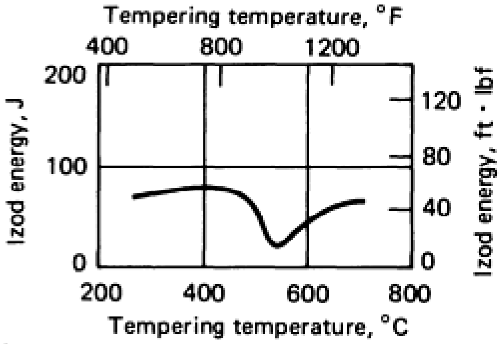
(a)


Tempering temperature, °F
400
800
1200
80
40
0
%
Reduction in area
Elongation in 50 mm
200
400
600
800
Tempering temperature, °C

(b)

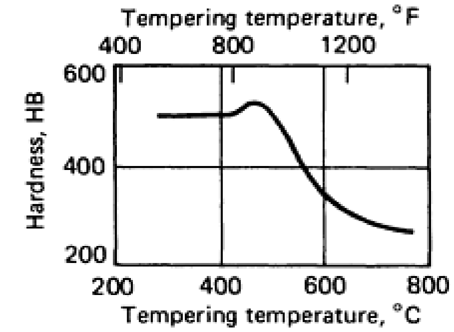

Tempering temperature, °F
400
800
1200
200
100
0
Izod energy, J
120
80
40
0
Izod energy, ft · lbf
200
400
600
800
Tempering temperature, °C

(a)

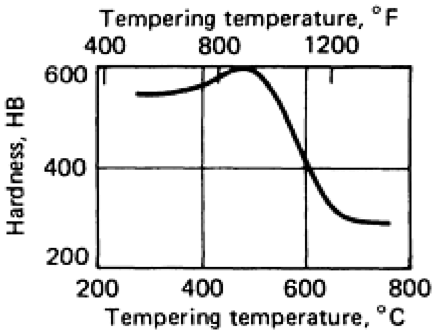

Tempering temperature, °F
400
800
1200
200
100
0
Izod energy, J
120
80
40
0
Izod energy, ft · lbf
200
400
600
800
Tempering temperature, °C

(b)

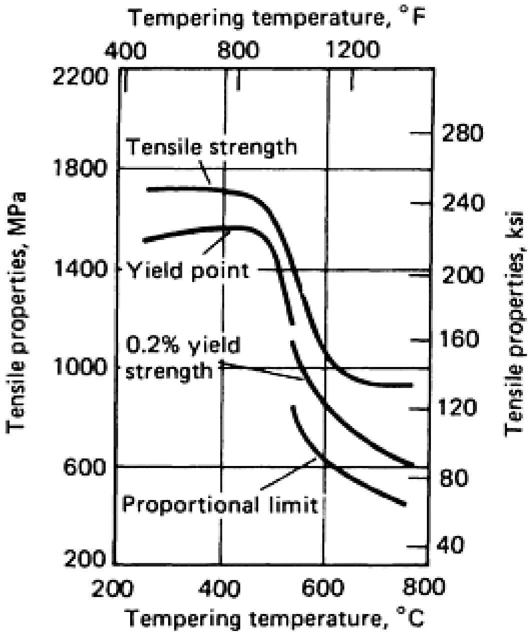
Fig. 13 Effect of austenitizing and tempering temperatures on typical mechanical properties of type 431 martensitic stainless steel. Austenitized 30 min; oil quenched to 65 to 95 °C (150 to 200 °F); double stress relieved at 175 °C (350 °F) for 15 min and water quenched; tempered 2 h. (a) Quenched from 925 °C (1700 °F). (b) Quenched from 1040 °C (1900 °F)


Tempering temperature, °F
400
800
1200
600
400
200
Hardness, HB
200
400
600
800
Tempering temperature, °C

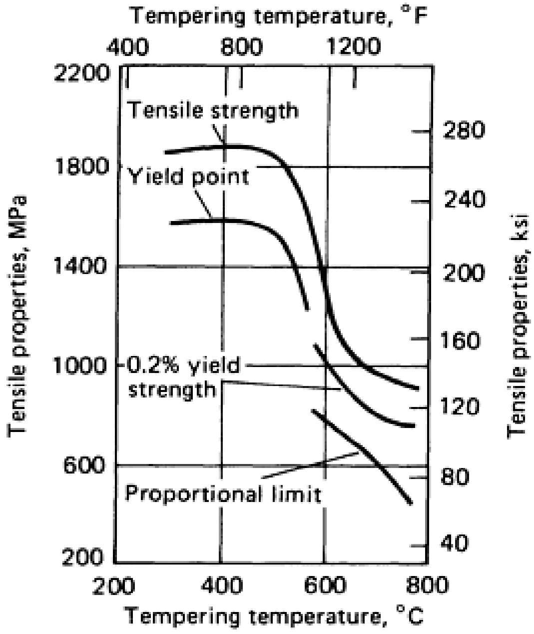
(a)


Tempering temperature, °F
400
800
1200
600
400
200
Hardness, HB
200
400
600
800
Tempering temperature, °C

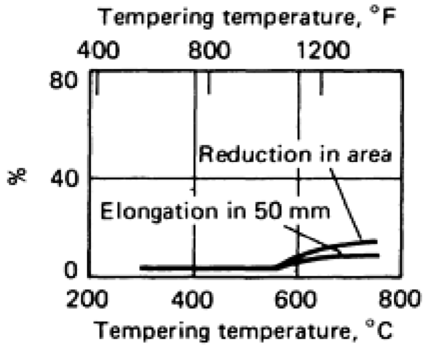
(b)


Tempering temperature, °F
400
800
1200
2200
1800
1400
1000
600
200
Tensile properties, MPa
280
240
200
160
120
80
40
Tensile properties, ksi
Tensile strength
Yield point
0.2% yield strength
Proportional limit
200
400
600
800
Tempering temperature, °C

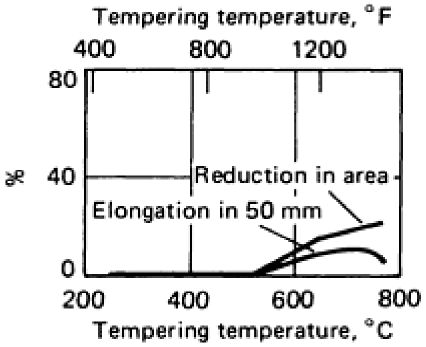
(a)


Tempering temperature, °F
400
800
1200
2200
1800
1400
1000
600
200
Tensile properties, MPa
280
240
200
160
120
80
40
Tensile properties, ksi
Tensile strength
Yield point
0.2% yield strength
Proportional limit
200
400
600
800
Tempering temperature, °C

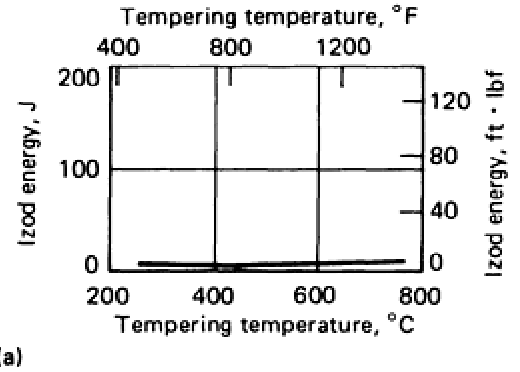
(b)


Tempering temperature, °F
400
800
1200
80
40
0
%
Reduction in area
Elongation in 50 mm
200
400
600
800
Tempering temperature, °C

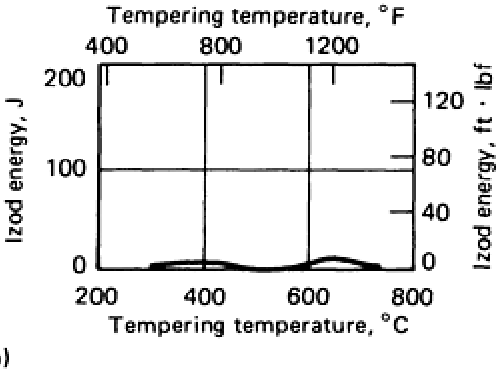
(a)


Tempering temperature, °F
400
800
1200
80
40
0
%
Reduction in area
Elongation in 50 mm
200
400
600
800
Tempering temperature, °C

(b)


Tempering temperature, °F
400
800
1200
200
100
0
Izod energy, J
120
80
40
0
Izod energy, ft · lbf
200
400
600
800
Tempering temperature, °C

(a)


Tempering temperature, °F
400
800
1200
200
100
0
Izod energy, J
120
80
40
0
Izod energy, ft · lbf
200
400
600
800
Tempering temperature, °C

(b)

Fig. 14 Effect of austenitizing and tempering temperatures on typical mechanical properties of type 440C martensitic stainless steel. Austenitized 1 h at 925 °C (1700 °F) and 2 h at 1040 °C (1900 °F); oil quenched to 65 to 95 °C (150 to 200 °F); double stress relieved at 175 °C (350 °F) for 15 min and water quenched; tempered 2 h. (a) Quenched from 925 °C (1700 °F). (b) Quenched from 1040 °C (1900 °F)

The Izod impact curves in Fig. 9, 10, 11, 12, 13, and 14 reveal a loss of impact strength when parts are tempered within the range of 370 to 650 °C (700 to 1200 °F). Tempering within this range also results in decreased corrosion resistance, particularly resistance to stress-corrosion cracking (Fig. 15). Double tempering (cooling parts to room temperature after the first tempering treatment) also is beneficial for resistance to stress corrosion.

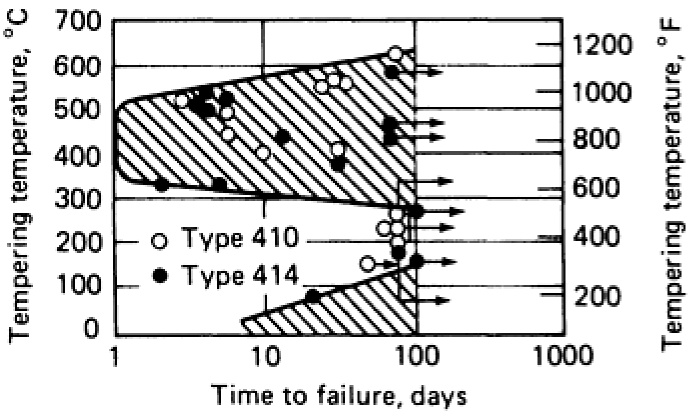


Fig. 15 Effect of tempering temperature on the stress-corrosion characteristics of two wrought martensitic stainless steels at high stress. Data apply to a stress level of 350 MPa (80 ksi) for tests in a salt fog cabinet.

Annealing. Temperatures and resulting hardnesses for process (subcritical) annealing, full annealing, and isothermal annealing are given in Table 12.

Table 12 Annealing temperatures and procedures for wrought martensitic stainless steels

Type	Process (subcritical) annealing			Full annealing			Isothermal annealing[c]	
	Temperature[a]		Hardness	Temperature[b][c]		Hardness		
	°C	°F		°C	°F		Procedure[d] °C (°F)	Hardness
403, 410	650-760	1200-1400	86-92 HRB	830-885	1525-1625	75-85 HRB	Heat to 830-885 (1525-1625); hold 6 h at 705 (1300)	**85 HRB**
414	650-730	1200-1345	99 HRB-24 HRC		Not recommended		**Not recommended**	
416, 416Se	650-760	1200-1345	86-92 HRB	830-885	1525-1625	75-85 HRB	Heat to 830-885 (1525-1625); hold 2 h at 720 (1330)	**85 HRB**
420	675-	1245-	94-97 HRB	830-	1525-	86-95 HRB	Heat to 830-885 (1525-1625);	**95 HRB**

	760	1400		885	1625		hold 2 h at 705 (1300)	
431	620-705	1150-1300	99 HRB-30 HRC		Not recommended		**Not recommended**	
440A	675-760	1245-1400	90 HRC-22 HRC	845-900	1555-1650	94-98 HRB	Heat to 845-900 (1555-1650); hold 4 h at 690	**98 HRB**
440B	675-760	1245-1400	98 HRB-23 HRC	845-900	1555-1650	95 HRB-20 HRC	Same as 440A	**20 HRC**
440C, 440F	**675-760**	**1245-1400**	**98 HRB-23 HRC**	**845-900**	**1555-1650**	**98 HRB-25 HRC**	**Same as 440A**	**25 HRC**

(a) Air cool from temperature; maximum softness is obtained by heating to temperature at high end of range.

(b) Soak thoroughly at temperature within range indicated; furnace cool to 790 °C (1455 °F); continue cooling at 15 to 25 °C/h (27 to 45 °F/h) to 595 °C (1100 °F); air cool to room temperature.

(c) Recommended for applications in which full advantage may be taken of the rapid cooling to the transformation temperature and from it to room temperature.

(d) Preheating to a temperature within the process annealing range is recommended for thin-gage parts, heavy sections, previously hardened parts, parts with extreme variations in section or with sharp reentrant angles, and parts that have been straightened or heavily ground or machined to avoid cracking and minimize distortion, particularly for types 420 and 431, and 440A, B, C, and F.

Full annealing is an expensive and time-consuming treatment; it should be used only when required for subsequent severe forming. Types 414 and 431 do not respond to full or isothermal annealing procedures within a reasonable soaking period.

Isothermal annealing is recommended where maximum softening is required and adequate facilities for controlled slow cooling are not available.

Subcritical annealing is recommended for all applications that do not require maximum softness.

Full annealing, isothermal annealing, and especially repeated process annealing promote the formation of coarse carbides that take longer to dissolve at austenitizing temperatures.

Salt Baths. Many stainless steel parts are heat treated in molten salt, with excellent results. The baths usually employed consist of barium chloride with 5 to 35% sodium or potassium chloride. Alkaline-earth and other metallic oxides build up in these baths through use, but these oxides are not harmful to low-carbon stainless steels. However, if these salt baths are also to be used for hardening other alloy steels, to avoid surface decarburization it is necessary to rectify the baths with graphite to remove the metallic oxides and with methyl chloride gas to convert the alkaline-earth oxides back to chlorides. A bath treated with methyl chloride will carburize low-carbon stainless steels unless it is aged for at least 24 h before the stainless is treated in it. To avoid this problem, stainless steel parts should be heat treated in a salt bath reserved exclusively for stainless steels.

Protective Atmospheres. Argon or helium, if used as protective atmospheres, should be exceptionally dry (with a dew point below -50 °C, or -60 °F). Because they are expensive and cannot be generated, they are rarely used. Exothermic and endothermically generated gas can be used with excellent results (see the article "Furnace Atmospheres" in this Volume). These require dew-point or infrared control so as not to carburize or decarburize the stainless grade being

heat treated. Endothermic gas containing approximately 40% hydrogen can embrittle martensitic stainless steels that are oil quenched.

An exothermic gas ratio of 6.5 or 7 to 1 is satisfactory for grades of stainless containing not more than 0.15% C. For endothermic atmospheres, dew points for specific steels and austenitizing temperatures are listed in Table 13.

Table 13 Dew points of selected wrought martensitic stainless steels at various austenitizing temperatures

Alloy	**Austenitizing temperature**		Dew point	
	°C	**°F**	**°C**	°F
420	1010	1850	10-12	**50-54**
403,410, 414, 416, 431	980	1795	16-18	**61-64**

Hydrogen embrittlement can become an important concern in the martensitic grades, generally increasing with hardness and carbon content. (It is variable and less acute in ferritic steels, and is virtually unknown in the austenitic grades.)

The embrittling hydrogen may be acquired as a result of the melting process, a heat-treating atmosphere, or chemical and electrochemical processes such as pickling and electroplating.

Most heat-treating atmospheres contain hydrogen in the form of moisture, hydrocarbons, or elemental hydrogen as an atmosphere or a dissociation product. The use of pure hydrogen or dissociated ammonia for bright annealing in one plant was associated with cracking of wire coils of types 431 and 440C, although other plants have reported no similar difficulty. Nevertheless, it is possible that some loss in ductility may result from the bright annealing of any of the martensitic stainless steels.

Less severe, the use of H_2 annealing gas with a titanium- or aluminum-bearing ferritic or martensitic grade, such as type 409, can lead to H_2 pickup and a resultant loss of bend ductility as-annealed. Low-temperature soaks of 175 to 230 °C (350 to 450 °F) in air will outgas embrittled ferritic alloys. Mill specifications outlining such baking procedures do exist.

Embrittlement has been found in oil-quenched types 403, 410, 414, and 431. Air quenching or the subsequent tempering of oil-quenched material releases the entrapped hydrogen, and ductility is restored. If a green oxide appears on the oil-quenched alloy, this must be removed prior to tempering or it will interfere with the release of entrapped hydrogen.

Additional information is available in the article "Embrittlement of Steels" in *Properties and Selection: Irons, Steels, and High-Performance Alloys,* Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.*

Precipitation-Hardening Stainless Steels

In the heat treating of precipitation-hardening (PH) stainless steels, areas of primary interest include:

- Cleaning prior to heat treatment
- Furnace atmospheres
- Time-temperature cycles
- Effect of variations in cycles

- Scale removal after heat treatment

Prior Cleaning. All parts must be cleaned thoroughly prior to heat treating. Because the chemical composition of these steels is delicately balanced, failure to remove drawing lubricants, cutting oils, and grease can lead to surface carburization and improper response to heat treatment. As a secondary benefit, thorough cleaning promotes the formation of a uniform surface scale that is readily removable.

The recommended cleaning procedure comprises vapor degreasing or solvent cleaning, followed by mechanical scrubbing with a mild abrasive alkaline cleaner to remove insoluble soils. All traces of cleaners should be removed by thoroughly rinsing with warm water.

Wet or dry abrasive blasting may be substituted for the above procedures. Recommended grits and operating details for blasting are given in Table 14. After blasting, all traces of abrasive must be removed from the work by scrubbing thoroughly.

Table 14 Recommended conditions for abrasive blast cleaning of precipitation-hardening stainless steels prior to heat treatment. All abrasives must be removed by thorough scrubbing.

Abrasive		Nozzle			Air pressure		Cleaning speed	
		Size		Angle, °				
Material	Grit No.	mm	in.		kPa	psi	mm^2/s	$in.^2/min$
Alumina (dry)	30	6.4	$\frac{1}{4}$	45-60	170-655[(a)]	25-95[(a)]	130-215	**12-20**
Garnet or alumina (dry)	36	9.5	$\frac{3}{8}$	60	240	35	645	**60**

(a) Depending on metal thickness

In some applications, cleaning prior to heat treating may be accomplished by closely controlled pickling in a 10% HNO_3-2% HF aqueous solution at 45 to 60 °C (110 to 140 °F). Time should be limited to 2 or 3 min. This method is not recommended for cleaning severely formed or previously heat-treated parts. Proprietary inhibited scale-removal preparations are available.

Furnaces fired with oil or natural gas are not entirely satisfactory for the heat treatment of these steels where finished surfaces are not to be subsequently machined. In such units, it is difficult to control combustion contaminants and to eliminate flame impingement on the parts being treated. Electric furnaces or gas-fired radiant-tube furnaces are generally used for heat treating precipitation-hardening stainless steels.

Furnace Atmospheres. Air is a satisfactory furnace atmosphere for austenite-conditioning and annealing operations. Controlled reducing atmospheres, such as dissociated ammonia or bright-annealing gas, introduce the potential hazard of nitriding or carburizing, either of which has a deleterious effect on mechanical properties.

Bright annealing may be done in hydrogen, argon, or helium atmospheres, provided a dew point of -55 °C (-65 °F) or lower is maintained. The cooling rate from the annealing temperature must be approximately equal to that of cooling in still air. Austenite-conditioning treatments at temperatures as high as 925 to 955 °C (1700 to 1750 °F) may also be performed in dry hydrogen, argon, or helium, maintaining the same low dew point. A scale-free surface will be obtained.

The lower austenite-conditioning temperatures, such as 760 °C (1400 °F), present difficulties in achieving scale-free surfaces in dry hydrogen, argon, or helium. An air atmosphere is generally used at these temperatures. For complete freedom from scale or discoloration at the lower temperatures, a vacuum furnace is required.

Final hardening of these steels is performed at relatively low temperatures, and an air atmosphere is acceptable for these treatments.

Heat-Treating Procedures. Recommended procedures for full annealing, austenite conditioning, transformation cooling, and age tempering (precipitation hardening) are given in Table 15.

Table 15 Recommended heat-treating procedures for semiaustenitic precipitation-hardenable stainless steels

UNS S17400

Homogenization. 1175 ± 15 °C (2150 ± 25 °F) for 2 h + 30 min per 25 mm (1 in.) [(a)]

Austenite conditioning (solution treatment). 1040 ± 15 °C (1900 ± 25 °F) for 30 min + 30 min per 25 mm (1 in.) [(a)]

Transformation cooling. To below +30 °C (+90 °F)

Precipitation hardening. To obtain minimum tensile strengths shown, use the following treatments for wrought alloys [(b)] :

MPa	**ksi**	**°C**	**°F**	h
1310	190	480 ± 5	(900 ± 10)	**1**
1170	170	495 ± 5	(925 ± 10)	**4**
1070	155	555 ± 5	(1030 ± 10)	**4**
1030	150	565 ± 5	(1050 ± 10)	**4**
1000	145	580 ± 5	(1075 ± 10)	**4**
930	**135**	**620 ± 5**	**(1150 ± 10)**	4

Comparable treatments for cast materials [(b)] :

MPa	**ksi**	**°C**	**°F**	h
1240	180	480 ± 5	(900 ± 10)	**4**
1170	170	495 ± 5	(925 ± 10)	**4**

1035	150	540 ± 5	(1000 ± 10)	**4**
895	**130**	**595 ± 5**	**(1100 ± 10)**	**4**

UNS S17700

Solution annealing. 1065 ± 15 °C (1950 ± 25 °F) for 3 min + 1 min per 0.25 mm (0.01 in.); air cool

RH treatments

Austenite conditioning. 955 ± 15 °C (1750 ± 25 °F) for 10 rain + 1 min per 0.25 mm (0.01 in.); air cool [(c)]

Transformation cooling. To below -70 °C (-90 °F) for 8 h

Precipitation hardening. To obtain minimum tensile strengths shown, the following treatments are recommended [(b)] :

MPa	**ksi**	**°C**	**°F**	h
1450	210	510 ± 5	(950 ± 10)	**1**
1240	180	565 ± 5	(1050 ± 10)	**1**
1170	170	580 ± 5	(1075 ± 10)	**1**
1035	**150**	**595 ± 5**	**(1100 ± 10)**	**1**

TH Treatments

Austenite conditioning. 760 ± 15 °C (1400 ± 25 °F) for $1\frac{1}{2}$ h; cool within 1 h to below 15 °C (60 °F) but above 0 °C (32 °F), and hold at least $\frac{1}{2}$ h before precipitation hardening

Precipitation hardening. To obtain minimum tensile strengths shown, the following treatments are recommended [(b)] :

MPa	**ksi**	**°C**	**°F**	h
1240	180	565 ± 5	(1050 ± 10)	$1\frac{1}{2}$
1170	170	580 ± 5	(1075 ± 10)	$1\frac{1}{2}$
1035	**150**	**595 ± 5**	**(1100 ± 10)**	$1\frac{1}{2}$

UNS S15700

Solution annealing. Same as for 17-7 PH

RH treatments

Austenite conditioning. Same as for 17-7 PH

Transformation cooling. Same as 17-7 PH

Precipitation hardening. To obtain minimum tensile strengths shown, the following treatments are recommended [(b)] :

MPa	**ksi**	**°C**	**°F**	h
1550	225	510 ± 5	(950 ± 10)	**1**
1310	**190**	**565 ± 5**	**(1050 ± 10)**	**1**

TH treatments

Austenite conditioning. 760 ± 15 °C (1400 ± 25 °F') for 1 $\frac{1}{2}$ h; cool within 1 h to below 15 °C (60 °F) but above 0 °C (32 °F), and hold at least $\frac{1}{2}$ h before precipitation hardening

Precipitation hardening. For minimum tensile strength of 1310 MPa (190 ksi) [(b)] : 565 ± 5 °C (1050 ± 10 °F) for 1 $\frac{1}{2}$ h

UNS S35000

Solution annealing. Wrought materials only: 1065 ± 15 °C (1950 ± 25 °F) for 3 min + 1 min per 0.25 mm (0.01 in.); air cool

Austenite conditioning. 930 ± 5 °C (1710 ± 10 °F) for 10 min + 1 min per 0.25 mm (0.01 in.); air cool [(c)]

Transformation cooling. To -75 ± 5 °C (-100 ± 10 °F) for 3 h (minimum)

Precipitation hardening. To obtain minimum tensile strengths shown, the following treatments are recommended [(b)] :

MPa	**ksi**	**°C**	**°F**	h
1275	185	455 ± 5	(850 ± 10)	**3**
1170	170	510 ± 5	(950 ± 10)	**3**
1140	**165**	**540 ± 5**	**(1000 ± 10)**	**3**

UNS S35500

Homogenization. Castings only: 1095 ± 15 °C (2000 ± 25 °F) for 2 h; air cool (water quench sections over 50 mm, or 2 in.). Bar and

forgings: 1050 ± 15 °C (1925 ± 25 °F) for 1 to 3 h; water quench. Cool all forms to below -70 °C (-90 °F) and hold 3 h minimum.

Solution annealing. 1025 ± 15 °C (1875 ± 25 °F) for 1 h per 25 mm (1 in.); water quench

Machinability treatment. 760 ± 15 °C (1400 ± 25 °F) for 3 h; air cool. Refrigerate to -70 °C (-90 °F) and hold for 3 h. Reheat to 565 ± 15 °C (1050 ± 25 °F) for 3 h.

For -70 °C (-90 °F) transformation:

Austenite conditioning. Castings: 980 ± 15 °C (1800 ± 25 °F) for 2 h; air cool (oil quench sections over 3 mm, or 0.125 in.). Wrought materials: 930 ± 15 °C (1710 ± 25 °F) for 15 min per in.; air cool (oil quench sections over 3 mm, or 0.125 in.)

Transformation cooling. To -75 ± 5 °C (-100 ± 10 °F) for 3 h

Precipitation hardening. To obtain minimum tensile strengths shown, use the following treatments for wrought alloys [b] :

MPa	**ksi**	**°C**	**°F**	h
1310	190	455 ± 5	(850 ± 10)	**3**
1170	**170**	**540 ± 5**	**(1000 ± 10)**	**3**

For castings, to obtain minimum tensile strength of 1240 MPa (180 ksi) [b] : 455 ± 5 °C (850 ± 10 °F) for 2 h

UNS S45000

Solution annealing. 1040 ± 15 °C (1900 ± 25 °F) for 1 h at heat [d] , water quench

Precipitation hardening. Typical tensile strengths shown may be obtained by the following treatments:

MPa	**ksi**	**°C**	**°F**	h
1345	195	480 ± 5	(900 ± 10)	**4, air cool**
1170	170	540 ± 5	(1000 ± 10)	**4, air cool**
1105	160	565 ± 5	(1050 ± 10)	**4, air cool**
965	**140**	**620 ± 5**	**(1150 ± 10)**	**4, air cool**

UNS S45500

Solution annealing. 830 ± 15 °C (1525 ± 25 °F) for 1 h at heat [d] , water quench

Precipitation hardening. Typical tensile strengths shown may be obtained by the following treatments:

MPa	**ksi**	**°C**	**°F**	h

1725	250	480 ± 5	(900 ± 10)	**4, air cool**
1620	235	510 ± 5	(950 ± 10)	**4, air cool**
1450	210	540 ± 5	(1000 + 10)	**4, air cool**
1310	**190**	**565 ± 5**	**(1050 ± 10)**	**4, air cool**

UNS S15500

Solution annealing. 1040 ± 15 °C (1900 ± 25 °F) for 1 h [(d)] , water quench

Precipitation hardening. Typical tensile strengths shown may be obtained by the following treatments:

MPa	**ksi**	**°C**	**°F**	h
1380	200	480 ± 5	(900 ± 10)	**1, air cool**
1170	170	550 ± 5	(1025 ± 10)	**4, air cool**
1000	**145**	**620 ± 5**	**(1150 ± 10)**	**4, air cool**

H1150M condition (after annealing). 760 ± 8 °C (1400 ± 15 °F) for 2 h, air cool + 620 ± 5 °C (1150 ± 10 °F) for 4 h, air cool

Typical tensile strength. 860 MPa (125 ksi)

UNS S13800

Solution annealing. 925 ± 8 °C (1700 ± 15 °F) for 1 h [(d)] , air cool or oil quench

Precipitation hardening. Typical tensile strengths shown may be obtained by the following treatments:

MPa	**ksi**	**°C**	**°F**	h
1550	225	510 ± 5	(950 ± 10)	**4, air cool**
1310	190	565 ± 5	(1050 ± 10)	**4, air cool**
1000	**145**	**620 ± 5**	**(1150 ± 10)**	**4, air cool**

H1150M condition (after annealing). 760 ± 8 °C (1400 ± 15 °F) for 2 h, air cool + 620 ± 5 °C (1150 ± 10 °F) for 4 h, air cool

Typical tensile strength. 895 MPa (130 ksi)

(a) To prevent cracking and ensure uniform properties, cool as follows: 75 mm (3 in.) and less, oil quench or air cool; 75 to 150 mm (3 to 6 in.), air cool; 150 mm (6 in.) and over, air cool under cover. *All parts must be cooled to below 30 °C (90 °F)* prior to the precipitation-hardening cycle.

(b) If hardness exceeds maximum specified, reheat treat at a slightly higher temperature for a minimum of 30 min.

(c) Air cool to room temperature; *do not reheat before transformation cooling.*

(d) Time at heat is dependent upon section size. Normally, a 1 h hold at temperature is suggested.

17-4 PH (UNS S17400) is a precipitation-hardening steel that has an essentially martensitic structure and limited formability when supplied in the solution-treated condition. Fabrication is followed by hardening in the range of 480 to 620 °C (900 to 1150 °F) (Table 15).

Care should be taken in using this alloy in the solution-treated condition because in this condition its ductility can be relatively low. Hardening to any of the strength levels shown in Table 15 improves toughness.

17-7 PH (UNS S17700) is normally supplied in the solution-annealed condition (condition A), in which it is soft and formable. Heat treatment is accomplished through the use of the transformation-hardened (TH) or refrigeration-hardened (RH) procedures indicated in Table 15. The choice of method of heat treatment is usually dictated by the ease with which the particular sequence fits into the production techniques of the user. Parts that receive significant deformation should be heat treated to RH 950, or soft spots may result.

This alloy is also supplied in the cold-rolled condition (condition C). Here, transformation has been achieved by cold rolling, and heat treatment is reduced to a single step: 480 °C (900 °F) for 1 h. Although strength and stress-corrosion resistance are greatly increased by this treatment, ductility is reduced and formability is limited.

PH 15-7 Mo (UNS S15700) is a high-strength modification of 17-7 PH. It is supplied in the same condition as 17-7 PH and requires identical heat-treating procedures. Table 15 illustrates the strength levels obtainable with PH 15-7 Mo.

15-5 Ni alloys (UNS S15500) are normally supplied in the solution-treated condition. As with 17-4 PH, care should be used in applying the material in the solution-treated condition. The alloy can be hardened by heating to a temperature in the range of 480 to 620 °C (900 to 1150 °F) for 1 to 4 h, depending on the temperature, and then air cooling. Table 15 illustrates typical strength levels versus hardening procedures.

13-8 Mo alloys (UNS S13800) are normally supplied in the solution-treated condition. They can be hardened to high strength levels by a single low-temperature treatment. Table 15 illustrates typical strength levels versus hardening procedures.

AM-350 and Pyromet 350 (UNS S35000) are normally purchased in the solution-treated condition; however, after severe forming or cold working, it may require a second annealing treatment. The annealing temperature limits, indicated in Table 15, are critical. High temperatures reduce strength; lower temperatures adversely affect formability.

After annealing and conditioning at 930 °C (1710 °F), AM-350 is usually subzero cooled, and then aged at 455 °C (850 °F) for 3 h; this treatment produces maximum strength. Maximum toughness is achieved by aging in the range of 480 to 540 °C (900 to 1000 °F). The recommended temperature for subzero cooling must be carefully observed. Cooling to much lower temperatures, such as -195 °C (-320 °F), results in incomplete transformation, as does failure to hold at the recommended temperature for at least 3 h.

AM-355 and Pyromet 355 (UNS S35500) flat products are supplied in either the solution-treated or solution-treated and cold-rolled condition, whereas bar products are usually supplied in the equalized and over-tempered condition for best machinability. Most castings are supplied in the as-cast condition.

Although, as indicated in Table 15, the homogenizing and austenite-conditioning treatments applied to castings differ from those applied to wrought materials (higher temperatures being used for castings in both treatments), subzero cooling is required for all forms to obtain maximum toughness and corrosion resistance. The full annealing treatment shown in Table 15 would normally be applicable only to flat products. The machinability treatment is required for obtaining good machining characteristics in this alloy.

Wrought materials should be aged at 455 °C (850 °F) for maximum strength, and at 540 °C (1000 °F) for maximum ductility and toughness. The usual aging treatment for castings consists of holding at 455 °C (850 °F) for 2 h.

Custom 450 (UNS S45000) stainless is normally supplied in the solution-treated condition, requiring no further heat treatment for many applications. It is easily fabricated in the annealed condition. A single-step hardening treatment develops higher strength with good ductility and toughness.

The recommended minimum hardening temperature of 480 °C (900 °F) produces the optimum combination of strength, ductility, and toughness. Hardening at temperatures up to 620 °C (1150 °F) increases the ductility and decreases strength (Table 15).

Custom 455 (UNS S45500) stainless is normally in the annealed condition. It is relatively soft and easily formable in the annealed condition. A single-step hardening treatment develops exceptionally high yield strengths with good ductility and toughness. Harden by heating in the range of 480 to 565 °C (900 to 1050 °F). See Table 15.

Variations in Heat-Treating Cycles. One of the principal advantages of these materials is their versatility. Although certain heat treatments have been classified as standard, there are applications where deviations from these standards are desirable. The series of curves in Fig. 16, 17, 18, 19, and 20 shows how these deviations affect mechanical properties.

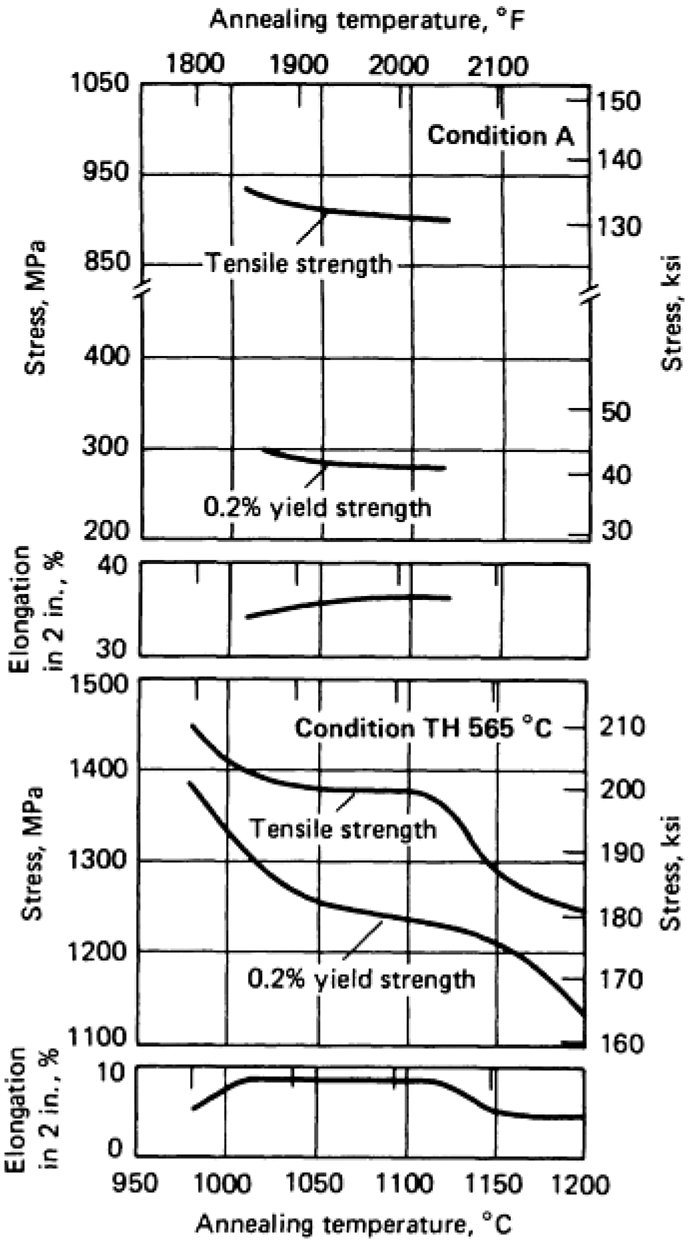


Fig. 16 Effect of variations in annealing temperature on typical mechanical properties of 17-7 PH sheet, strip, and plate

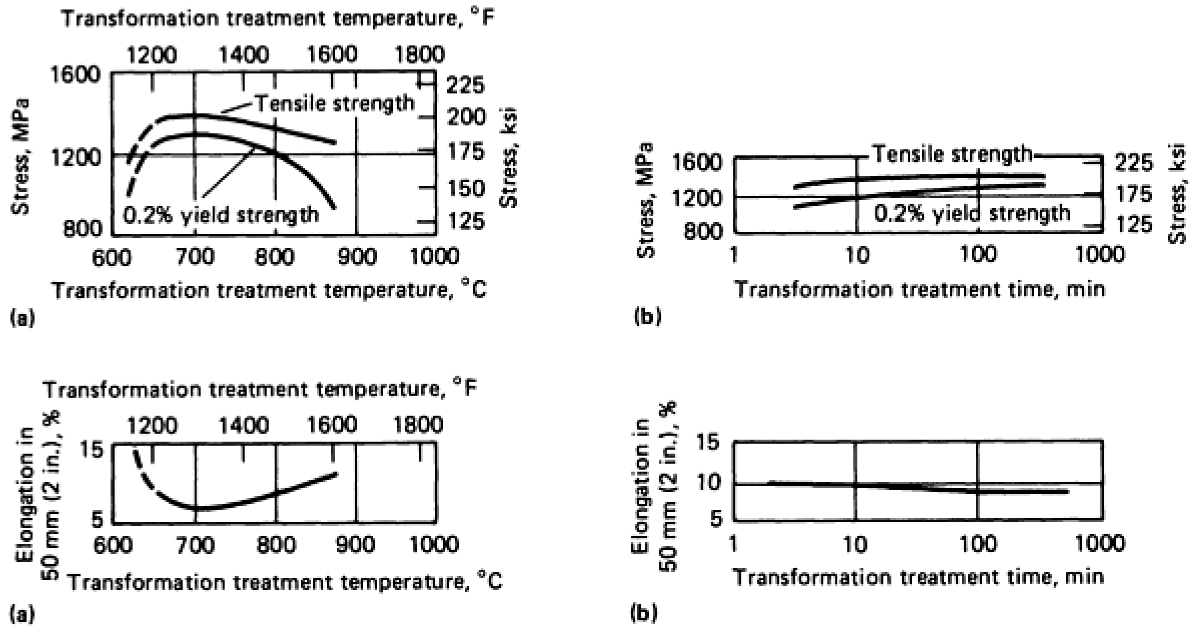


Fig. 17 Effect of variations in transformation treatment temperature and time on typical mechanical properties of 17-7 PH sheet, strip, and plate. (a) Heated for 90 min; cooled to 15 °C (60 °F); hardened at 565 °C (1050 °F). (b) Heated at 760 °C (1400 °F); hardened at 565 °C (1050 °F) for 90 min

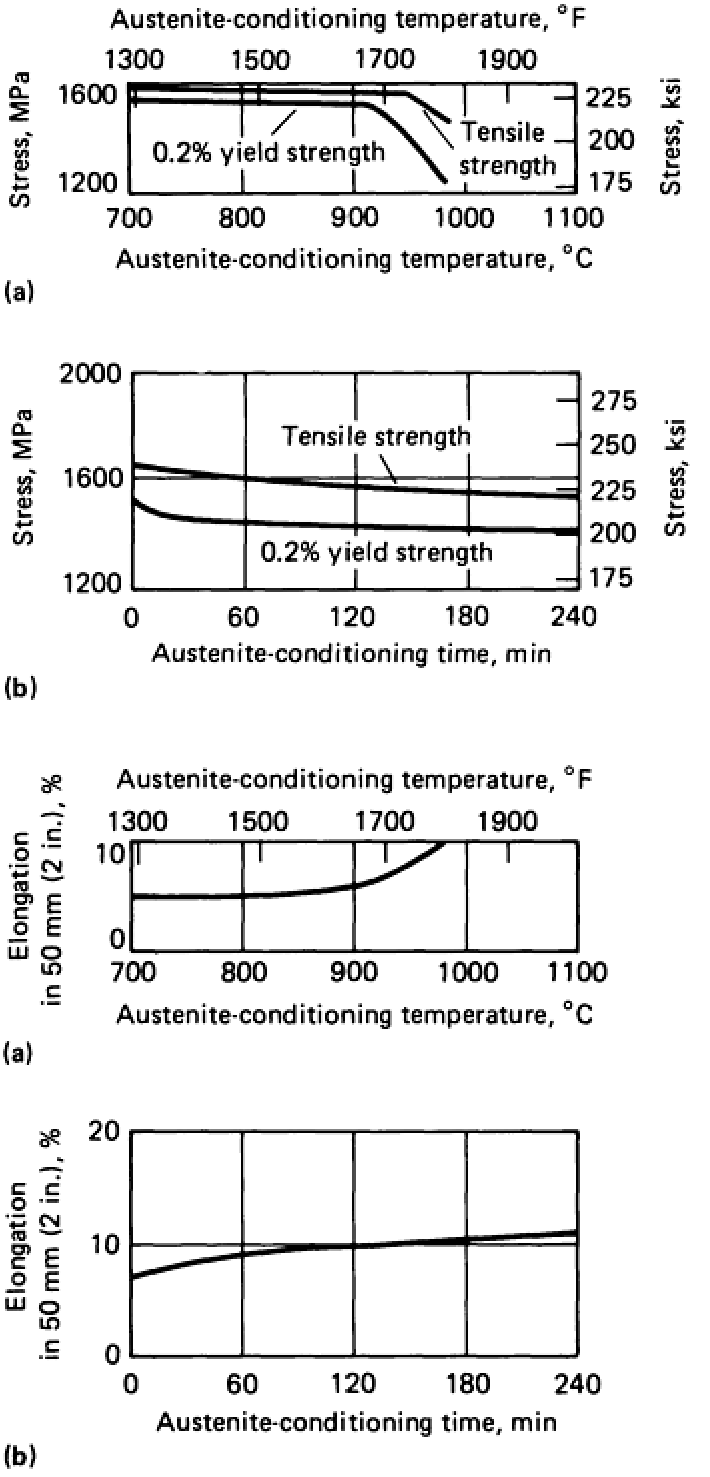
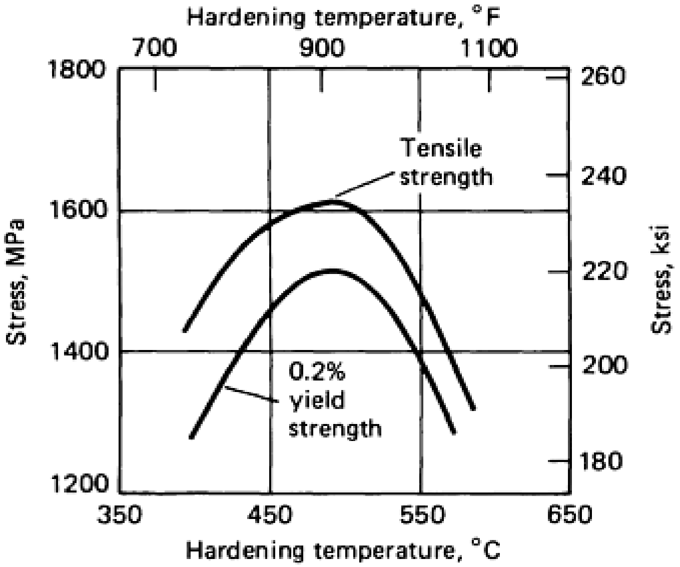
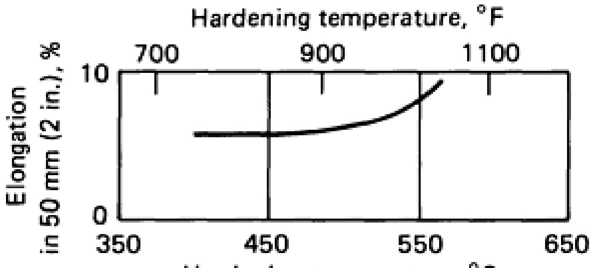


Fig. 18 Effect of variations in austenite-conditioning temperature and time on typical mechanical properties of 17-7 PH sheet, strip, and plate. (a) Heated for 10 min; air cooled; liquid cooled to -75 °C (-100 °F) for 8 h; hardened at 510 °C (950 °F) for 1 h. (b) Heated at 955 °C (1750 °F); air cooled; liquid cooled to -75 °C (-100 °F) for 8 h; hardened at 510 °C (950 °F) for 1 h



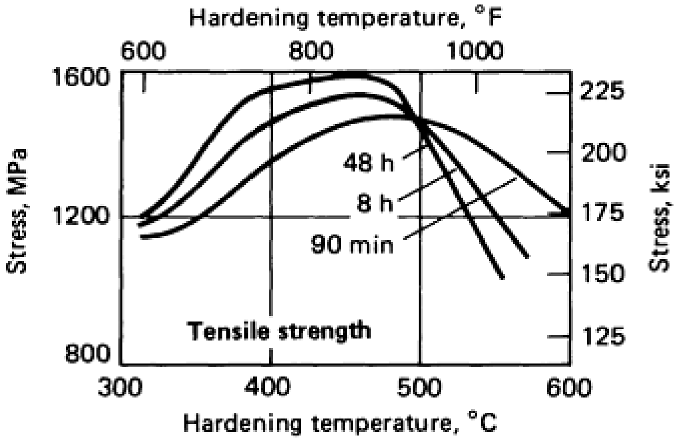
Hardening temperature, °F
700
900
1100
1800
1600
1400
1200
Stress, MPa
260
240
220
200
180
Stress, ksi
Tensile strength
0.2% yield strength
350
450
550
650
Hardening temperature, °C

(a)



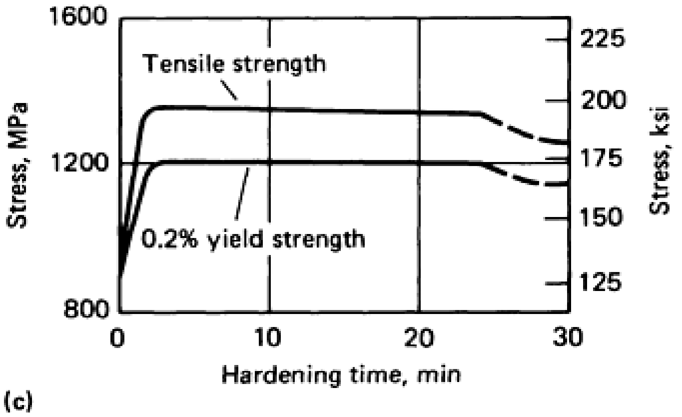
Hardening temperature, °F
700
900
1100
Elongation in 50 mm (2 in.), %
10
0
350
450
550
650
Hardening temperature, °C

(a)



Hardening temperature, °F
600
800
1000
1600
1200
800
Stress, MPa
225
200
175
150
125
Stress, ksi
48 h
8 h
90 min
Tensile strength
300
400
500
600
Hardening temperature, °C

(b)



1600
1200
800
Stress, MPa
225
200
175
150
125
Stress, ksi
Tensile strength
0.2% yield strength
0
10
20
30
Hardening time, min

(c)

Fig. 19 Effect of variations in hardening temperature and time on typical mechanical properties of 17-7 PH sheet, strip, and plate. (a) Heated at 955 °C (1750 °F) for 10 min; air cooled; liquid cooled to -75 °C (-100 °F) for 8 h; hardened for 1 h. (b) Heated at 760 °C (1400 °F) for 90 min; air cooled to room temperature; water quenched to 15 °C (60 °F); hardened as indicated. Elongation data not available. (c) Heated at 760 °C (1400 °F) for 90 rain; air cooled to room temperature; water quenched to 15 °C (60 °F); hardened at 565 °C (1050 °F). Elongation data not available

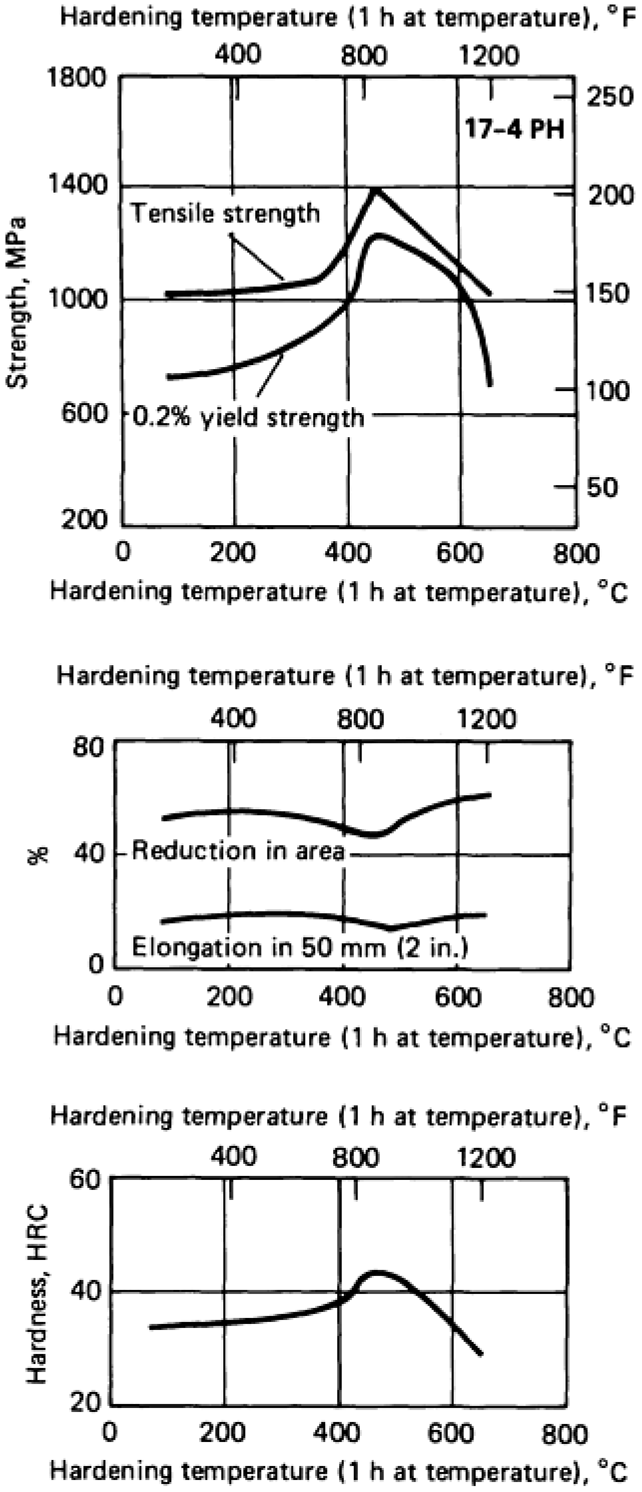


Fig. 20 Effect of hardening temperature on typical room-temperature properties of 17-4 PH that was solution treated at 1040 °C (1900 °F) for 30 min, air cooled. Data are average values for bars 25 to 89 mm (1 to $3\frac{1}{2}$

in.) in diameter from four heats.

Scale Removal after Heat Treating. The amount and nature of scale vary with the degree of cleanness of the work being treated, the furnace atmosphere, and the temperature and duration of heat treatment. In the following discussion, it will be assumed that all heat-treating operations are performed in an air atmosphere. A variety of descaling methods may be employed; the choice depends on the type of steel and the facilities available.

In removing scale formed during homogenization or full annealing, the use of a 10% HNO_3-2% HF aqueous solution at 45 to 60 °C (110 to 140 °F) has been effective. Exposure to the acid solution should be limited to a period of 3 min. Removal of loosened scale may be facilitated by the use of high-pressure water or steam. A uniform surface is evidence of a well-cleaned part. The use of molten salts to condition the scale is limited because the temperature involved (about 450 °C, or 850 °F) can age harden any martensite in the microstructure.

The austenite-conditioning treatments produce a scale that is best removed by mechanical means. Acids should be avoided because they are a possible source of intergranular attack. Wet grit-blasting processes have been widely used to remove these scales and have been found to be highly satisfactory.

The final step in heat treating (precipitation hardening) produces a discoloration of heat tint. It is desirable to use mechanical means to remove this oxide from 17-7 PH, PH 15-7 Mo, AM-350, and AM-355. The HNO_3-HF solution has been used on these steels, but extreme care is required to prevent intergranular attack. The acid solution may be used satisfactorily with 17-4 PH. To a lesser extent, electropolishing has also been used to remove the final heat tint resulting from precipitation hardening. Also available are proprietary cleaners that have been successful in removing the heat tint discoloration.

Stainless Steel Castings

The heat treatment of stainless steel castings follows closely in purpose and procedure the thermal processing of comparable wrought materials. However, the differences in detail warrant separate consideration here.

Because they are not cold worked or cold formed, castings of the older, conventional martensitic grades CA-15 and CA-40 (UNS J91150 and J91153) do not require subcritical annealing to remove the effects of cold working. However, in work-hardenable ferritic alloys, machining and grinding stresses are relieved at temperatures from about 260 to 540 °C (500 to 1000 °F). Casting stresses in the martensitic castings noted above should be relieved by subcritical annealing prior to further heat treatment. When these hardened martensitic castings are stress relieved, the stress-relieving temperature must be kept below the final tempering or aging temperature.

An improved, cast martensitic alloy, CA-6NM (UNS J91540), possesses better casting behavior, improved weldability, and equals or exceeds all of the mechanical, corrosion, and cavitation resistance properties of CA-15, and, as a result, has largely replaced the older alloy. Both CA-6NM and CA-15 castings are usually supplied in the normalized condition at 955 °C (1750 °F) minimum and tempered at 595 °C (1100 °F) minimum. However, when it is necessary or desirable to anneal CA-6NM castings, a temperature of 790 to 815 °C (1450 to 1500 °F) should be used. The alloy should be furnace cooled or otherwise slow cooled to 595 °C (1100 °F), after which it may be cooled in air. When stress relieving is required, CA-6NM may be heated to 620 °C (1150 °F) maximum and followed by slow cooling to prevent the formation of martensite.

Homogenization

Alloy segregation and dendritic structures may occur in castings and may be particularly pronounced in heavy sections. Because castings are not subjected to the high-temperature mechanical reduction and soaking treatments entailed in the mill processing of wrought alloys, it is frequently necessary to homogenize some alloys at temperatures above 1095 °C (2000 °F) to promote uniformity of chemical composition and microstructure. Full annealing of martensitic castings results in recrystallization and maximum softness, but it is less effective than homogenization in eliminating segregation. Homogenization is a common procedure in the heat treatment of precipitation-hardening castings.

Ferritic and Austenitic Alloys

The ferritic, austenitic, and mixed ferritic-austenitic alloys are not hardenable by heat treatment. They can be heat treated to improve their corrosion resistance and machining characteristics. The ferritic alloys CB-30 and CC-50 (UNS J91803 and J92615) are annealed to relieve stresses and reduce hardness by being heated above 790 °C (1450 °F) (Table 16).

Table 16 Annealing of ferritic and austenitic stainless steel castings

Type	**Minimum temperature**		**Quench**[(a)]	Typical ultimate tensile strength[(b)]	
	°C	**°F**		**MPa**	ksi
For full softness					
CB-30	790	1450	FC + A[(c)]	655	**95**
CC-50	790	1450	A	670	**97**
For maximum corrosion resistance					
CE-30	1095	2000	W, O, A	670	**97**
CF-3, CF-3M	1040	1900	W, O, A	530	**77**
CF-8, CF-8C[(d)]	1040	1900	W, O, A	530	**77**
CF-8M, CF-12M[(e)]	1040	1900	W, O, A	550	**80**
CF-16F, CF-20	1040	1900	W, O, A	530	**77**
CH-20	1095	2000	W, O, A	605	**88**
CK-20	1095	2000	W, O, A	525	**76**

(a) FC, furnace cool; W, water; O, oil; A, air.

(b) Approximate.

(c) Furnace cool to 540 °C (1000 °F), and then air cool.

(d) CF-8C may be reheated to 870 to 925 °C (1600 to 1700 °F), and then air cooled, for precipitation of niobium carbides.

(e) CF-12M should be quenched from a temperature above 1095 °C (2000 °F).

Solution Annealing. The austenitic alloys achieve maximum resistance to intergranular corrosion by the high-temperature heating and quenching procedure known as solution annealing (Table 16). As-cast structures, or castings exposed to temperatures in the range from 425 to 870 °C (800 to 1600 °F), may contain complex chromium carbides precipitated preferentially along grain boundaries in wholly austenitic alloys. This microstructure is susceptible to intergranular corrosion, especially in oxidizing solutions. (In partially ferritic alloys, carbides tend to precipitate in the discontinuous ferrite pools; thus, these alloys are less susceptible to intergranular attack.) The purpose of solution annealing is to ensure complete solution of carbides in the matrix and to retain these carbides in solid solution.

Solution-annealing procedures for all austenitic alloys are similar, and consist of heating to a temperature of about 1095 °C (2000 °F), holding for a time sufficient to accomplish complete solution of carbides, and quenching at a rate fast enough to prevent reprecipitation of the carbides--particularly while cooling through the range from 870 to 540 °C (1600 to 1000 °F). Temperatures to which castings should be heated prior to quenching vary somewhat, depending on the alloy (Table 16).

Stabilizing Treatment. As shown in Table 16, a two-step heat-treating procedure may be applied to the niobium-containing CF-8C (UNS J92710) alloy. The first treatment consists of solution annealing. This is followed by a stabilizing treatment at 870 to 925 °C (1600 to 1700 °F), which precipitates niobium carbides, prevents formation of the damaging chromium carbides, and provides maximum resistance to intergranular attack.

Because of their low carbon contents, CF-3 and CF-3M (UNS J92700 and J92800) as-cast do not contain enough chromium carbides to cause selective intergranular attack, and hence may be used in some corrodents in this condition; for maximum corrosion resistance, however, these grades require solution annealing.

Martensitic Alloys

Castings of the CA-6NM composition should be hardened by air cooling or oil quenching from a temperature of 1010 to 1065 °C (1850 to 1950 °F). Even though the carbon content of this alloy is lower than that of CA-15, this fact in itself and the addition of molybdenum and nickel enable the alloy to harden completely without significant austenite retention when cooled as suggested.

The choice of cooling medium is determined primarily by the maximum section size. Section sizes in excess of 125 mm (5 in.) will harden completely when cooled in air. CA-6NM is not prone to cracking during cooling from elevated temperatures. For this reason, no problem should arise in the air cooling or oil quenching of configurations that include thick as well as thin sections.

A wide choice of mechanical properties is available through the choice of tempering temperature. Castings of CA-6NM are normally supplied normalized and tempered at 595 to 620 °C (1100 to 1150 °F). Reaustenitizing occurs upon tempering above 620 °C (1150 °F), the amount of reaustenitization increasing with increasing temperature. Depending on the amount of this transformation, cooling from such tempering temperatures may adversely affect both ductility and toughness through the transformation to untempered martensite.

Even though the alloy is characterized by a decrease in impact strength when tempered in the range of 370 to 595 °C (700 to 1100 °F), the minimum reached is significantly higher than that of CA-15. This improvement in impact toughness results from the presence of molybdenum and nickel in the composition and from the lower carbon content. The best combination of strength with toughness is obtained when the alloy is tempered above 510 °C (950 °F).

Figure 21 describes the effect of tempering temperature on the hardness, strength, ductility, and toughness properties of CA-6NM and illustrates that strengths even higher than those considered typical can be obtained by tempering at lower temperatures without a disturbing loss of ductility or toughness.

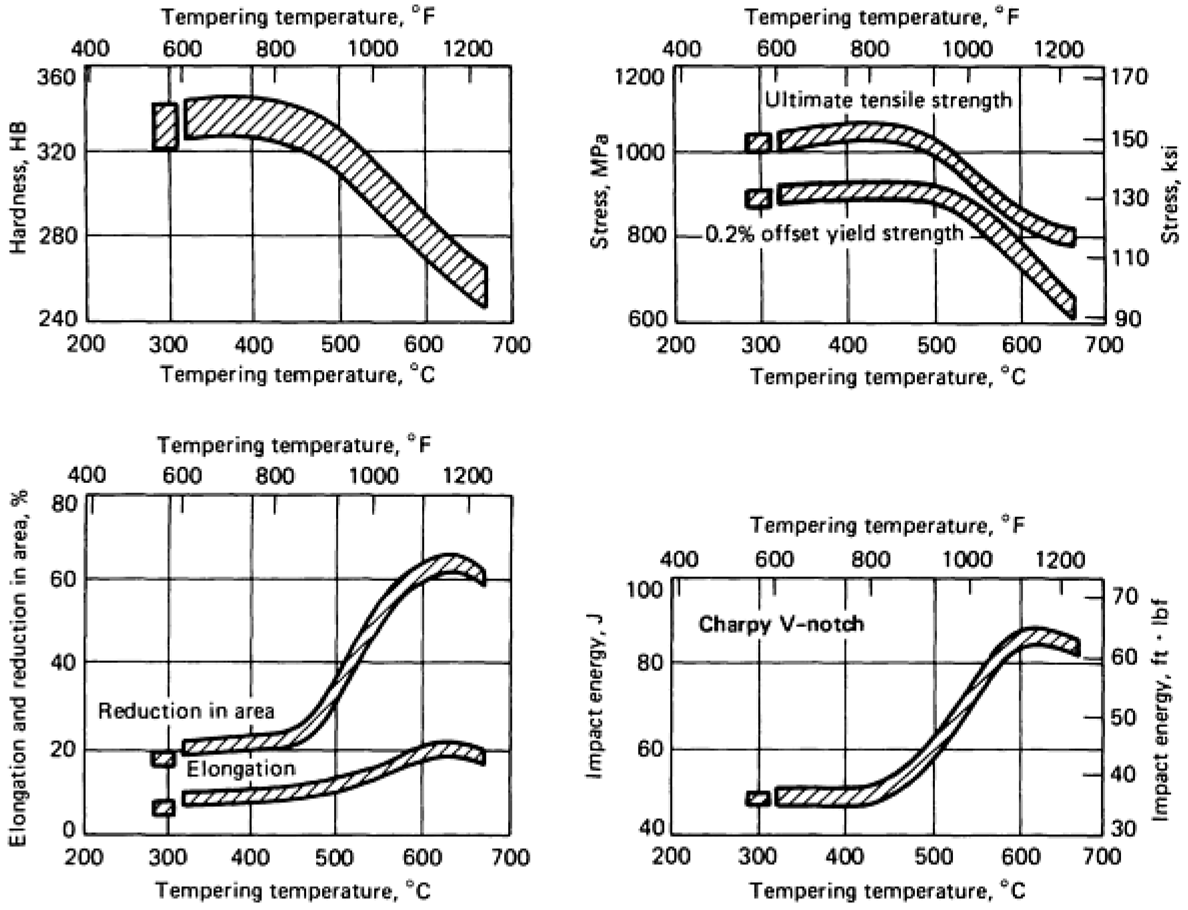


Fig. 21 Effect of tempering temperature on the mechanical properties of a CA-6NM standard keel block. Courtesy of ESCO Corporation

The minor loss of toughness and ductility that does occur is associated with the lesser degree of tempering that takes place at the lower temperature and not with embrittlement, as might be the situation with other 12% Cr steels that contain no molybdenum. The addition of molybdenum to 12% Cr steels makes them unusually stable thermally and normally not susceptible to embrittlement in the annealed or annealed and cold-worked conditions, even when exposed for long periods at 370 to 480 °C (700 to 900 °F). There are no data currently available on such steels in the quenched and tempered or normalized and tempered conditions.

Another significant practical advantage of CA-6NM is its relative freedom from the rapid drop in hardness when tempered above about 510 °C (950 °F). Figure 22 shows clearly that a given increase in tempering temperature produces a much more gradual decrease in hardness as compared with CA-15. This makes heat treating much easier and cheaper and decreases the frequency of rejects and/or the necessity for reheat treatment.

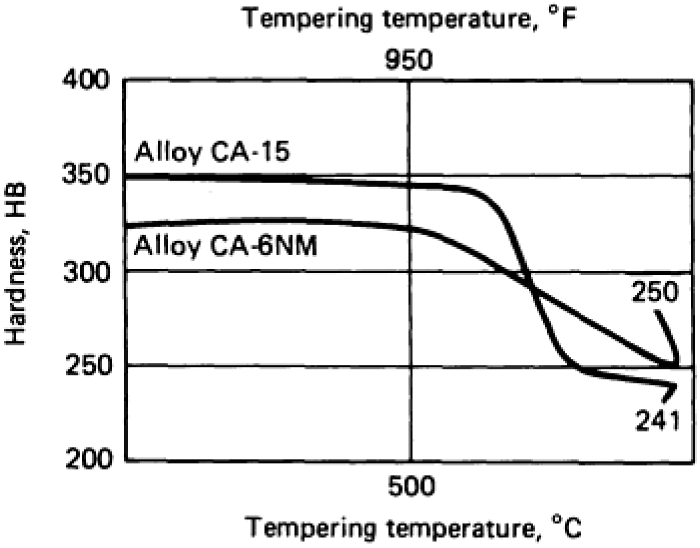


Fig. 22 Influence of tempering temperature on the hardness of CA-6NM and CA-15. Courtesy of ESCO Corporation

The hardening procedures for CA-15 castings are similar to those used for the comparable wrought alloy (type 410). Austenitizing consists of heating to 955 to 1010 °C (1750 to 1850 °F) and soaking for a minimum of 30 min; the high side of this temperature range is normally employed. Parts are then cooled in air or quenched in oil. To reduce the probability of cracking in the brittle, untempered martensitic condition, tempering should take place immediately after quenching.

Tempering is performed in two temperature ranges: up to 370 °C (700 °F) for maximum strength and corrosion resistance, and from 595 to 760 °C (1100 to 1400 °F) for improved ductility at lower strength levels. Tempering in the range of 370 to 595 °C (700 to 1100 °F) is normally avoided because of the resultant low impact strength. Figure 23 shows the nominal mechanical properties obtained in CA-15 castings as a function of tempering temperature. Additional data on mechanical properties are given in Table 17. These data are based on several heats of shell cast CA-15 alloy. The standard heat-treating procedures for CA-15, CA-40, and CA-6NM are given in Table 18. In the hardened and tempered condition, CA-40 provides higher tensile strength and lower ductility than CA-15 tempered at the same temperature. Both alloys can be annealed by cooling slowly from the range 845 to 900 °C (1550 to 1650 °F).

Table 17 Effects of four methods of heat treatment on typical mechanical properties of cast CA-15

Specimens were taken from shell mold cast keel blocks; data indicate results obtained on four specimens treated by each method.

Heat treatment[(a)]	**Ultimate tensile strength**		**Yield strength**		**Elongation in 50 mm (2 in.), %**	Reduction in area, %
	MPa	**ksi**	**MPa**	**ksi**		
Treatment 1	1230	178	1005	146	9.0	**13.0**
Homogenize: 1 h at 1040 °C (1900 °F), AC	1250	181	970	141	12.5	**28.0**
Solution anneal: $\frac{1}{2}$ h at 955 °C (1750 °F), OQ	1275	185	985	143	7.0	**14.0**

Temper: 3 h at 300 °C (575 °F), AC	1315	191	1020	148	8.0	**12.5**
Treatment 2	1260	183	1115	162	6.5	**9.5**
Anneal: 1 h at 900 °C (1650 °F), FC	1296	188	1130	164	5.5	**16.0**
Solution anneal: $1\frac{1}{4}$ h at 1010 °C (1850 °F), OQ	1340	194	1070	155	9.0	**23.0**
Temper: 3 h at 370 °C (700 °F), OQ	1380	200	1050	152	12.0	**42.0**
Treatment 3[(b)]	795	115	485	70	15.5	**60.0**
Anneal: 1 h at 900 °C (1650 °F), FC	810	117	630	91	16.5	**37.0**
Solution anneal: $1\frac{1}{4}$ h at 1010 °C (1850 °F), OQ	830	120	680	98	9.5	**23.0**
Temper: 2 h at 620 °C (1150 °F), AC	860	125	585	85	12.5	**32.0**
Treatment 4[(c)]	685	99	525	76	21.0	**65.0**
Anneal: 1 h at 900 °C (1650 °F), FC	710	103	545	79	20.5	**56.0**
Solution anneal: $1\frac{1}{2}$ h at 995 °C (1825 °F), FAC	710	103	545	79	18.5	**61.5**
Temper: 2 h at 705 °C (1300 °F), AC	**720**	**104**	**550**	**80**	**20.5**	60.0

(a) Each treatment comprised three processes as listed. AC, air cool; OQ, oil quench; FC, furnace cool; FAC, forced-air cool.

(b) AMS 5351-B.

(c) MIL-S-16993

Table 18 Heat treatment of martensitic stainless steel castings

Alloy	**Annealing temperature[(a)]**	**Hardening treatment**		Typical ultimate tensile strength[(c)]
		Austenitizing temperature[(b)]	**Tempering temperature**	

	°C	°F	°C	°F	°C	°F	MPa	ksi
CA-15	845-900	1550-1650	. . .	. . .	. . .	. . .	550	**80**
	. . .	. . .	925-1010[d]	1700-1850[d]	370 max[e]	700 max[e]	1380	**200**
	. . .	. . .	925-1010[d]	1700-1850[d]	595-760	1100-1400	690-930	**100-135**
CA-40	845-900	1550-1650	. . .	. . .	. . .	. . .	620	**90**
	. . .	. . .	980-1010	1800-1850	315 max[e]	600 max[e]	1515	**220**
	. . .	. . .	980-1010	1800-1850	595	1100	1035	**150**
	. . .	. . .	980-1010	1800-1850	650	1200	965	**140**
	. . .	. . .	980-1010	1800-1850	760	1400	760	**110**
CA-6NM	790-815	1450-1500	. . .	. . .	. . .	. . .	550	**80**
	. . .	**. . .**	**950-980**	**1750-1800**	**595-620**	**1100-1150**	**830**	**120**

(a) Annealing for maximum softness; slow furnace cool from temperature.

(b) Quench in oil or air.

(c) Approximate.

(d) Hold at temperature for a minimum of 30 min.

(e) Tempering at 370 to 595 °C (700 to 1100 °F) is not recommended because low-impact ductility results.

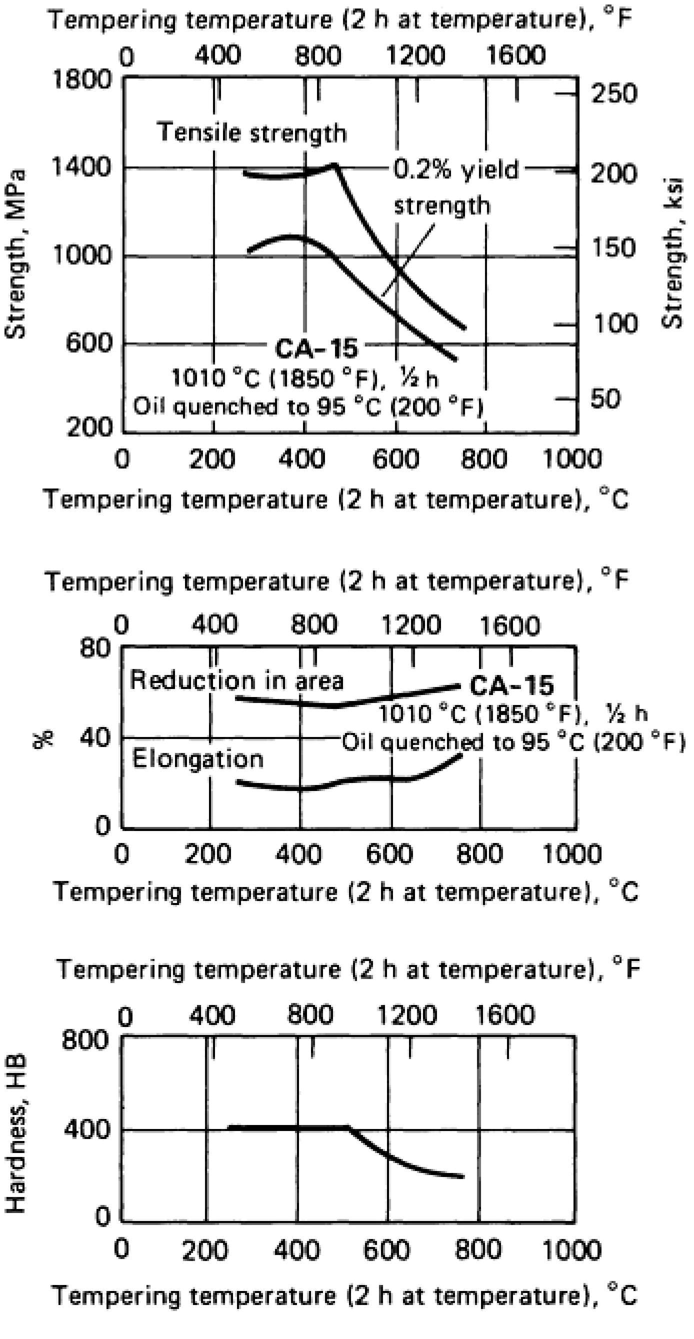


Fig. 23 Effect of tempering temperature on typical room-temperature mechanical properties of CA-15 castings

Additional information is available in the article "High-Alloy Steels," in Casting, Volume 15 of *ASM Handbook*, formerly 9th Edition *Metals Handbook.*

Precipitation-Hardening Alloys

It is desirable to subject precipitation-hardenable castings to a high-temperature homogenization treatment to reduce alloy segregation and to obtain more uniform response to subsequent heat treatment. Even investment castings that are cooled slowly from the pouring temperature exhibit more nearly uniform properties when they have been homogenized. Recommended homogenizing treatments for precipitation-hardening alloys 17-4 PH and AM-350 are included in Table 15.

17-4 PH Castings. When 17-4 PH (ASTM CB-7Cu-1 and CB-7Cu-2) is cast in plastic-bonded shell molds, the surface is carburized by decomposition of the binder. The added carbon prevents proper heat-treating response of the casting surface. Satisfactory response is obtained when surface carbon is removed prior to the homogenization treatment.

In addition to homogenization, other heat-treating procedures for 17-4 PH castings include solution annealing and precipitation hardening. Details of these procedures are given in Table 15. The preferred temperature range for precipitation hardening is 480 to 595 °C (900 to 1100 °F). The mechanical properties obtained at different aging temperatures are given in Table 19.

Table 19 Effect of temperature of 1-h aging treatment on typical properties of investment cast 17-4 PH stainless steels. Data obtained using cast test bars.

Aging temperature[(a)]		**Ultimate tensile strength**		**Yield strength, 0.2%**		**Elongation in 50 mm (2 in.), %**	Hardness, HRC
°C	**°F**	**MPa**	**ksi**	**MPa**	**ksi**		
Alloy with 0.IS to 0.40% Nb							
As-cast	. . .	1055	153	770	112	3.5	. . .
480	900	1380	200	1055	153	15	**44**
510	950	1360	197	1082	157	13	**42**
540	1000	1130	164	970	141	14	**39**
565	1050	1125	163	1040	151	16	**35**
595	1100	1115	162	985	143	16	**34**
650	1200	1015	147	860	125	15	**30**
Alloy without niobium							
As-cast	. . .	1115	162	985	143	2.7	**38**
480	900	1365	198	1145	166	12	**43**
510	950	1255	182	1110	161	13	**42**
540	1000	1280	186	1095	159	14	**38**
565	1050	980	142	910	132	16	**35**

595	1100	1080	157	840	122	16	**34**
650	**1200**	**1055**	**153**	**895**	**130**	**12**	**32**

(a) Before aging, specimens were homogenized ($1\frac{1}{2}$ at 1150 °C, or 2100 °F, air cool) and solution annealed ($\frac{1}{2}$ h at 1040 °C, or 1900 °F, oil quench); subzero transformation not employed. After 1 h at aging temperature, specimens were air cooled.

The tendency of 17-4 PH castings to overage is reduced by the addition of about 0.25% combined niobium plus tantalum to the alloy. The effect of time at aging temperature on the mechanical properties of niobium-free and niobium-containing 17-4 PH investment castings are shown in Table 20.

Table 20 Effect of aging time at 480 °C (900 °F) on typical properties of investment cast 17-4 PH stainless steels[(a)]

Aging time, h	**Ultimate tensile strength**		**Yield strength**		**Elongation in 25 mm (1 in.), %**	Hardness, HRC
	MPa	**ksi**	**MPa**	**ksi**		
Alloy with 0.15 to 0.40% Nb						
$\frac{1}{2}$	1385	201	1275	185	7	**45**
1	1380	200	1070	155	15	**44**
2	1340	194	1055	153	13	**45**
4	1295	188	1075	156	9	**43**
Alloy without niobium						
$\frac{1}{2}$	1385	201	1075	156	10	**43**
1	1365	198	1130	164	12	**43**
2	1395	202	1080	157	12	**44**
4	1180	171	980	142	16	**38**

(a) Treatment prior to aging: $1\frac{1}{2}$ h at 1150 °C (2100 °F), air cool; 1 h at 1040 °C (1900 °F), oil quench

AM-350 and AM-355. Although investment castings made of these alloys do not necessarily require a homogenizing treatment, this treatment provides a more uniform response to subsequent heat treatment. Shell mold and sand castings made of AM-355 that were extremely brittle without homogenization regained ductility after homogenizing at 1095 °C (2000 °F) for 2 h minimum. Heat-treating procedures and effects of tempering temperatures up to 650 °C (1200 °F) on mechanical properties of AM-355 shell mold castings are given in Table 21.

Table 21 Effects of tempering temperature on typical properties of shell mold cast AM-355[(a)]

Condition	Ultimate tensile strength		Yield strength[(b)]		Elongation in 50 mm (2 in.), %	Reduction in area, %
	MPa	ksi	MPa	ksi		
Annealed	1290	187	485	70	6	**3.5**
Subzero transformed	1400	203	965	140	6	**2.5**
Tempered 3 h at, °C (°F):						
480 (900)	1440	209	1170	170	20	**9**
540 (1000)	1325	192	1095	159	34	**13**
595 (1100)	1195	173	940	136	35	**14**

(a) Treatment prior to tempering: $1\frac{1}{2}$ h at 1095 °C (2000 °F) and then furnace cool to 980 °C (1800 °F); soak at 980 °C (1800 °F) for $1\frac{1}{2}$ h and then water quench; subzero cool at -85 °C (-120 °F) for 6 h.

(b) 0.2% offset

When AM-355 castings are welded, maximum mechanical properties are obtained when the castings are fully heat treated after welding (Table 22). Heat treatments prior to welding have little effect on properties when a complete heat treatment follows welding.

Table 22 Effect of heat treating and welding sequence on typical properties of AM-355 castings

Sequence[(a)]	Ultimate tensile strength	Yield strength, 0.2%	Elongation in 50 mm (2 in.), %

					(2 in.), %
	Mpa	**ksi**	**MPa**	**ksi**	
Heat treated after welding					
A	1450	210	1105	160	**15**
B	1380	200	1115	162	**12**
C	1415	205	1070	155	**12**
D	1415	205	1105	160	**8**
Not heat treated after welding					
E	**1070**	**155**	**830**	**120**	**11**

(a) Heat treating and welding procedures and sequences were as follows: A, 2 h at 1095 °C (2000 °F) and then air cool; 2 h at 1010 °C (1850 °F) and then water quench; 3 h at -75 °C (-100 °F); 3 h at 455 °C (850 °F) and then air cool; 3 h at 510 °C (950 °F) and then air cool; helium-shielded arc welding; repeat heat treatment. B, 2 h at 1095 °C (2000 °F) and then air cool; 2 h at 1010 °C (1850 °F) and then water quench; 3 h at -75 °C (-100 °F); 3 h at 455 °C (850 °F) and then air cool; 3 h at 510 °C (950 °F) and then air cool; 2 h at 1010 °C (1850 °F) and then water quench; helium-shielded arc welding, repeat heat treatment through 510 °C (950 °F) tempering. C, Helium-shielded arc welding; 2 h at 1095 °C (2000 °F) and then air cool; 2 h at 1010 °C (1850 °F} and then water quench; 3 h at -75 °C (-100 °F); 3 h at 455 °C (850 °F) and then air cool; 3 h at 510 °C (950 °F) and then air cool. D, 2 h at 1095 °C (2000 °F) and then air cool; 2 h at 1010 °C (1850 °F) and then water quench; helium-shielded arc welding; 2 h at 1095 °C (2000 °F) and then air cool; 2 h at 1010 °C (1850 °F) and then water quench; 3 h at -75 °C (-100 °F); 3 h at 455 °C (850 °F) and then air cool; 3 h at 510 °C (950 °F) and then air cool. E, 2 h at 1095 °C (2000 °F) and then air cool; 2 h at 1010 °C (1850 °F} and then water quench; 3 h at -75 °C (-100 °F); 3 h at 455 °C (850 °F) and then air cool; 3 h at 510 °C (950 °F) and then air cool; helium-shielded arc welding

Heat Treating of Superalloys

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Introduction

SUPERALLOYS are heat-resistant alloys based on nickel, iron-nickel, and cobalt-nickel that exhibit a good combination of mechanical strength and resistance to surface degradation. Compositions of wrought and cast superalloys are listed in Tables 1 and 2, respectively. The high-temperature strength of all superalloys is based on the principle of a stable face-centered cubic (fcc) matrix combined with either precipitation strengthening and/or solid-solution hardening. In age-hardenable nickel-base alloys the γ' intermetallic (Ni_3Al, Ti) is generally present for strengthening, while the non-hardenable nickel-, cobalt-, and iron-base alloys rely on solid-solution strengthening of the fcc (γ) matrix. Iron-base and nickel-iron superalloys may also develop, in addition to γ', second-phase strengthening from the γ'' (Ni_3Nb) intermetallic and perhaps η(Ni_3Ti). Cobalt-base superalloys may develop some precipitation strengthening from carbides (Cr_7C_3, $M_{23}C_6$), but no intermetallic-phase strengthening equal to the γ' strengthening in nickel-base alloys has been discovered in cobalt-base superalloys.

Table 1 Nominal compositions of wrought superalloys

Alloy	**UNS Number**	Composition, %										
		Cr	**Ni**	**Co**	**Mo**	**W**	**Nb**	**Ti**	**Al**	**Fe**	**C**	Other
Solid-solution alloys												
Iron/nickel-base												
Alloy N-155 (Multimet)	R30155	21.0	20.0	20.0	3.00	2.5	1.0	. . .	. . .	32.2	0.15	**0.15 N, 0.2 La, 0.02 Zr**
Haynes 556	R30556	22.0	21.0	20.0	3.0	2.5	0.1	. . .	0.3	29.0	0.10	**0.50 Ta, 0.02 La, 0.002 Zr**
19-9 DL	S63198	19.0	9.0	. . .	1.25	1.25	0.4	0.3	. . .	66.8	0.30	**1.10 Mn, 0.60 Si**
Nickel-base												
Haynes 214	. . .	16.0	76.5	. . .	. . .	. . .	. . .	. . .	4.5	3.0	0.03	
Haynes 230	N06230	22.0	55.0	5.0 max	2.0	14.0	. . .	. . .	0.35	3.0 max	0.10	**0.015 max B, 0.02 La**
Inconel 617	N06617	22.0	55.0	12.5	9.0	. . .	. . .	. . .	1.0	. . .	0.07	**. . .**
Alloy 625	N06625	21.5	61.0	. . .	9.0	. . .	3.6	0.2	0.2	2.5	0.05	**. . .**
RA 333	N06333	25.0	45.0	3.0	3.0	3.0	. . .	. . .	. . .	18.0	0.05	**. . .**
Hastelloy B	N10001	1.0 max	63.0	2.5 max	28.0	. . .	. . .	. . .	. . .	5.0	0.05 max	**0.03 V**
Hastelloy N	N10003	7.0	72.0	. . .	16.0	. . .	. . .	0.5 max	. . .	5.0 max	0.06	
Hastelloy S	N06635	15.5	67.0	. . .	15.5	. . .	. . .	. . .	0.2	1.0	0.02 max	**0.02 La**
Hastelloy W	N10004	5.0	61.0	2.5 max	24.5	. . .	. . .	. . .	. . .	5.5	0.12 max	**0.6 V**
Hastelloy X	N06002	22.0	49.0	1.5 max	9.0	0.6	. . .	. . .	2.0	15.8	0.15	**. . .**

Alloy	UNS Number	Composition, %										
		Cr	**Ni**	**Co**	**Mo**	**W**	**Nb**	**Ti**	**Al**	**Fe**	**C**	Other
Hastelloy C-276	N10276	15.5	59.0	. . .	16.0	3.7	. . .	. . .	. . .	5.0	0.02 max	**. . .**
Nimonic 75	N06075	19.5	75.0	. . .	. . .	. . .	. . .	0.4	0.15	2.5	0.12	**0.25 max Cu**
Nimonic 86	. . .	25.0	65.0	. . .	10.0	. . .	. . .	. . .	. . .	. . .	0.05	**0.03 Ce, 0.015 Mg**
Cobalt-base												
Haynes 25 (L605)	R30605	20.0	10.0	50.0	. . .	15.0	. . .	. . .	. . .	3.0	0.10	**1.5 Mn**
Haynes 188	R30188	22.0	22.0	37.0	. . .	14.5	. . .	. . .	. . .	3.0 max	0.10	**0.90 La**
Alloy S-816	R30816	20.0	20.0	42.0	4.0	4.0	4.0	. . .	. . .	4.0	0.38	**. . .**
MP35-N	R30035	20.0	35.0	35.0	10.0	. . .	. . .	. . .	. . .	. . .	. . .	**. . .**
MP159	R30159	19.0	25.0	36.0	7.0	. . .	0.6	3.0	0.2	9.0	. . .	**. . .**
Precipitation-hardening alloys												
Iron-base												
A-286	S66286	15.0	26.0	. . .	1.25	. . .	. . .	2.0	0.2	55.2	0.04	**0.005 B, 0.3 V**
Discaloy	S66220	14.0	26.0	. . .	3.0	. . .	. . .	1.7	0.25	55.0	0.06	**. . .**
Incoloy 903	N19903	0.1 max	38.0	15.0	0.1	. . .	3.0	1.4	0.7	41.0	0.04	**. . .**
Pyromet CTX-1	. . .	0.1 max	37.7	16.0	0.1	. . .	3.0	1.7	1.0	39.0	0.03	**. . .**
Incoloy 907	N19907	. . .	38.4	13.0	. . .	. . .	4.7	1.5	0.03	42.0	0.01	**0.15 Si**
Incoloy 909	N19909	. . .	38.0	13.0	. . .	. . .	4.7	1.5	0.03	42.0	0.01	**0.4 Si**

Alloy	**UNS Number**	Composition, %										
		Cr	**Ni**	**Co**	**Mo**	**W**	**Nb**	**Ti**	**Al**	**Fe**	**C**	Other
Incoloy 925	N09925	20.5	44.0	. . .	2.8	. . .	. . .	2.1	0.2	29	0.01	**1.8 Cu**
V-57	. . .	14.8	27.0	. . .	1.25	. . .	. . .	3.0	0.25	48.6	0.08 max	**0.01 B, 0.5 max V**
W-545	S66545	13.5	26.0	. . .	1.5	. . .	. . .	2.85	0.2	55.8	0.08 max	**0.05 B**
Nickel-base												
Astroloy	N13017	15.0	56.5	15.0	5.25	. . .	. . .	3.5	4.4	<0.3	0.06	**0.03 B, 0.06 Zr**
Custom Age 625 PLUS	N07716	21.0	61.0	. . .	8.0	. . .	3.4	1.3	0.2	5.0	0.01	**. . .**
Haynes 242	. . .	8.0	62.5	2.5 max	25.0	. . .	. . .	. . .	0.5 max	2.0 max	0.10 max	**0.006 max B**
Inconel 100	N13100	10.0	60.0	15.0	3.0	. . .	. . .	4.7	5.5	<0.6	0.15	**1.0 V, 0.06 Zr, 0.015 B**
Inconel 102	N06102	15.0	67.0	. . .	2.9	3.0	2.9	0.5	0.5	7.0	0.06	**0.005 B, 0.02 Mg, 0.03 Zr**
Incoloy 901	N09901	12.5	42.5	. . .	6.0	. . .	. . .	2.7	. . .	36.2	0.10 max	**. . .**
Inconel 702	N07702	15.5	79.5	. . .	. . .	. . .	. . .	0.6	3.2	1.0	0.05	**0.5 Mn, 0.2 Cu, 0.4 Si**
Inconel 706	N09706	16.0	41.5	. . .	. . .	. . .	. . .	1.75	0.2	37.5	0.03	**2.9 (Nb + Ta), 0.15 max Cu**
Inconel 718	N07718	19.0	52.5	. . .	3.0	. . .	5.1	0.9	0.5	18.5	0.08 max	**0.15 max Cu**
Inconel 721	N07721	16.0	71.0	. . .	. . .	. . .	. . .	3.0	. . .	6.5	0.04	**2.2 Mn, 0.1 Cu**
Inconel 722	N07722	15.5	75.0	. . .	. . .	. . .	. . .	2.4	0.7	7.0	0.04	**0.5 Mn, 0.2 Cu, 0.4 Si**

Alloy	**UNS Number**	Composition, %										
		Cr	**Ni**	**Co**	**Mo**	**W**	**Nb**	**Ti**	**Al**	**Fe**	**C**	Other
Inconel 725	N07725	21.0	57.0	. . .	8.0	. . .	3.5	1.5	0.35 max	9.0	0.03 max	
Inconel 751	N07751	15.5	72.5	. . .	. . .	. . .	1.0	2.3	1.2	7.0	0.05	**0.25 max Cu**
Inconel X-750	N07750	15.5	73.0	. . .	. . .	. . .	1.0	2.5	0.7	7.0	0.04	**0.25 max Cu**
M252	N07252	19.0	56.5	10.0	10.0	. . .	. . .	2.6	1.0	<0.75	0.15	**0.005 B**
Nimonic 80A	N07080	19.5	73.0	1.0	. . .	. . .	. . .	2.25	1.4	1.5	0.05	**0.10 max Cu**
Nimonic 90	N07090	19.5	55.5	18.0	. . .	. . .	. . .	2.4	1.4	1.5	0.06	**. . .**
Nimonic 95	. . .	19.5	53.5	18.0	. . .	. . .	. . .	2.9	2.0	5.0 max	0.15 max	**+B, +Zr**
Nimonic 100	. . .	11.0	56.0	20.0	5.0	. . .	. . .	1.5	5.0	2.0 max	0.30 max	**+B, +Zr**
Nimonic 105	. . .	15.0	54.0	20.0	5.0	. . .	. . .	1.2	4.7	. . .	0.08	**0.005 B**
Nimonic 115	. . .	15.0	55.0	15.0	4.0	. . .	. . .	4.0	5.0	1.0	0.20	**0.04 Zr**
C-263	N07263	20.0	51.0	20.0	5.9	. . .	. . .	2.1	0.45	0.7 max	0.06	**. . .**
Pyromet 860	. . .	13.0	44.0	4.0	6.0	. . .	. . .	3.0	1.0	28.9	0.05	**0.01 B**
Pyromet 31	N07031	22.7	55.5	. . .	2.0	. . .	1.1	2.5	1.5	14.5	0.04	**0.005 B**
Refractaloy 26	. . .	18.0	38.0	20.0	3.2	. . .	. . .	2.6	0.2	16.0	0.03	**0.015 B**
René 41	N07041	19.0	55.0	11.0	10.0	. . .	. . .	3.1	1.5	<0.3	0.09	**0.01 B**
René 95	. . .	14.0	61.0	8.0	3.5	3.5	3.5	2.5	3.5	<0.3	0.16	**0.01 B, 0.05 Zr**
René 100	. . .	9.5	61.0	15.0	3.0	. . .	. . .	4.2	5.5	1.0 max	0.16	**0.015 B, 0.06 Zr, 1.0 V**

Alloy	**UNS Number**	Composition, %										
		Cr	**Ni**	**Co**	**Mo**	**W**	**Nb**	**Ti**	**Al**	**Fe**	**C**	Other
Udimet 500	N07500	19.0	48.0	19.0	4.0	. . .	. . .	3.0	3.0	4.0 max	0.08	**0.005 B**
Udimet 520	. . .	19.0	57.0	12.0	6.0	1.0	. . .	3.0	2.0	. . .	0.08	**0.005 B**
Udimet 630	. . .	17.0	50.0	. . .	3.0	3.0	6.5	1.0	0.7	18.0	0.04	**0.004 B**
Udimet 700	. . .	15.0	53.0	18.5	5.0	. . .	. . .	3.4	4.3	<1.0	0.07	**0.03 B**
Udimet 710	. . .	18.0	55.0	14.8	3.0	1.5	. . .	5.0	2.5	. . .	0.07	**0.01 B**
Unitemp AF2-1DA	N07012	12.0	59.0	10.0	3.0	6.0	. . .	3.0	4.6	<0.5	0.35	**1.5 Ta, 0.015 B, 0.1 Zr**
Waspaloy	**N07001**	**19.5**	**57.0**	**13.5**	**4.3**	**. . .**	**. . .**	**3.0**	**1.4**	**2.0 max**	**0.07**	**0.006 B, 0.09 Zr**

Table 2 Nominal compositions of cast superalloys

Alloy designation	Nominal composition, %											
	C	**Ni**	**Cr**	**Co**	**Mo**	**Fe**	**Al**	**B**	**Ti**	**Ta**	**W**	**Zr**	Other
Nickel-base													
B-1900	0.1	64	8	10	6	. . .	6	0.015	1	4[(a)]	. . .	0.10	**. . .**
CMSX-2	. . .	66.2	8	4.6	0.6	. . .	56	. . .	1	6	8	6	**. . .**
Hastelloy X	0.1	50	21	1	9	18	. . .	. . .	. . .	. . .	1	. . .	**. . .**
Inconel 100	0.18	60.5	10	15	3	. . .	5.5	0.01	5	. . .	. . .	0.06	**1 V**
Inconel 713C	0.12	74	12.5	. . .	4.2	. . .	6	0.012	0.8	1.75	. . .	0.1	**0.9 Nb**
Inconel 713LC	0.05	75	12	. . .	4.5	. . .	6	0.01	0.6	4	. . .	0.1	**. . .**
Inconel 738	0.17	61.5	16	8.5	1.75	. . .	3.4	0.01	3.4	. . .	2.6	0.1	**2 Nb**

Alloy designation	Nominal composition, %												
	C	**Ni**	**Cr**	**Co**	**Mo**	**Fe**	**Al**	**B**	**Ti**	**Ta**	**W**	**Zr**	Other
Inconel 792	0.2	60	13	9	2.0	. . .	3.2	0.02	4.2	. . .	4	0.1	**2 Nb**
Inconel 718	0.04	53	19	. . .	3	18	0.5	. . .	0.9	. . .	. . .	. . .	**0.1 Cu, 5 Nb**
X-750	0.04	73	15	. . .	. . .	7	0.7	. . .	2.5	. . .	. . .	. . .	**0.25 Cu, 0.9 Nb**
M-252	0.15	56	20	10	10	. . .	1	0.005	2.6	. . .	. . .	. . .	**. . .**
MAR-M 200	0.15	59	9	10	. . .	1	5	0.015	2	. . .	12.5	0.05	**1 Nb[(b)]**
MAR-M 246	0.15	60	9	10	2.5	. . .	5.5	0.015	1.5	1.5	10	0.05	**. . .**
MAR-M 247	0.15	59	8.25	10	0.7	0.5	5.5	0.015	1	3	10	0.05	**1.5 Hf**
PWA 1480	. . .	bal	10	5.0	. . .	. . .	5.0	. . .	1.5	12	4.0	. . .	**. . .**
René 41	0.09	55	19	11.0	10.0	. . .	1.5	0.01	3.1	. . .	. . .	. . .	**. . .**
René 77	0.07	58	15	15	4.2	. . .	4.3	0.015	3.3	. . .	. . .	0.04	**. . .**
René 80	0.17	60	14	9.5	4	. . .	3	0.015	5	. . .	4	0.03	**. . .**
René 80 Hf	0.08	60	14	9.5	4	. . .	3	0.015	4.8	. . .	4	0.02	**0.75 Hf**
René 100	0.18	61	9.5	15	3	. . .	5.5	0.015	4.2	. . .	. . .	0.06	**1 V**
René N4	0.06	62	9.8	7.5	1.5	. . .	4.2	0.004	3.5	4.8	6	. . .	**0.5 Nb, 0.15 Hf**
Udimet 500	0.1	53	18	17	4	2	3	. . .	3	. . .	. . .	. . .	**. . .**
Udimet 700	0.1	53.5	15	18.5	5.25	. . .	4.25	0.03	3.5	. . .	. . .	. . .	**. . .**
Udimet 710	0.13	55	18	15	3	. . .	2.5	. . .	5	. . .	1.5	0.08	**. . .**
Waspaloy	0.07	57.5	19.5	13.5	4.2	1	1.2	0.005	3	. . .	. . .	0.09	**. . .**
WAX-20 (DS)	0.20	72	. . .	. . .	. . .	. . .	6.5	. . .	. . .	. . .	20	1.5	**. . .**

Alloy designation	Nominal composition, %											
	C	**Ni**	**Cr**	**Co**	**Mo**	**Fe**	**Al**	**B**	**Ti**	**Ta**	**W**	**Zr**	Other
Cobalt-base													
AiResist 13	0.45	. . .	21	62	. . .	. . .	3.4	. . .	. . .	2	11	. . .	**0.1 Y**
AiResist 213	0.20	0.5	20	64	. . .	0.5	3.5	. . .	. . .	6.5	4.5	0.1	**0.1 Y**
AiResist 215	0.35	0.5	19	63	. . .	0.5	4.3	. . .	. . .	7.5	4.5	0.1	**0.1 Y**
FSX-414	0.25	10	29	52.5	. . .	1	. . .	0.010	. . .	. . .	7.5	. . .	**. . .**
Haynes 21	0.25	3	27	64	. . .	1	. . .	. . .	. . .	. . .	. . .	. . .	**5 Mo**
Haynes 25; L-605	0.1	10	20	54	. . .	1	. . .	. . .	. . .	. . .	15	. . .	**. . .**
J-1650	0.20	27	19	36	. . .	. . .	. . .	0.02	3.8	2	12	. . .	**. . .**
MAR-M 302	0.85	. . .	21.5	58	. . .	0.5	. . .	0.005	. . .	9	10	0.2	**. . .**
MAR-M 322	1.0	. . .	21.5	60.5	. . .	0.5	. . .	. . .	0.75	4.5	9	2	**. . .**
MAR-M 509	0.6	10	23.5	54.5	. . .	. . .	. . .	. . .	0.2	3.5	7	0.5	**. . .**
MAR-M 918	0.05	20	20	52	. . .	. . .	. . .	. . .	. . .	7.5	. . .	0.1	**. . .**
NASA Co-W-Re	0.40	. . .	3	67.5	. . .	. . .	. . .	. . .	1	. . .	25	1	**2 Re**
S-816	0.4	20	20	42	. . .	4	. . .	. . .	. . .	. . .	4	. . .	**4 Mo, 4 Nb, 1.2 Mn, 0.4 Si**
V-36	0.27	20	25	42	. . .	3	. . .	. . .	. . .	. . .	2	. . .	**4 Mo, 2 Nb, 1 Mn, 0.4 Si**
WI-52	0.45	. . .	21	63.5	. . .	2	. . .	. . .	. . .	. . .	11	. . .	**2 Nb + Ta**
X-40 (Stellite alloy 31)	**0.50**	**10**	**22**	**57.5**	**. . .**	**1.5**	**. . .**	**. . .**	**. . .**	**. . .**	**7.5**	**. . .**	**0.5 Mn, 0.5 Si**

(a) B-1900 + Hf also contains 1.5% Hf.

(b) MAR-M 200 + Hf also contains 1.5% Hf.

This article describes the procedures for heat treatment of superalloys and the resulting properties. The first part briefly reviews the heat-treating processes and the special considerations required by superalloys. The later sections describe these processes for both the wrought (Table 1) and cast (Table 2) versions of the age-hardenable and solid-solution-strengthened superalloys.

Heat-Treating Operations

Stress relieving of superalloys frequently entails a compromise between maximum relief of residual stress and effects deleterious to high-temperature properties and/or corrosion resistance. True stress relieving of wrought material is usually, but not always, confined to non-age-hardenable alloys because a full-solution treatment is useful prior to age-hardening. In addition, the stress-relieving temperature would typically fall within the upper temperature range for age-hardening.

Time and temperature cycles vary considerably, depending on the metallurgical characteristics of the alloy and on the type and magnitude of the residual stresses developed in the prior fabrication processes. Stress-relieving temperatures are usually below the annealing or recrystallization temperatures.

Annealing. When applied to superalloys, annealing implies full annealing, that is, complete recrystallization and attaining maximum softness. The practice is usually applied to non-hardening wrought alloys. For most of the age-hardenable alloys, the annealing cycles are the same as for solution treating. However, the two treatments serve different purposes. Annealing is used mainly to reduce hardness and increase ductility to facilitate forming or machining, prepare for welding, relieve stresses after welding, produce specific microstructures, or soften age-hardened structures by resolution of second phases. Solution treating is intended to dissolve second phases to produce maximum corrosion resistance or to prepare for age hardening.

Most wrought superalloys can be cold formed but are more difficult to form than austenitic stainless steels. Severe cold-forming operations may require several intermediate annealing operations. Full annealing must be followed by fast cooling.

Annealing should be conducted after welding the age-hardenable alloys if highly restrained joints are involved. For alloys sensitive to strain age cracking, heating rates must be rapid. If the configuration of the weldment does not permit annealing, aging may be used for stress relieving in alloys not prone to strain age cracking.

Reheating for hot working is similar to annealing in that the aim is to promote adequate formability of the metal being deformed. Control of temperature can be critical to resultant properties, as varying degrees of recrystallization and control of grain growth may be desired. In most standard operations, heating or reheating for hot working is a full annealing step with recrystallization and dissolution of all or most secondary phases. Additional discussion of controlled heating for hot working can be found in the section "Thermomechanical Processing" in this article.

Solution Treating and Quenching. The first step in heat treating superalloys is usually solution treatment. In some wrought alloys, the solution-treating temperature will depend on the properties desired. A higher temperature is specified for optimum creep-rupture properties; a lower temperature is used for optimum short-time tensile properties at elevated temperature, improved fatigue resistance (via finer grain size), or improved resistance to notch rupture sensitivity.

The higher solution-treating temperature will result in some grain growth and more extensive dissolving of carbides. The principal objective is to put hardening phases into solution and dissolve some carbides. After aging, the resulting microstructure of these wrought alloys consists of large grains that contain the principal aging phases (γ', γ'', η) and a heavy concentration of carbides in the grain boundaries. The lower solution-treating temperature dissolves the principal aging phases without grain growth or significant carbide solution.

For some wrought superalloys (such as Nimonic 80A and Nimonic 90), an intermediate solution-treating temperature is selected to produce a compromise of the properties. For other alloys (such as Udimet 500 and Udimet 700), the intermediate-temperature aging treatment is used to tailor the grain boundaries for improved creep-rupture properties.

Quenching. The purpose of quenching after solution treating is to maintain, at room temperature, the supersaturated solid solution obtained during solution treating. Quenching permits a finer age-hardening precipitate size. Cooling methods commonly used include oil and water quenching as well as various forms of air or inert gas cooling. Internal stresses resulting from quenching can also accelerate overaging in some age-hardenable alloys.

Aging treatments strengthen age-hardenable alloys by causing the precipitation of additional quantities of one or more phases from the supersaturated matrix that is developed by solution treating. Factors that influence the selection and number of aging steps and aging temperature include:

- Type and number of precipitating phases available
- Anticipated service temperature
- Precipitate size
- The combination of strength and ductility desired and heat treatment of similar alloys

Typical heat treatments of wrought age-hardenable superalloys are given in Table 3. Because dimensional changes can occur during aging, it is recommended that finish machining be done after aging.

Table 3 Typical solution-treating and aging cycles for wrought superalloys

Alloy	**Solution treating**				Aging			
	Temperature		**Time, h**	**Cooling procedure**	**Temperature**		**Time, h**	Cooling procedure
	°C	**°F**			**°C**	**°F**		
Iron-base alloys								
A-286	980	1800	1	Oil quench	720	1325	16	**Air cool**
Discaloy	1010	1850	2	Oil quench	730	1350	20	**Air cool**
					650	1200	20	**Air cool**
N-155	1165-1190	2125-2175	1	Water quench	815	1500	4	**Air cool**
Incoloy 903	845	1550	1	Water quench	720	1325	8	**Furnace cool**
					620	1150	8	**Air cool**
lncoloy 907	980	1800	1	Air cool	775	1425	12	**Furnace cool**
					620	1150	8	**Air cool**
Incoloy 909	980	1800	1	Air cool	720	1325	8	**Furnace cool**

					620	1150	8	**Air cool**
Incoloy 925	1010	1850	1	Air cool	730[a]	1350[a]	8	**Furnace cool**
					620	1150	8	**Air cool**
Nickel-base alloys								
Astroloy	1175	2150	4	Air cool	845	1550	24	**Air cool**
	1080	1975	4	Air cool	760	1400	16	**Air cool**
Custom Age 625 PLUS	1038	1900	1	Air cool	720	1325	8	**Furnace cool**
					620	1150	8	**Air cool**
Inconel 901	1095	2000	2	Water quench	790	1450	2	**Air cool**
					720	1325	24	**Air cool**
Inconel 625	1150	2100	2	[b]	. . .	. . .	. . .	**. . .**
Inconel 706	925-1010	1700-1850	. . .	. . .	845	1550	3	**Air cool**
					720	1325	8	**Furnace cool**
					620	1150	8	**Air cool**
Inconel 706[c]	980	1800	1	Air cool	730	1350	8	**Furnace cool**
					620	1150	8	**Air cool**
lnconel 718	980	1800	1	Air cool	720	1325	8	**Furnace cool**
					620	1150	8	**Air cool**
Inconel 725	1040	1900	1	Air cool	730[a]	1350	8	**Furnace cool**
					620	1150	8	**Air cool**
Inconel X-750	1150	2100	2	Air cool	845	1550	24	**Air cool**

					705	1300	20	**Air cool**
Nimonic 80A	1080	1975	8	Air cool	705	1300	16	**Air cool**
Nimonic 90	1080	1975	8	Air cool	705	1300	16	**Air cool**
René 41	1065	1950	$\frac{1}{2}$	Air cool	760	1400	16	**Air cool**
Udimet 500	1080	1975	4	Air cool	845	1550	24	**Air cool**
					760	1400	16	**Air cool**
Udimet 700	1175	2150	4	Air cool	845	1550	24	**Air cool**
	1080	1975	4	Air cool	760	1400	16	**Air cool**
Waspaloy	1080	1975	4	Air cool	845	1550	24	**Air cool**
					760	1400	16	**Air cool**
Cobalt-base alloys								
S 816	**1175**	**2150**	**1**	(b)	**760**	**1400**	**12**	**Air cool**

Note: Alternate treatments may be used to improve specific properties.

(a) If furnace size/load prohibits fast heat up to initial age temperature, a controlled ramp up from 590 to 730 °C (1100 to 1350 °F) is recommended.

(b) To provide adequate quenching after solution treating, it is necessary to cool below about 540 °C (1000 °F) rapidly enough to prevent precipitation in the intermediate temperature range. For sheet metal parts of most alloys, rapid air cooling will suffice. Oil or water quenching is frequently required for heavier sections that are not subject to cracking.

(c) Heat treatment of lnconel 706 to enhance tensile properties instead of creep resistance for tensile-limited applications

Aging Precipitates. Principal aging phases in the superalloys usually include one or more of the following: γ' (Ni_3Al or Ni_3Al,Ti), η (Ni_3Ti), or γ" (body-centered tetragonal Ni_3Nb). Secondary phases that may be present include: carbides ($M_{23}C_6$, M_7C_3, M_6C, and MC), nitrides (MN), carbonitrides (MCN), and borides (M_3B_2), as well as Laves phase (M_2Ti) and δ phase (orthorhombic Ni_3Nb). The above phases occur principally in nickel-base alloys. The primary phases in cobalt-base alloys are $M_{23}C_6$, M_7C_3, M_6C, and MC. The primary phases in iron-base superalloys will be similar to those in nickel alloys, although η is more apt to be found because the Ti-to-Al ratio is generally higher in iron alloys than in nickel alloys.

When more than one phase is capable of precipitating from the alloy matrix, judicious selection of a single aging temperature (or a double aging treatment that produces different sizes and types of precipitates at different temperatures) is important. The principal strengthening precipitates are γ' or γ", while other precipitates such as η, δ, or Laves phase can provide grain size control in nickel-iron superalloys (see, for example, the next section "Thermomechanical Processing"). In some alloys, if composition has not been carefully controlled, undesirable phases, such as σ and μcan also form either during heat treatment or, more commonly, during service. These precipitates, known as TCP (topologically close-packed) phases, are composed of close-packed layers of atoms parallel to {111} planes of the γmatrix. Usually harmful, they may appear as long plates or needles, often nucleating on grain-boundary carbides. The formulae for σ and μ are given in Table 4. Alloys containing a high level of body-centered cubic (bcc) transition metals (tantalum, niobium, chromium, tungsten, and molybdenum) are most susceptible to TCP phase formation.

Table 4 Constituents observed in superalloys

Phase	**Crystal structure**	**Lattice parameter, nm**	**Formula**	Comments
γ'	fcc (ordered *L*1$_2$)	0.3561 for pure Ni_3Al to 0.3568 for $Ni_3(Al_{0.5}Ti_{0.5})$	Ni_3Al $Ni_3(Al, Ti)$	**Principal strengthening phase in many nickel- and nickel-iron-base superalloys; crystal lattice varies slightly in size (0 to 0.5%) from that of austenite matrix; shape varies from spherical to cubic; size varies with exposure time and temperature. Gamma prime is spherical in iron-nickel-base and in some of the older nickel-base alloys, such as Nimonic 80A and Waspaloy. In the more recently developed nickel-base alloys, γ' is generally cuboidal. Experiments have shown that variations in molybdenum content and in the aluminum/titanium ratio can change the morphology of γ. With increasing γ/γ' mismatch, the shape changes in the following order: spherical, globular, blocky, cuboidal. When the γ/γ' lattice mismatch is high, extended exposure above 700 °C (1290 °F) causes undesirable η(Ni_3Ti) or δ(Ni_3Nb) phases to form.**
η	hcp (*D*0$_{24}$)	a_o = 0.5093 c_o = 0.8276	Ni_3Ti (no solubility for other elements)	**Found in iron-, cobalt-, and nickel-base superalloys with high titanium/aluminum ratios after extended exposure; may form intergranularly in a cellular form or intragranularly as acicular platelets in a Widmanstätte pattern**
γ"	bct (ordered *D*0$_{22}$)	a_o = 0.3624 c_o = 0.7406	Ni_3Nb	**Principal strengthening phase in Inconel 718; γ'' precipitates are coherent disk-shaped particles that form on the {100} planes (avg diam approximately 600 Å, thickness approximately 50 to 90 Å); Bright-field TEM examination is unsatisfactory for resolving γ'' due to the high density of the precipitates and the strong contrast from the coherency strain field around the precipitates. However, dark-field TEM examination provides excellent imaging of the γ'' by selective imaging of precipitates that produce specific superlattice reflections. In addition, γ'' can be separated from γ' using the dark-field mode, because the γ'' dark-field image is substantially brighter than that of γ'.**
Ni_3Nb (δ)	Orthorhombic (ordered Cu_3Ti)	a_o = 0.5106-0.511 b_o = 0.421-0.4251 c_o = 0.452-0.4556	Ni_3Nb	**Observed in overaged Inconel 718; has an acicular shape when formed between 815 and 980 °C (1500 and 1800 °F); forms by cellular reaction at low aging temperatures and by intragranular precipitation at high aging temperatures**

MC	Cubic	a_o = 0.430-0.470	TiC NbC HfC	**Titanium carbide has some solubility for nitrogen, zirconium, and molybdenum; composition is variable; appears as globular, irregularly shaped particles that are gray to lavender; "M" elements can be titanium, tantalum, niobium, hafnium, thorium, or zirconium.**
$M_{23}C_6$	fcc	a_o = 1.050-1.070 (varies with composition)	$Cr_{23}C_6$ $(Cr,Fe,W,Mo)_{23}C_6$	**Form of precipitation is important; it can precipitate as films, globules, platelets, lamellae, and cells; usually forms at grain boundaries; "M" element is usually chromium, but nickel-cobalt, iron, molybdenum, and tungsten can substitute.**
M_6C	fcc	a_o = 1.085-1.175	Fe_3Mo_3C Fe_3W_3C-Fe_4W_2C Fe_3Nb_3C Nb_3Co_3C Ta_3Co_3C	**Randomly distributed carbide; may appear pinkish; "M" elements are generally molybdenum or tungsten; there is some solubility for chromium, nickel-niobium, tantalum, and cobalt.**
M_7C_3	Hexagonal	a_o = 1.398 c_o = 0.4523	Cr_7C_3	**Generally observed as a blocky intergranular shape; observed only in alloys such as Nimonic 80A after exposure above 1000 °C (1830 °F), and in some cobalt-base alloys**
M_3B_2	Tetragonal	a_o = 0.560-0.620 c_o = 0.300-0.330	Ta_3B_2 V_3B_2 Nb_3B_2 $(Mo,Ti,Cr,Ni,Fe)_3B_2$ Mo_2FeB_2	**Observed in iron-nickel- and nickel-base alloys with about 0.03% B or greater; borides appear similar to carbides, but are not attacked by preferential carbide etchants; "M" elements can be molybdenum, tantalum, niobium, nickel, iron, or vanadium.**
MN	Cubic	a_o = 0.4240	TiN (Ti,Nb,Zr)N (Ti,Nb,Zr)(C,N) ZrN NbN	**Nitrides are observed in alloys containing titanium, niobium, or zirconium; they are insoluble at temperatures below the melting point; easily recognized as-polished, having square to rectangular shapes and ranging from yellow to orange**
μ	Rhombohedral	a_o = 0.475 c_o = 2.577	Co_2W_6 $(Fe,Co)_7(Mo,W)_6$	**Generally observed in alloys with high levels of molybdenum or tungsten; appears as coarse, irregular Widmanstätten platelets; forms at high temperatures**
Laves	Hexagonal	a_o = 0.475-0.495 c_o = 0.770-0.815	Fe_2Nb Fe_2Ti Fe_2Mo Co_2Ta Co_2Ti	**Most common in iron-base and cobalt-base superalloys; usually appears as irregularly shaped globules, often elongated, or as platelets after extended high-temperature exposure**
σ	**Tetragonal**	**a_o = 0.880-0.910 c_o = 0.450-0.480**	**FeCr FeCrMo CrFeMoNi CrCo CrNiMo**	**Most often observed in iron- and cobalt-base superalloys, less commonly in nickel-base alloys; appears as irregularly shaped globules, often elongated; forms after extended exposure between 540 and 980 °C (1005 to 1795 °F)**

The size distribution of precipitates is affected by aging temperature. Exposure to temperatures higher than the optimum aging temperature results in a decrease in strength through the process of overaging (coarsening of precipitates); at still higher temperatures, resolution may occur. High aging temperatures will produce coarser γ' particles than lower

temperatures and result in higher creep-rupture properties. For optimum short-time elevated-temperature properties, small, finely dispersed particles of γ' precipitate are desired. Therefore, final aging temperatures are lower than those used to obtain high creep-rupture properties. For all γ' dispersions, care must be taken to ensure the correct carbide distribution.

Double-Aging Treatment. A two-step aging treatment is commonly used to control the size distribution of γ' and γ'' precipitates. A principal reason for two-step aging sequences, in addition to γ' or γ'' control, is to precipitate or control grain boundary carbide morphology. In some alloys, such as Incoloy 901 and A-286, MC films may form along grain boundaries and reduce ductility.

Double or multistep aging treatments vary according to the alloy type and design objectives. In some alloys, a second aging step up to about 850 °C (1560 °F) is added (see Examples 1 and 2 below).

In other alloys, however, aging may involve an initial treatment in the range of 850 to 1100 °C (1560 to 2010 °F) over a period of up to 24 h. Aging at one or more lower temperatures, for example at 760 °C (1400 °F) for 16 h, completes the precipitation of γ'. The finer γ' produced in the second aging treatment is advantageous for tensile strength as well as for rupture life. This type of aging treatment is used for nickel-base superalloys such as Udimet 700, Astroloy, and Udimet 710.

Example 1: Double-Aging Treatment of A-286.

Adding a second aging treatment can improve properties to meet a requirement. For example, borderline values of yield strength, 615 and 630 MPa (89 and 91 ksi), were obtained in two heats of material with a heat treatment of:

- 900 °C (1650 °F) solution treatment for 2 h and oil quench
- Aging treatment of 705 °C (1300 °F) for 16 h with air cooling

By aging a second time at 650 °C (1200 °F) for 16 h (air cooled), the yield strengths were improved to 635 and 698 MPa (92 and 101 ksi).

Example 2: Double-Aging Sequence of Udimet 500 for Stabilization of Grain Boundary Carbides.

Udimet 500 is typical of wrought precipitation-hardened superalloys that contain MC and $M_{23}C_6$ carbides and are strengthened by γ'. For a good balance of tensile strength and stress-rupture life, the alloy is:

- Solution heat treated at 1080 °C (1975 °F) for 4 h (air cooled)
- Stabilized at 845 °C (1550 °F) for 24 h (air cooled)
- Aged at 760 °C (1400 °F) for 16 h (air cooled)

The solution exposure dissolves all phases except MC carbides, and γ' precipitates nucleate during cooling from the solution temperature. The stabilization at 845 °C (1550 °F) precipitates discontinuous $M_{23}C_6$ at grain boundaries as well as γ'. Final aging increases the volume fraction of γ'. The grain boundary $M_{23}C_6$ increases stress-rupture life as long as it is not a continuous carbide film, which markedly decreases rupture ductility.

Thermomechanical Processing. In recent years there has been more interest in the interdependence of hot working and heat-treating operations. In many critical applications the desired final properties are not attainable via heat treatment if the hot working operation has not been conducted under controlled temperature and deformation parameters. This requires a study of hot working and heat treating, known as thermomechanical processing. One application of thermomechanical processing is the development of direct age 718 for turbine disk applications (Ref 1). Proper heating temperatures and forging operations also influence the microstructure and distribution of phases in alloys such as 718.

Grain Size Control. An important objective of thermomechanical processing is grain size control (Ref 2, 3, 4). For example, grain structure may be controlled by thermomechanical processing in several iron-nickel-base alloys that have two precipitates present, such as the primary strengthening precipitate (γ'' Ni_3Nb in Inconel 718 and γ' Ni_3Ti in Inconel

901) and a secondary precipitate (δ in Inconel 718 and ηNi_3Ti in Inconel 901) (Ref 3, 4). The secondary precipitate is produced first, by an appropriate heat treatment (8 h at 900 °C, or 1650 °F, for 901), followed by working at about 950 °C (1740 °F), below the η solvus. Final working is carried out below the recrystallization temperature, and the alloy is subsequently recrystallized below the η solvus. Finally, the alloy is aged by standard procedures. The result is a fine-grain alloy with higher tensile strength and improved fatigue resistance.

Other thermomechanical working schedules are used to produce a double necklace structure of fine grains surrounding the large grains formed during high-temperature recrystallization. Reductions of 25 to 50% are needed in the final working operations at 1080 to 1110 °C (1975 to 2030 °F) to produce the small recrystallized grains in cast/wrought René 95.

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General Guidelines and Potential Problems

Surface-Related Problems. Although superalloys offer resistance to surface degradation during elevated-temperature service, heat treatment temperatures (particularly solution treatment) can degrade surface characteristics. The potential forms of surface degradation include oxidation, carbon pickup, alloy depletion, and contamination.

Oxidation. In general, superalloys have good oxidation resistance within their normal range of service temperature and above their aging temperatures (typical range 760 to 980 °C, or 1400 to 1800 °F) depending on the alloy. Others may require coatings to provide suitable resistance in the service environment, such as blade and vane alloys for turbine engines and compressors. However, at higher temperatures, such as those used for solution treating, these alloys are susceptible to intergranular oxidation, a defect that adversely affects thermal fatigue.

Oxidation resistance is enhanced by adding chromium, aluminum, and certain other elements. Chromium allows formation of a protective chromium oxide and is most beneficial at intermediate temperatures and below ($\lesssim$870 °C, or 1600 °F), or in the presence of adequate aluminum permits the formation of aluminum oxide, which is more protective at higher temperatures (>870 °C, or 1600 °F). The principal mode of intergranular attack involves preferential oxidation of chromium, aluminum, titanium, zirconium, and boron. Molybdenum increases susceptibility to intergranular attack in age-hardenable alloys. In relation to intergranular oxidation, aluminum is preferable to titanium as a hardening element because:

- Increased aluminum reduces formation of the η phase from γ'
- Aluminum oxide provides a denser and less permeable barrier to the diffusion of oxygen
- Lower density

However, a smooth tight oxide layer is not possible in chromium-free low-expansion (Invar-type) superalloys such as Incoloy alloys 903, 907, and 909 and Pyromet alloys CTX-1, CTX-3, and CTX-909.

Carbon pickup can occur if the solution-treating atmosphere has a carburizing potential. For instance, the carbon content of the surface of A-286 has been observed to increase from 0.05 to 0.30%. The added carbon forms a stable carbide (TiC), thus removing titanium from solid solution and preventing normal precipitation hardening in the surface layers. TiN can be formed in the same manner as a result of nitrogen contamination.

Alloy Depletion. In addition to oxidation, exposure to high-temperature environments can cause changes in the composition of the alloy near the surface. As certain elements are preferentially consumed by the scale layer, the bulk composition can become depleted. In addition, some alloys can be very susceptible to deboronization. This can affect the properties of the surface layers and can be of considerable concern, for instance in sheet products.

Miscellaneous Contaminants. All exposed surfaces of superalloy parts should be kept free of dirt, fingerprints, oil, grease, forming compounds, lubricants, and scale. Lubricants or fuel oils that contain sulfur compounds are particularly active in corroding and embrittling the metal surface by first forming Cr_2S_3 and then, as the attack progresses, also forming a $Ni\text{-}Ni_3S_2$ eutectic that melts at 645 °C (1190 °F), particularly at low pressures of less than 10^{-2} Pa (10^{-4} torr) in vacuum.

Scale and slag from furnace hearths are another source of contamination. Contact with steel scale, slag, and furnace spallings should be avoided; low-melting constituents can form on the metal surface and promote corrosion.

Protective atmospheres are used in annealing or solution treating if heavy oxidation cannot be tolerated. If oxidation can be tolerated, because of subsequent stock removal, superalloys can be solution-treated in air or in the normal mixture of air and combustion products found in gas-fired furnaces. A vacuum environment is desirable.

Vacuum atmosphere, generally below $\frac{1}{4}$ Pa (2×10^{-3} torr), is commonly used above 815 °C (1500 °F). It is particularly desirable when parts are at or close to final dimensions.

Inert Gas. Dry argon, with a dew point of -50 °C (-60 °F) or lower, should be used if no oxidation can be tolerated. It is mandatory that this type of atmosphere be used in a sealed retort or sealed furnace chamber. A purge of at least ten times the volume of the retort is recommended before the retort is placed in the furnace. The argon must be kept flowing continually during and after the treatment until the workpieces have cooled nearly to room temperature, to prevent the formation of an oxide film.

Alloys containing stable-oxide formers such as aluminum and titanium, with or without boron, must be bright annealed in a vacuum or in a chemically inert gas such as argon. If used, argon must be pure and dry with a dew point of -50 °C (-60 °F) or lower. If the argon has a slightly higher dew point, but not more than -40 °C (-40 °F), oxidation will be limited to a thin surface film that can usually be tolerated.

Hydrogen. Dry hydrogen, with a dew point of -50 °C (-60 °F) or lower, is used in preference to dissociated ammonia for bright annealing. If the hydrogen is prepared by catalytic gas reactions instead of by electrolysis, residual hydrocarbons, such as methane, should be limited to about 50 ppm, to prevent carburizing. Hydrogen is not recommended for bright annealing of alloys containing significant amounts of elements (such as aluminum or titanium) that form stable oxides not reducible at normal heat-treating temperatures and dew points. Hydrogen is not recommended for annealing or solution treating alloys that contain boron, because of the danger of deboronization through formation of boron hydrides. Titanium hydrides can also form.

Exothermic Atmosphere. A lean and dilute exothermic atmosphere is relatively safe and economical. The surface scale formed in such an atmosphere can be removed by pickling or by salt bath descaling and pickling. Such an atmosphere, formed by burning fuel gas with air, contains about 85% nitrogen, 10% carbon dioxide, 1.5% carbon monoxide, 1.5% hydrogen, and 2% water vapor. This atmosphere will produce a scale rich in chromium oxides.

Endothermic atmospheres prepared by reacting fuel gas with air in the presence of a catalyst are not recommended, because of their carburizing potential. Similarly, the endothermic mixture of nitrogen and hydrogen formed by dissociating ammonia is not used, because of the probability of nitriding.

Atmosphere for Aging. Air is the most common aging atmosphere. The smooth, tight oxide layer that is formed is usually unobjectionable on the finished product (except when heat treating chromium-free low-expansion superalloys). However, if this oxide layer must be minimized, a lean exothermic gas (air-to-gas ratio, about 10 to 1) or vacuum can be employed. It will not entirely prevent oxidation, but the oxide layer will be very light. The use of gases containing hydrogen and carbon monoxide for aging cycles is dangerous because of the explosion hazard at temperatures below 760 °C (1400 °F).

Furnace Equipment. Basic equipment considerations seldom differ from those influencing the selection of furnaces for heat treating steel. In general, the temperature-control limits are ±14 °C (±25 °F) and temperature may range up to about 1315 °C (2400 °F). Belt conveyor furnaces, although widely used for production annealing, are less gastight than roller-hearth furnaces of the same volume. Batch heating for annealing or solution treating is usually done in box furnaces. These may have provisions for purging, preheating, and quenching, if the high-temperature compartment is supplemented by other chambers.

Aging of precipitation-hardenable superalloys, commonly in the range of 650 to 900 °C (1200 to 1650 °F), is usually done in box furnaces, with or without protective atmospheres. The usual operating-temperature tolerance is ±14 °C (±25 °F). Continuous furnaces are seldom used, because of the long aging cycles. Salt baths are not recommended, because reaction could occur between chloride in the bath and the alloy surface during the long-time immersion required for aging. Salt baths can be used satisfactorily for solution treating, however.

Vacuum furnaces are used for heat treating some alloys. Heating may be accomplished by resistance elements or by induction. Furnace design dictates a batch operation. Cooling can be accomplished in a vacuum retort pressurized with an inert gas that provides conductive cooling after heating is discontinued. Further details are provided in the article "Heat Treating in Vacuum Furnaces and Auxiliary Equipment" in this Volume.

Fixtures for holding finished parts or assemblies during heat treatment may be either the support type or the restraint type. For alloys that must be cooled rapidly from the solution-treating temperature, the best practice is to employ minimum fixtures during solution treating and quenching and to control dimensional relations by using restraining fixtures during aging.

Support fixtures are used when restraint is not required or when the part itself provides sufficient self-restraint. A support fixture also aids in handling parts and helps the part to support its own weight. Long narrow pieces, such as tubes or bolts, are most easily fixtured by hanging vertically. Parts that have a large flat surface, such as rings, cylinders, and beams, can be placed on a flat furnace tray or plate. For slightly asymmetrical parts, special supports can be built up from a flat tray. If these supports are fabricated by welding, they must be stress relieved prior to use.

Asymmetrical parts can be supported in several ways. One method is to lay the part on a tray of sand, making certain that most of the bottom area is well supported. Alluvial garnet sand is most commonly used as the supporting medium. Another method of support is a ceramic casting formed to the shape of the part. However, this method is costly and subject to size limitations. Turbine blades and asymmetrical ducting are examples of parts that can be supported either in a sand tray or by ceramic castings.

Restraint fixtures are generally more complicated than support fixtures and may require machined grooves, lugs, or clamps to hold parts to a given shape. For example, to maintain symmetry and roundness in an alloy A-286 frame assembly during aging, the assembly was processed on a flat plate into which grooves had been machined. These grooves accepted the rims on the outer and inner shrouds and held them in restraint during heat treatment. To prevent the center hub from rising or dropping in relation to the outer shroud, both the hub and the shroud were clamped to the grooved-plate fixture.

Some straightening of parts is possible in aging fixtures of the type described above. A slightly distorted part can be forced into the fixture and clamped. Some stress relieving will occur along with aging. However, fixtures for hot sizing are not always successful, because of the high creep strength of these alloys at the aging temperature.

Threaded fasteners are not recommended for clamping because they are difficult to remove after heat treatment. A slotted bar held in place by wedges is preferable.

Usually, the coefficient of expansion of both the fixture and part should be nearly the same. However, in some applications, the fixture is purposely made from a material having different expansion characteristics, in order to apply pressure to the part as the temperature increases.

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Wrought Superalloy Heat Treatment

The heat treatment of wrought superalloys can be subdivided according to the following alloy categories:

- Precipitation-strengthened nickel-iron-base superalloys
- Precipitation-strengthened nickel-base superalloys
- Solution-strengthened iron-, nickel-, and cobalt-base superalloys

Solid-solution-strengthened iron-, nickel-, and cobalt-base superalloys are generally distinguishable from the precipitation-strengthened superalloys by their relatively low content of precipitate-forming elements such as aluminum, titanium, or niobium. There are, of course, some exceptions to this, particularly as regards niobium content. Typical compositions for precipitation-strengthened and solid-solution-strengthened superalloys are given in Table 1.

Precipitation-Strengthened Nickel-Iron-Base Superalloys

There is also an important distinction between the nickel-base and nickel-iron precipitation-strengthened superalloys. Many of the nickel-iron alloys allow precipitation of additional intermetallics (such as η, δ, and Laves phases) in addition to the principal strengthening precipitates (γ' and/or γ"). These additional precipitates, with appropriate heat treatment, can provide some grain size control in nickel-iron superalloys. For example:

- The η phase in Inconel 901 and A-286 reduces grain growth when temperatures are below the η solvus
- The δ phase can control grain size in γ"-strengthened superalloys such as Inconel 718
- The Laves phase (solvus at about 1040 °C, or 1900 °F) in Incoloy 909 and Pyromet CTX3M controls grain size when annealing in a temperature range of 980 to 1010 °C (1800 to 1850 °F)

A specific example of grain size control with the η phase is described below.

Example 3: Control of Grain Growth in A-286 with η.

In A-286, the γ' solvus is approximately 855 °C (1575 °F) and the η solvus is approximately 910 °C (1675 °F). The alloy can be worked and heat treated above the η solvus, or the γ' can be fully dissolved with some η phase retained for grain size control. A-286 has been processed to fine grain sizes by finish forging at temperatures in the vicinity of the η solvus, solution treating below the η solvus but above the γ' solvus (for example, hold at 900 °C, or 1650 °F) for 2 h and oil quench), then aging below the γ' solvus (for example, 720 °C, or 1325 °F, for 16 h and air cool). Recrystallization occurs above the γ' solvus either during forging or solution heat treatment, but the η phase controls grain growth. If the alloy is solution heat treated above the η solvus (for example, at 980 °C, or 1800 °F, for 1 h with oil quenching), a coarser grain size results. Table 5 shows typical tensile and stress-rupture data for A-286 obtained by each approach. The finer-grain-size material has better room-temperature tensile strength, better stress rupture ductility (including notched bar rupture ductility), but lower stress-rupture life.

Table 5 Effect of heat treatment on the properties of A-286

Heat treatment	**Tensile properties at 21 °C (70 °F)**	Stress rupture at 650 °C (1200 °F)

	0.2% Yield strength		Ultimate tensile strength		Elongation %	Reduction in area, %	with 450 MPa (65 ksi)		
	MPa	ksi	MPa	ksi			Life, h	Elongation, %	Reduction in area, %
980 °C (1800 °F) for 1 h, oil quench (OQ) + 720 °C (1325 °F) for 16 h, air cool	690	100	1070	156	24	46	85	10	**15**
900 °C (1650 °F) for 2 h, OQ + 720 °C (1325 °F) for 16 h, air cool	**740**	**108**	**1100**	**160**	**25**	**46**	**64**	**15**	**20**

Source: Ref 5

Alloy Types. Precipitation-strengthened nickel-iron-base superalloys can be grouped into two classes according to the main strengthening phase. One class consists of alloys strengthened by the γ' phase. This class includes alloys such as A-286, which contain relatively low levels of nickel (25 to 35 wt%), and alloys such as Incoloy 901 and Inconel X-750, which contain higher levels of nickel (more than 40 wt%) and also contain higher volume fractions of γ' for increased strength. Iron-rich Incoloy 903 and 909, which are iron-nickel-cobalt alloys developed to exhibit low coefficient of thermal expansion properties along with high strength, are also strengthened by γ' precipitates.

The second class of nickel-iron-base superalloys includes alloys strengthened primarily by the γ" phase. These alloys are nickel-rich and contain niobium for formation of γ", and are represented by Inconel alloys 706 and 718. Inconel 718 is particularly important. In 1989, 45% of all wrought nickel-base and nickel-iron-base superalloys produced was Inconel 718.

Effects of Cold Working on Heat Treatment Response. Cold working of age-hardenable nickel-iron-base superalloys affects the response of the alloy during heat treatment. Cold work affects the recrystallization and grain growth behavior during subsequent solution treatment, and also the reaction kinetics of aging. The cold working itself is usually performed on solution-treated alloys because of the markedly lower strength and increased ductility of the material before aging (see Table 6).

Table 6 Typical effects of aging on room-temperature mechanical properties of solution-treated heat-resisting alloys

Alloy	Yield strength (0.2% offset				Elongation in 50 mm (2 in.), %	
	Not aged		Aged			
	MPa	ksi	MPa	ksi	Not aged	Aged
A-286	240	35	760	110	52	**33**
René 41	620	90	1100	160	45	**15**
X-750	410	60	650	92	45	**24**

Haynes alloy 25	**480**	**69**	**480**	**70**	**55**	**45**

Effect of Cold Work on Grain Growth during Solution Treatment. Larger amounts of cold work refine the grain size during solution treatment, but smaller amounts of cold work can lead to critical grain growth. The effect of varying amounts of cold work on grain growth in A-286 during solution treating is illustrated in Fig. 1. The initial material was solution treated with a maximum grain size of ASTM 5. Cold working in the range of 1 to 5% caused excessive grain growth during subsequent solution treating at 900 °C (1650 °F). Above about 5% of cold work, critical grain growth did not occur, and the recrystallized grain size decreased with increasing cold work. Excessive grain growth, especially excessive localized grain growth, would likely degrade tensile properties. Therefore, on parts subjected to cold or hot work prior to solution treating, the critical amount of work (about 1 to 6% cold work, depending on the alloy, and about 10% hot work) must be exceeded in all areas to avoid the growth of abnormally large grains. This rule applies to items such as cold-headed bolts, spun or stretch-formed sheets, and parts formed by simple bending.

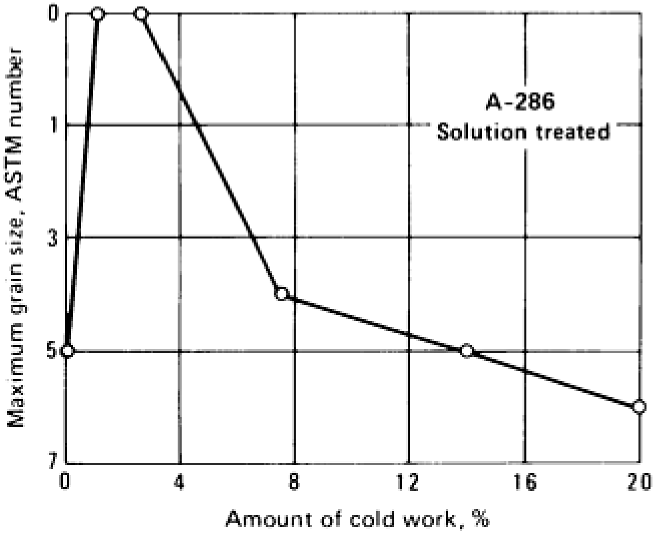

Fig. 1 Effect of cold work on grain size of A-286 alloy solution treated at 900 °C (1650 °F) for 1 h and oil quenched

Effect of Cold Work on Aging Response. Cold working accelerates the aging reaction, causing the early appearance of precipitates at normal aging temperature and the appearance of a precipitate at temperatures below the normal aging temperature if the alloy is cold worked sufficiently and held at temperature long enough. In other words, cold working can make a material more prone to overaging at the normal aging temperature. Even relatively small amounts of residual strain can lead to strain-induced overaging of the low-expansion (Invar-type) superalloys such as Incoloy 907, 909, and Pyromet CTX-3 and CTX-909. This effect can result in an extreme loss in tensile properties. Thus, care must be taken to provide strain (dislocation)-free structures prior to aging. Properly charted information correlating cold work with aging response, however, can be used to shorten the required aging period or to lower the normal aging temperature. The effect of cold work and aging on hardness in A-286 is shown in Fig. 2.

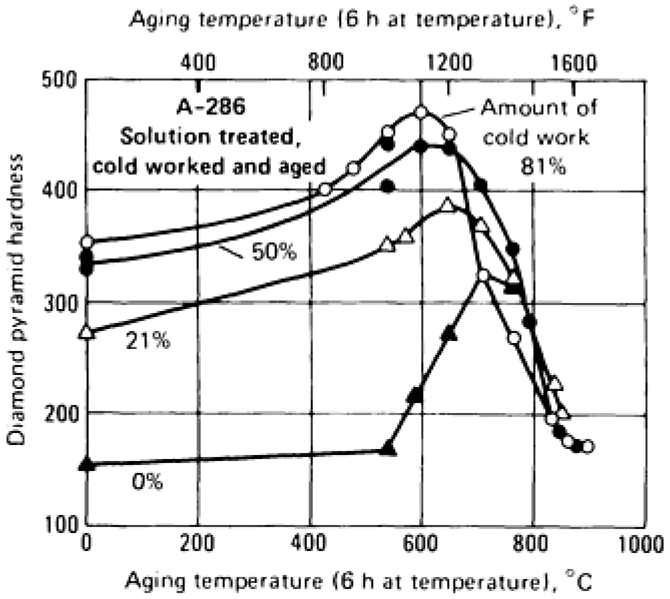

Fig. 2 Effect of cold work and aging on diamond pyramid hardness of A-286

The hardness after cold working and before aging, as well as the peak hardness after aging, increases greatly with increasing amounts of cold rolling. The temperature at which peak hardness is attained decreases with increasing amounts of reduction. The temperature at which softening occurs also decreases with increasing amounts of deformation. In Fig. 2, for example, the material cold worked 81% and then aged at 760 °C (1400 °F) for 16 h is softer than material that was not cold worked before being aged.

Double Aging of Cold Worked Parts to Obtain Uniformity of Properties. In parts that have been cold worked nonuniformly, higher-than-normal aging temperatures are sometimes used, followed by a second aging cycle at lower-than-normal aging temperature. For example, in A-286 parts with varying amounts of cold work, double aging at 760 °C (1400 °F) and 720 °C (1300 °F), respectively, provides more uniform hardness, short-time tensile properties, and creep-rupture properties than the normal 720 °C (1325 °F) aging treatment. The higher aging temperature also improves the structural stability of the part in service.

Heat Treatment of Nickel-Iron-Base Alloys Strengthened by γ'. For the nickel-iron-base superalloys strengthened by γ', heat treatments are designed to control grain size and develop the desired morphology of possible phases, primarily γ', η, and MC carbides. Precipitation of the η phase occurs at temperatures higher than the γ' solvus, and can provide control of grain growth during thermomechanical processing or during heat treatment (see, for instance, Example 3 in this article). Adding a second aging treatment can also improve properties (see Example 1).

Acceptable mechanical properties do not always result from the solution treating and aging procedure first tried for a given alloy or application. To develop specified properties, changes of the following kinds are often required:

- Adjust the solution temperature or time
- Adjust the aging temperature
- Add an intermediate (stabilizing) aging treatment at a temperature higher than that of the final aging
- Add a second (final) aging treatment at a lower temperature
- Adjust one or both aging temperatures in a double aging cycle
- Add a third aging treatment
- Increase aging time

An example for A-286 is shown in Table 7, which shows the effects of alternative approaches to the problem of insufficient notch ductility in heat treated A-286 alloy (namely, an additional aging treatment and the substitution of a higher aging temperature for single aging). Although both approaches provided required creep-rupture properties, the

higher aging temperature (with no increase in the solution-treating temperature) is recommended over the additional aging treatment.

Table 7 Effects of alternative aging treatments on rupture properties of A-286

Treatment	Creep rupture[a]		
	Life, h	**Elongation in 50 mm (2 in.), %**	Location of failure
Original heat treatment[b]			
900 °C (1650 °F), 2 h, oil quench; 720 °C (1325 °F), 16 h, air cool	7-69	. . .	**Notch**
Revised heat treatments[c]			
Original plus additional age at 650 °C (1200 °F), 12 h, air cool	74-142	5.6-7.7	**Smooth bar**

(a) Specification requirements for creep-rupture at 650 °C 1200 °F) and 450 MPa (65 ksi); life, 23 h min; no failure in notch permitted.

(b) Ten specimens tested.

(c) Five specimens for each treatment

Such procedures can be especially important when high-temperature annealing (such as during brazing) results in a coarse-grain microstructure. This is definitely the case for low-expansion superalloys, because initial aging temperature and time must be increased to provide overaging necessary for improved notched bar rupture strength if grain size is coarse.

Heat Treatment of Incoloy 901. Incoloy 901 has a γ' solvus of approximately 940 °C (1725 °F) and an η solvus of approximately 995 °C (1825 °F). Just as for A-286 (Example 3), solution heat treating above the γ' solvus but below the η solvus is used to obtain a finer grain structure (for improved tensile properties), and solution heat treating above the η solvus is used to yield a coarser grain structure (for improved creep characteristics). In addition, for Incoloy 901, a stabilization heat treatment is carried out before aging to achieve a desirable grain-boundary carbide morphology. The stabilization heat treatment promotes formation of globular MC (primarily TiC) carbides as opposed to a continuous grain boundary film. Low stress-rupture ductility is associated with a continuous intergranular MC film, while the globular MC morphology promotes good rupture life and ductility.

Heat treatment to achieve a coarser grain size of ASTM 2 to 4, with discrete intergranular carbides and a γ' strengthened matrix might be:

- Solution heat treating at 1080 to 1105 °C (1975 to 2025 °F) for 2 h (air cooling or faster)
- Stabilizing at 775 to 800 °C (1425 to 1475 °F) for 2 to 4 h (air cooling)
- Aging at 705 to 745 °C (1300 to 1375 °F) for 24 h (air cooling)

To preserve a finer grain size achieved by forging, lower solution, stabilizing, and aging temperatures are chosen. Heat treatment for finer grain size would be:

- Solution heat treating at 980 to 1040 °C (1800 to 1900 °F) for 1 to 2 h (air cooling or faster)
- Stabilizing at 705 to 730 °C (1300 to 1350 °F) for 6 to 20 h (air cooling or faster)
- Aging at 635 to 665 °C (1175 to 1225 °F) for 12 to 20 h (air cooling)

This approach typically yields a dynamically recrystallized grain size of ASTM 5 to 7, with grain boundaries strengthened by discrete carbides and possibly containing some η phase, and a matrix strengthened by γ' precipitates. Tensile properties for an Incoloy 901 forged and heat-treated turbine disk that are representative of the above two heat treatment approaches are presented for room temperature and 540 °C (1000 °F) in Tables 8 and 9, respectively. The lower solution temperature yields higher tensile strengths and ductility.

Table 8 Tensile properties at various locations in disk forgings of Incoloy 901 in two heat-treated conditions

Condition	**Test location**	**Yield strength**		**Ultimate tensile strength**		**Elongation in 50 mm (2 in.), %**	Reduction in area, %
		MPa	**ksi**	**MPa**	**ksi**		
1095 °C (2000 °F) for 2 h, water quench + 790 °C (1450 °F) for 2 h, water quench + 730 °C (1350 °F) for 24 h, air cool	Rim-radial-top	859	124.6	1178	170.8	15	**16**
	Rim-radial-bottom	907	131.6	1168	169.4	13	**14**
	Rim-radial-middle	880	127.6	1179	171.0	15	**17**
	Rim-axial-middle	858	124.4	1054	152.9	. . .	**. . .**
	Rim-tangent-middle	883	128.0	1175	170.4	13	**17**
	Bore-radial-top	874	126.8	1200	174.0	14	**17**
	Bore-radial-bottom	889	129.0	1131	164.0	. . .	**. . .**
	Bore-radial-middle	869	126.0	1172	170.0	16	**20**
	Bore-axial-middle	840	121.8	1154	167.4	. . .	**. . .**

	Bore-tangent-middle	859	124.6	1167	169.2	15	**17**
1010 °C (1850 °F) for 2 h, water quench + 730 °C (1350 °F) for 20 h, water quench + 650 °C (1200 °F) for 20 h, air cool	Rim-radial-top	924	134.0	1234	179.0	17	**20**
	Rim-radial-bottom	952	138.0	1240	179.8	17	**21**
	Rim-radial-middle	980	142.0	1258	182.4	19	**29**
	Rim-axial-middle	972	141.0	1255	182.0	21	**31**
	Rim-tangent-middle	986	143.0	1274	184.8	18	**25**
	Bore-radial-top	978	141.9	1248	181.0	18	**24**
	Bore-radial-bottom	976	141.6	1255	182.0	20	**31**
	Bore-radial-middle	968	140.4	1252	181.6	21	**34**
	Bore-axial-middle	940	136.4	1081	156.8	5	**9**
	Bore-tangent-middle	**965**	**140.0**	**1253**	**181.8**	**20**	**31**

Source: Ref 6

Table 9 Tensile properties at 1000 °F at various locations in disk forgings of Incoloy 901 in two heat-treated conditions

Condition	**Test location**	**Yield strength**		**Ultimate tensile strength**		**Elongation in 50 mm (2 in.), %**	Reduction in area, %
		MPa	**ksi**	**MPa**	**ksi**		
1095 °C (2000 °F) for 2 h, water quench + 790 °C (1450 °F) for 2 h, water quench + 730 °C (1350 °F) for 24 h, air cool	Rim-radial-top	772	112.0	1037	150.4	13	**18**

24 h, air cool	Rim-tangent-middle	772	112.0	1048	152.0	12	**18**
	Web-radial-top	781	113.2	1049	152.1	13	**21**
	Web-tangent-middle	772	112.0	1041	151.0	14	**21**
	Bore-radial-top	782	113.4	1045	151.6	13	**20**
	Bore-tangent-middle	772	112.0	1027	149.0	14	**22**
1010 °C (1850 °F) for 2 h, water quench + 730 °C (1350 °F) for 20 h, water quench + 650 °C (1200 °F) for 20 h, air cool	Rim-radial-top	832	120.6	1066	154.6	14	**27**
	Rim-tangent-middle	910	132.0	1117	162.0	17	**38**
	Web-radial-top	853	123.7	1091	158.2	20	**39**
	Web-tangent-middle	876	127.0	1089	158.0	19	**39**
	Bore-radial-top	855	124.0	1069	155.0	17	**30**
	Bore-tangent-middle	**876**	**127.0**	**1105**	**160.2**	**17**	**38**

Source: Ref 6

It is important to note, however, that not only heat treatment influences tensile properties; the control of structure during thermomechanical processing is also important. A method for achieving fine grain structures in Incoloy 901 (less than ASTM 10) by controlling structure during thermomechanical processing with η phase (Ref 2) is briefly described in the section "Thermomechanical Processing" in this article. Figure 3 shows the effect of solution temperatures from 955 °C (1750 °F) to 1095 °C (2000 °F) and grain sizes from ASTM 2 to 12 on tensile properties of Incoloy 901 processed using this method. The high-cycle fatigue strength of Incoloy 901 doubled as a result of the reduction in grain size from ASTM 2 to 12 (Table 10). The low-cycle fatigue also improved greatly with decreasing grain size (Table 11).

Table 10 Effect of grain size on the high-cycle fatigue properties of Incoloy 901 at 455 °C (850 °F)

Incoloy 901 grain size	**455 °C (850 °F) Fatigue strength (10,$_7$ cycles)**	Fatigue ratio (FS/UTS)[(a)]

	MPa	ksi	
ASTM 2	315	46	**0.32**
ASTM 5	439	64	**0.42**
ASTM 12	**624**	**91**	**0.55**

Source: Ref 2

(a) FS/UTS, fatigue strength to ultimate tensile strength.

Table 11 Effect of grain size on the low-cycle fatigue properties of Incoloy 901 at 455 °C (850 °F)

Incoloy 901 grain size	**Stress**		**Temperature**		Cycles to failure[(a)]
	MPa	**ksi**	**°C**	**°F**	
ASTM 2	205 ± 448	30 ± 65	455	850	**9,000**
ASTM 5	205 ± 448	30 ± 65	455	850	**26,000**
ASTM 12	205 ± 448	30 ± 65	455	850	**200,000+**
ASTM 2	205 ± 530	30 ± 77	455	850	**5,000**
ASTM 5	205 ± 530	30 ± 77	455	850	**16,000**
ASTM 12	**205 ± 530**	**30 ± 77**	**455**	**850**	**137,000**

(a) Average of 8 tests at 455 °C (850 °F).

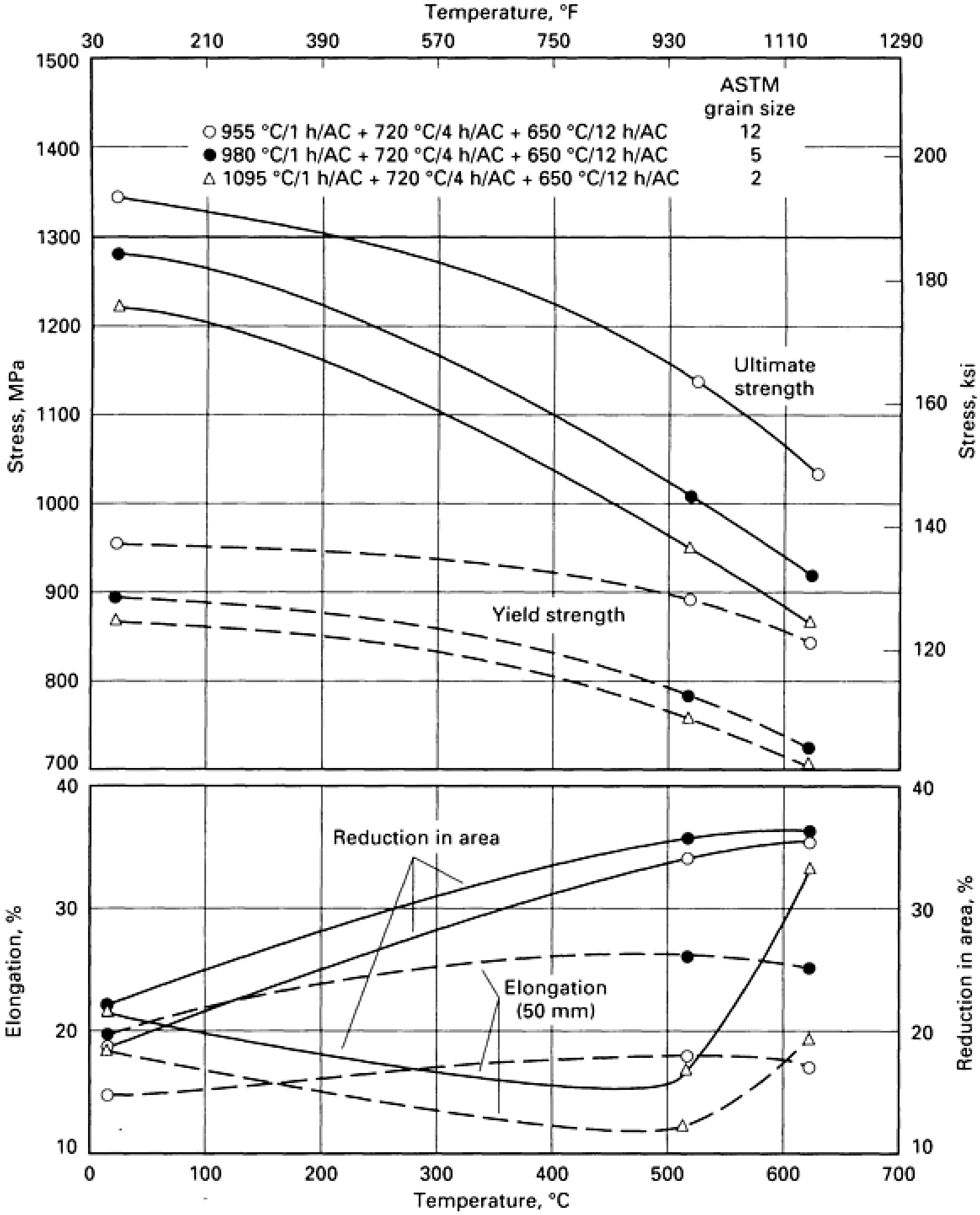

Fig. 3 Effects of temperature and grain size on tensile properties of Incoloy 901 forgings in the solution-treated, stabilized, and aged condition. AC, air cooled. Source: Ref 6

An example of the effect of the stabilization heat treatment for Incoloy 901 is given in Table 12. Adding the stabilization treatment greatly improved the rupture ductility, although at some sacrifice of yield strength and rupture life.

Table 12 Effect of stabilization on typical properties of Incoloy 901

	Ultimate tensile	**Yield strength**	**Elongation in 50 mm**	**Reduction in area, %**	Creep-rupture life, h

	strength				(2 in.), %		
	MPa	**ksi**	**MPa**	**ksi**			
Tested at 20 °C (70 °F)							
No intermediate aging[(a)]:							
Heat A	1050	152	790	115	12	13	. . .
Heat B	1080	157	790	114	17	16	. . .
With intermediate aging[(b)]:							
Heat A	1040	151	730	106	12	15	. . .
Heat B	1040	151	710	103	12	13	. . .
Tested at 650 °C (1200 °F)							
No intermediate aging[(a)]:							
Heat A	. . .	. . .	. . .	. . .	1.0	. . .	**76**
Heat B	. . .	. . .	. . .	. . .	1.5	. . .	**118**
With intermediate aging[(b)]:							
Heat A	. . .	. . .	. . .	. . .	11	. . .	**45**
Heat B	**. . .**	**. . .**	**. . .**	**. . .**	**7**		**54**

(a) Heat treatment: 1120 °C (2050 °F) for 2 h, water quench; 745 °C (1375 °F) for 24 h, air cool.

(b) Heat treatment: 1120 °C (2050 °F) for 24 h, water quench; 815 °C (1500 °F), 4 h; air cool; 745 °C (1375 °F), 24 h; air cool

Adding a second aging treatment can improve selected properties as needed. In one application, single aging at 720 °C (1325 °F) for 24 h (air cooled), after a 2-h 1085 °C (1985 °F) solution and stabilization (water quenched) failed to provide sufficient yield strength to meet specifications for room-temperature tensile strength. A second aging treatment at 650 °C (1200 °F) for 12 h (air cooled) provided additional strength to meet requirements. Table 13 lists the properties obtained by the two treatments.

Table 13 Effect of single and double aging on room-temperature properties of Incoloy 901

	Ultimate tensile strength		**Yield strength**		**Elongation in 50 mm (2 in.), %**	Reduction in area, %
	MPa	**ksi**	**MPa**	**ksi**		
Specification	1140	165	827	120	12	**15**
Single aging[(a)]	1150-1160	167-169	800-810	116-118	20-23	**24-29**
Double aging[(b)]	**1190-1210**	**173-175**	**830-890**	**121-129**	**18-22**	**24-29**

(a) Solution treated at 1085 °C (1985 °F) for 2 h, water quenched; aged at 770 °C (1450 °F) for 2 h, air cooled; aged at 720 °C (1325 °F) for 24 h, air cooled.

(b) Re-aged at 650 °C (1200 °F} for 12 h and air cooled

In another Incoloy 901 application, a problem of low room-temperature yield strength and low rupture ductility was solved by increasing the temperature of the 2-h stabilization (and air cooling) treatment from 775 °C (1425 °F) to 790 °C (1450 °F), and by adding a second aging treatment. Table 14 lists the mechanical properties obtained using the original and the revised heat treatments.

Table 14 Effects of adding a third aging treatment on properties of Incoloy 901

Ultimate tensile strength		**Yield strength**		**Elongation in 50 mm (2 in.), %**	**Reduction in area, %**	Creep-rupture elongation[(a)]
MPa	**ksi**	**MPa**	**ksi**			
Specification						
1140	165	830	120	12	15	**4% in 23 h[(b)]**
Double aging[(c)]						
160-1210[(d)]	169-175[(d)]	810-900[(d)]	118-131[(d)]	22-23[(d)]	25-30[(d)]	**4.9% in 31 h to 2.8% in 85 h[(e)]**
Triple aging[(f)]						

(a) At 650 °C (1200 °F) and 620 MPa (90 ksi).

(b) Minimum values.

(c) Solution treated at 1085 °C (1985 °F) for 2 h, water quenched; aged at 775 °C (1425 °F) for 2 h, air cooled; aged at 720 °C (1325 °F) for 24 h, air cooled.

(d) Seven tests.

(e) Three tests.

(f) Solution treated at 1085 °C (1985 °F) for 2 h; water quenched; aged at 790 °C (1450 °F) for 2 h, air cooled; aged at 720 °C (1325 °F) for 24 h, air cooled; aged at 650 °C (1200 °F) for 12 h, air cooled.

(g) Two tests

Another example showing the effect of a stabilization treatment on rupture ductility is presented in Table 15. Initially, the heat treatment included a solution treatment at 1085 °C (1985 °F) for 2 h (air cooling) and aging at 720 °C (1325 °F) for 24 h (air cooling). The rupture ductility was significantly improved, with a small penalty in rupture life, by adding an 810 °C (1490 °F) stabilization treatment.

Table 15 Effect of revision in aging treatment on creep-rupture properties of Incoloy 901

Test No.	Creep rupture[(a)]			
	Original treatment[(b)]		Revised treatment[(c)]	
	Life, h	**Elongation, %**	**Life, h**	Elongation, in 50 mm (2 in.), %
1	72	4	74	**13**
2	126	4	115	**12**
3	161	4	160	**13**
4	111	4	110	**9**
5	127	4	84	**9**
6	76	4	84	**8**

(a) At 650 °C (1200 °F) and 552 MPa (80 ksi) specified minimum: life, 23 h: elongation, 5%.

(b) Solution treated at 1085 °C (1985 °F) for 2 h, cooled; aged at 720 °C (1325 °F) for 24 h, air cooled.

(c) Same conditions as in (b) except that temperature of first aging was 810 °C (1490 °F)

Inconel X-750 heat treatment in general depends on the application and the properties desired. For service above 595 °C (1100 °F), optimum properties in rods, bars, and forgings are achieved by:

- Solution treating at 1150 °C (2100 °F) for 2 to 4 h (air cooling)
- Stabilization treating at 845 °C (1550 °F) for 24 h (air cooling)
- Aging at 705 °C (1300 °F) for 20 h (air cooling)

This treatment maximizes creep and rupture strength.

For service below 595 °C (1100 °F), the optimum heat treatment is:

- Solution heat treating at 980 °C (1800 °F) for 1 h (air cooling)
- Aging at 730 °C (1350 °F) for 8 h (furnace cooling) to 620 °C (1150 °F)
- Hold for total time of 18 h and then air cool

This treatment maximizes tensile properties. Heat treatments for various product forms of Inconel X-750 are summarized in Table 16.

Table 16 Typical thermal treatments for precipitation hardening of Inconel X-750 products

Form	**Desired property**	Thermal treatment
Rods, bars, and forgings	Strength and optimum ductility up to 595 °C (1100 °F)	**Equalize: 885 °C (1625 °F), 24 h, air cool Precipitation: 705 °C (1300 °F), 20 h, air cool**
	Optimum tensile strength up to 595 °C (1100 °F)	**Solution: 980 °C (1800 °F), air cool Furnace-cool, precipitation: 730 °C (1350 °F), 8 h, furnace cool to 620 °C (1150 °F), hold 8 h, air cool**
	Maximum creep strength above 595 °C (1100 °F)	**Full solution: 1150 °C (2100 °F), 2-4 h, air cool Stabilize: 845 °C (1550 °F), 24 h, air cool Precipitation: 705 °C (1300 °F), 20 h, air cool**
Sheet, strip, and plate	High strength at high temperatures	**Annealed + Precipitation: 705 °C (1300 °F), 20 h, air cool**
	High strength and higher tensile properties to 705 °C (1300 °F)	**Annealed + Furnace-cool, precipitation: 730 °C (1350 °F), 8 h, furnace cool to 620 °C (1150 °F), hold 8 h, air cool[(a)]**

Tubing	High strength at high temperatures	**Annealed + Precipitation: 705 °C (1300 °F), 20 h, air cool**
No. 1 temper wire	Service up to 540 °C (1000 °F)	**Solution treated + cold drawn (15-20%) + 730 °C (1350 °F), 16 h, air cool**
Spring temper wire	Service up to 370 °C (700 °F)	**Solution treated + cold drawn (30-65%) + 650 °C (1200 °F), 4 h, air cool**
	Service at 480-650 °C (900-1200 °F)	**Cold drawn (30-65%) + 1150 °C (2100 °F), 2 h, air cool + 845 °C (1550 °F), 24 h, air cool + 705 °C (1300 °F)). 20 h, air cool**

Source: Ref 7

(a) Equivalent properties in a shorter time can be developed by the following precipitation treatment: 760 °C (1400 °F)) for 1 h. furnace cool (FC) to 620 °C (1150 °F)). hold 3 h, air cool (AC).

Heat Treatment of Nickel-Iron-Base Alloys Strengthened by γ''. The heat treatment of nickel-iron-base superalloys strengthened by the γ'' phase are fashioned using many of the same principles that guide the heat treatments of A-286 and Incoloy 901. In these alloys, δ phase, which is present at temperatures above the γ'' solvus, can be used for grain size control, just as η phase can be utilized in A-286 or Incoloy 901. However, careful heat treatment is required to ensure adequate precipitation of γ'' instead of the δ(orthorhombic) phase of the same Ni_3Nb composition. The latter is invariably incoherent and does not confer strength when present in large quantities. In the absence of iron, or at temperatures and times shown in the transformation diagram of an iron-containing alloy (Fig. 4), the δ phase forms instead of the γ'' phase.

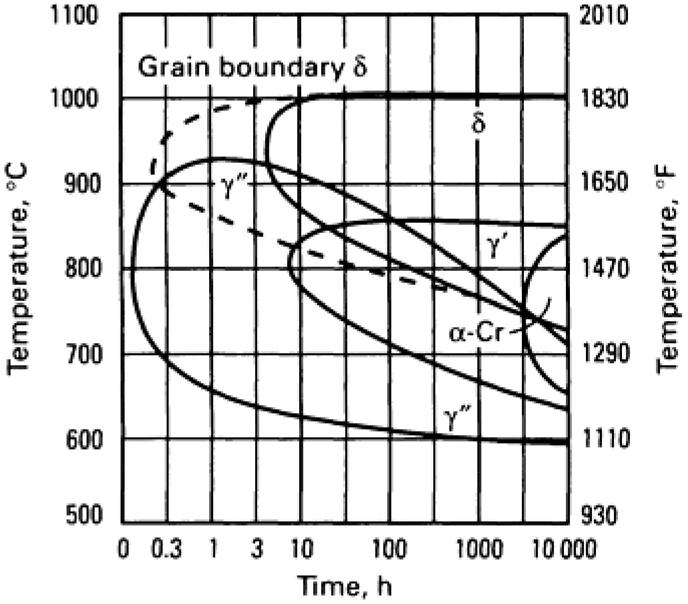

Fig. 4 Transformation diagram for vacuum-melted and hot-forged Inconel 718 bar. Source: Ref 8

The γ'' phase forms in alloys such as Inconel 718 and Inconel 706. In Inconel alloy 718, γ'' forms in the range of 705 °C (1300 °F) to 900 °C (1650 °F) and has a solvus temperature of about 910 °C (1675 °F). The δ phase, depending on exposure time (Fig. 4), precipitates in the approximate temperature range of 870 °C (1600 °F) to 1010 °C (1850 °F) and has a solvus temperature of about 1010 °C (1850 °F). The alloy can be worked and solution heat treated above the δ

solvus, or at a temperature below the δ solvus but above the γ'' solvus for grain size control. Gamma double prime often precipitates together with γ' in Inconel 718 (Fig. 4), but γ'' is the principal strengthening phase under such circumstances. Unlike γ', which causes strengthening through the necessity to disorder the particles as they are sheared, γ'' strengthens by virtue of high coherency strains in the lattice. More detailed descriptions of the physical metallurgy of γ'/γ'' alloys appear in Volume 1 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.*

Heat Treatment of Inconel 718. Inconel 718 is usually used in the solution and aged condition; the exact conditions of the temperatures, times, and cooling rates depend on the application and mechanical property needs. Many aerospace applications requiring high tensile and fatigue strength, as well as good stress-rupture properties, use a solution treatment below the δ solvus and a two-step aging treatment as follows:

- Solution heat treat at 925 to 1010 °C (1700 to 1850 °F) for 1 to 2 h (air cooling or faster)
- Age at 720 °C (1325 °F) for 8 h followed by furnace cooling to 620 °C (1150 °F)
- Hold at 620 °C (1150 °F) for a total aging time of 18 h (air cooled)

Higher strength levels are achieved by forging below the δ solvus, quenching after forging, and performing the two-step aging process directly without a solution treatment. This approach, termed direct aging, requires high quality, uniform billet material, and careful control of the forging process to achieve the high strengths and the uniform ASTM 10 grain size throughout the forging.

The effect of the solution temperature, or direct aging (no solution treatment), on tensile and stress-rupture properties of Inconel 718 is shown in Table 17. The highest tensile strength is achieved with the direct-aged material, at some sacrifice of stress-rupture life. The lower solution temperatures produce better strength, while the higher solution temperatures (up to 1010 °C, or 1850 °F) result in better stress-rupture strength.

Table 17 Properties of Inconel 718 as function of heat treatment

Solution treatment[(a)]	**0.2% yield strength**		Room-temperature tensile properties						
			Ultimate tensile strength		**Elongation, %**	**Reduction in area, %**	Stress rupture at 650 °C (1200 °F) with 690 MPa (100 ksi)		
	MPa	**ksi**	**MPa**	**ksi**			**Life, h**	**Elongation, %**	Reduction in area, %
None (direct aged)	1330	193	1525	221	19	34	95	24	**31**
940 °C (1725 °F), 1 h, air cooled	1240	180	1460	212	18	34	194	11	**16**
955 °C (1720 °F), 1 h, air cooled	1180	171	1420	206	20	38	122	14	**19**
970 °C (1775 °F), 1 h, air cooled	1145	166	1405	204	23	41	218	13	**15**
980 °C (1800 °F), 1 h, air cooled	1172	170	1405	204	24	43	200	6	**10**

1010 °C (1850 °F), 1 h, air cooled	1185	172	1390	202	22	46	270	6	**12**
1040 ° (1900 °F), 1 h, air cooled	**1165**	**169**	**1365**	**198**	**25**	**48**	**225**	**2**	**8**

Source: Ref 9

(a) All aged 720 °C (1325 °F) for 8 h, cool 55 °C/h (100 °F/h) to 620 °C (1150 °F), hold for 8 h, air cool (AC).

(b) (b) Notch sensitive at K_t = 3.8.

Typical properties for Inconel 718 in three forms are plotted as a function of temperature in Fig. 5. The standard solution-treated and aged condition of Inconel 718 with an average grain size of ASTM 4 to 6 is labeled STD 718. This material condition is used for noncritical or difficult-to-make shapes. High-strength 718, labeled HS 718, with ASTM 8 average grain size, is used for more highly stressed components with less complex configurations. This material is also solution-treated and aged, but tighter controls are placed on input billet material and the forging practice. The highest strengths and fatigue properties are achieved by Inconel 718 in the direct-aged condition, termed DA 718, with ASTM 10 average grain size. Figure 5(b) again illustrates that these strengths are obtained at some reduction of stress-rupture life at low stress and high temperature. To obtain the DA 718 properties in Fig. 5, very high-quality and uniform input material is required along with tightly controlled forging temperatures and processing.

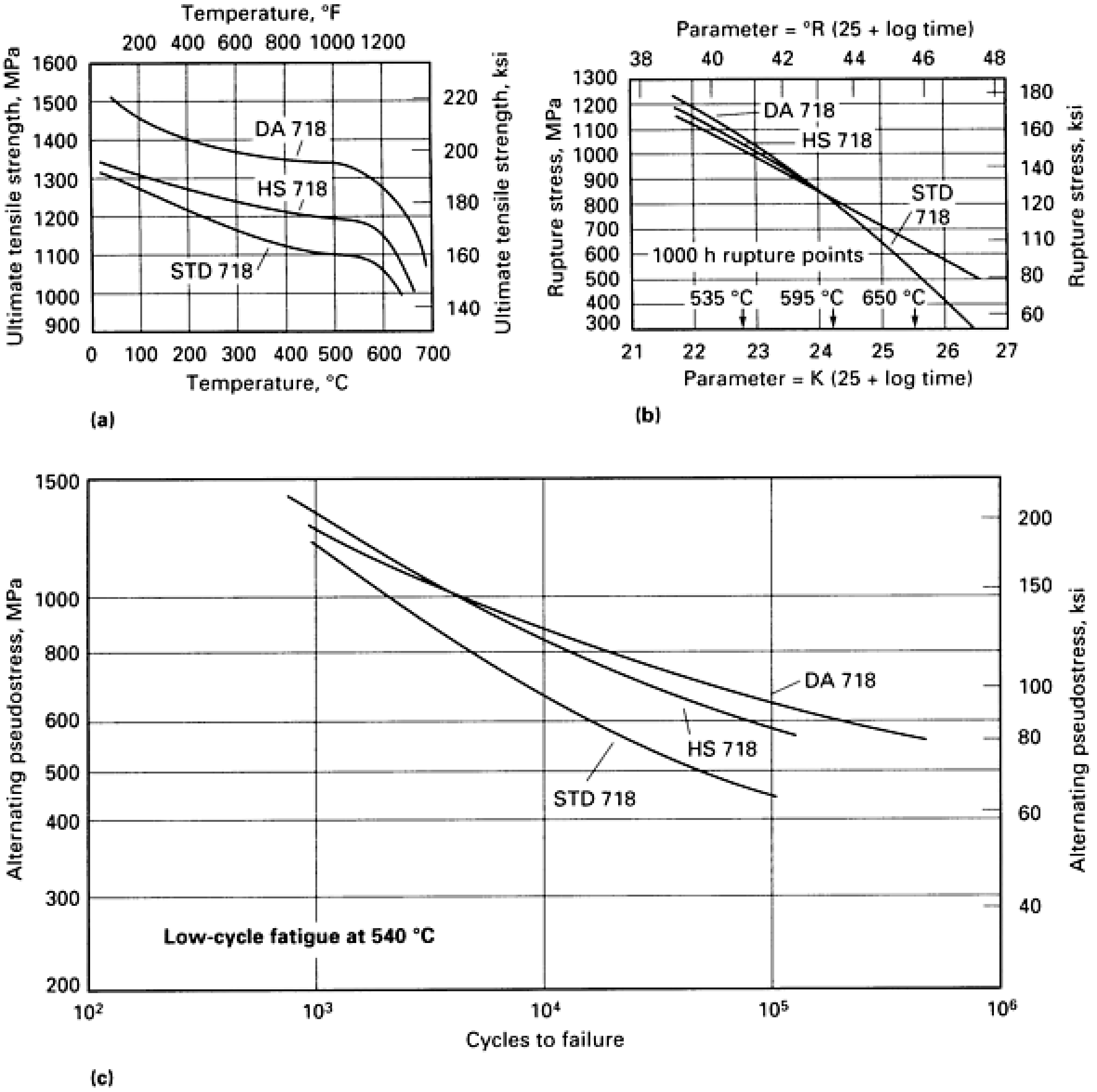

Fig. 5 Typical properties of Inconel 718 as a function of processing. (a) Ultimate tensile strength. (b) Rupture stress. (c) Fatigue at 540 °C (1000 °F). Source: Ref 1

A slightly different solution-and-age heat treatment is sometimes used for optimum ductility, impact properties, and low-temperature toughness in heavy sections, although it can also produce notch brittleness in stress rupture. This heat treatment involves:

- Solution heat treatment at 1040 to 1065 °C 1900 to 1950 °F) for $\frac{1}{2}$ to 1 h, air cooled (or faster)
- Aging at 760 °C (1400 °F) for 10 h with furnace cool to 650 °C (1200 °F)
- Hold at 650 °C (1200 °F) for a total aging time of 20 h (air cool)

Tensile properties as a function of the two heat treatment approaches are listed in Table 18 for hot-rolled rounds of various diameters and in Table 19 for pancake forgings.

Table 18 Tensile properties in longitudinal orientations of Inconel 718 hot-rolled rounds of several sizes and in various heat-treated conditions

Diameter		Condition	Yield strength		Ultimate tensile strength		Elongation in 50 mm (2 in.), %	Reduction in area, %
mm	in.		MPa	ksi	MPa	ksi		
16	$\frac{5}{8}$	As-rolled	566	82.1	962	139.5	46	**60**
		955 °C (1750 °F) 1 h, air cool	546	79.2	958	139.0	50	**49**
		1065 °C (1950 °F) 1 h, air cool	332	48.2	803	116.5	61	**66**
		955 °C (1750 °F) 1 h, air cool + age[(a)]	1239	179.8	1435	208.2	21	**39**
		1065 °C (1950 °F) 1 h, air cool + age[(b)]	1086	157.5	1339	194.2	22	**30**
25	1	As-rolled	448	65.0	896	130.0	54	**67**
		955 °C (1750 °F) 1 h, air cool	445	64.5	889	129.0	55	**61**
		1065 °C (1950 °F) 1 h, air cool	359	52.0	776	112.5	64	**68**
		955 °C (1750 °F) 1 h, air cool + age[(a)]	1206	175.0	1389	201.5	20	**36**
		1065 °C (1950 °F) 1 h, air cool + age[(b)]	1048	152.0	1296	188.0	21	**34**
38	$1\frac{1}{2}$	As-rolled	727	105.5	1013	147.0	40	**52**
		955 °C (1750 °F) 1 h, air cool	500	72.5	976	141.5	46	**45**
		1065 °C (1950 °F) 1 h, air cool	379	55.0	827	120.0	58	**60**
		955 °C (1750 °F) 1 h, air cool + age[(a)]	1155	167.5	1413	205.0	20	**28**
		1065 °C (1950 °F) 1 h, air cool + age[(b)]	1055	153.0	1316	191.0	24	**36**
100	4	955 °C (1750 °F) 1 h, air cool	379	55.0	810	117.5	53	**52**
		1065 °C (1950 °F) 1 h, air cool	331	48.0	776	112.5	60	**63**
		955 °C (1750 °F) 1 h, air cool + age[(a)]	1138	165.0	1323	192.0	17	**24**

		1065 °C (1950 °F) 1 h, air cool + age(b)	**1138**	**165.0**	**1348**	**195.5**	**21**	**34**

Source: Ref 10

(a) Age 720 °C (1325 °F) for 8 h, furnace cool to 620 °C (1150 °F), hold for a total age of 18 h, air cool.

(b) Age 760 °C (1400 °F) for 10 h, furnace cool to 650 °C (1200 °F), hold for a total age of 20 h, air cool.

Table 19 Tensile properties of Inconel 718 pancake forgings of various sizes in different heat-treated conditions

Forging size	**Condition**	**Orientation**	**Yield strength**		**Ultimate tensile strength**		**Elongation in 50 mm (2 in.), %**	Reduction in area,%
			MPa	**ksi**	**MPa**	**ksi**		
200 mm diam (8 in.) × 63.5 mm (2 $\frac{1}{2}$ in.)	Solutioned 925 °C (1700 °F) for 1 h and air cooled + age(a)	Radial:						
		Top edge	1096	159.0	1255	182.0	10	**10.5**
		Center	1103	160.0	1351	196.0	24	**33.0**
		Bottom edge	1100	159.5	1286	186.5	16	**19.0**
		Tangential:						
Top edge	1248	181.0	1441	209.0	19	27.5		
Bottom edge	1234	179.0	1448	210.0	18	29.5		
175 mm diam (7 in.) × 25 mm (1 in.)	Solutioned 1065 °C (1950 °F) for $\frac{1}{2}$ h and air cooled + age(b)	Radical	1055	153.0	1307	189.5	19	**29.8**
		Tangential	1056	153.2	1277	185.2	19	**27.2**
140 mm diam (5 $\frac{1}{2}$ in.) × 25 mm (1 in.)	Solutioned 980 °C (1800 °F) for 1 h, water quenched + age(a)	Radial	1189	172.5	1398	202.8	19	**25.6**
	Solutioned 1065 °C (1950 °F) for 1 h, water quenched + age(b)	**Radial**	**1048**	**152.0**	**1310**	**190.0**	**18**	**24.3**

(a) Age 720 °C (1325 °F) for 8 h, furnace cool to 620 °C (1150 °F), hold for total age of 18 h.

(b) Age 760 °C (1400 °F) for 10 h. furnace cool to 650 °C (1200 °F), hold for total age of 20 h.

For applications of Inconel 718 in the oil and gas industry, the very high strength levels needed in aerospace applications are unnecessary. Instead, heat treatments are designed to address other needs, including good toughness with adequate strength and resistance to hydrogen embrittlement and stress-corrosion cracking. Single-step aging treatments are used to develop mechanical properties in oil and gas applications. Solution treatment in the range of 1010 to 1065 °C (1850 to 1950 °F) is followed by a single-step aging at 650 to 815 °C (1200 to 1500 °F). Room-temperature properties achieved by single-step and two-step aging treatments are compared in Table 20. The single-step aging treatments result in lower strengths but higher fracture toughness. Both general and pitting corrosion resistance can be reduced at higher aging temperatures. This behavior has been attributed to carbide formation and chromium depletion in localized areas. The trade-off between strength and toughness is illustrated in Fig. 6, which shows yield strength and toughness as a function of aging temperature for material after solution-and-age treatment. The exact choice of heat treatment parameters depends on the balance of properties required.

Table 20 Effect of heat treatment on typical room-temperature properties of Inconel 718

Heat treatment	**Yield strength (0.2% offset)**		**Tensile strength**		**Elongation, %**	**Reduction in area, %**	**Hardness, HRC**	Fracture toughness J_{1c}	
	MPa	**ksi**	**MPa**	**ksi**				**MPa · m**	psi · in.
Solution anneal: 1025 °C (1875 °F) for 1 h, water quench; Age: 790 °C (1450 °F) for 6-8 h, air cool	855	124	1200	174	28	51	35	334	**1908**
Solution anneal: 1050 °C (1925 °F) for 1 h, water quench; Age: 760 °C (1400 °F) for 6 h, air cool	855	124	1205	175	27	42	38	286	**1631**
Solution anneal: 955 °C (1750 °F) for 2 h, water quench or air cool; Age: 720 °C (1325 °F) for 8 h, cool 55 °C/h (100 °F/h) to 620 °C (1150 °F), hold 8 h, air cool	1130	164	1330	193	23	48	42	100	**572**
Solution anneal: 1050 °C (1925 °F) for 1 h, air cool; Age: 760 °C (1400 °F) for 6 h, furnace cool 55 °C/h (100 °F/h) to 650 °C (1200 °F), hold 8 h, air cool	1255	182	1415	205	17	41	44	84	**480**
Solution anneal: 1065 °C (1950 °F) for 1 h, air cool	**1110**	**161**	**1310**	**190**	**19**	**. . .**	**40**	**96**	**546**

Source: Ref 11

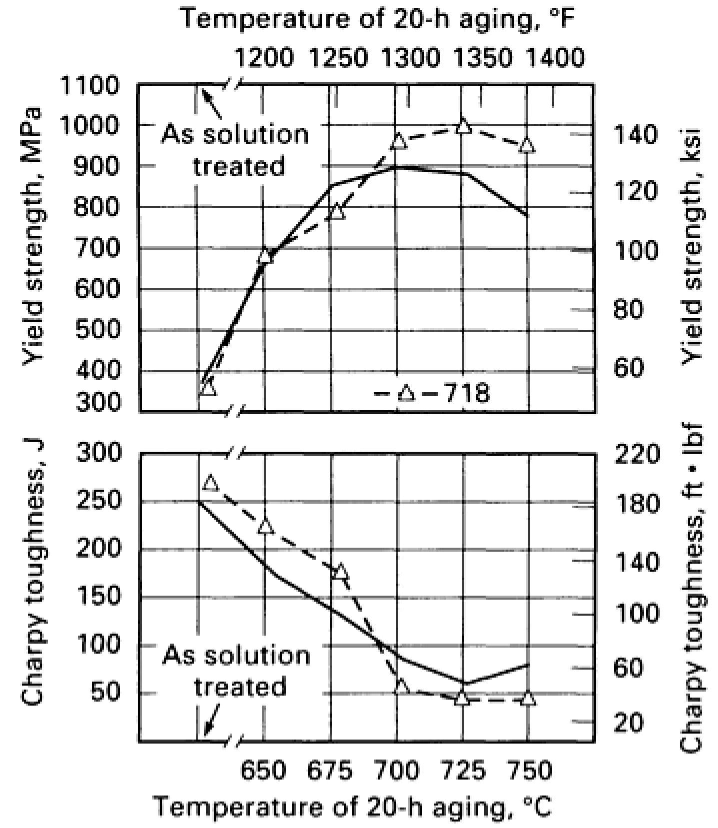

Fig. 6 Effect of aging temperature on the yield strength and toughness of Inconel 718. Source: Ref 12

Precipitation-Strengthened Nickel-Base Superalloys

To achieve optimal microstructures for the intended applications, wrought precipitation-strengthened nickel-base superalloys usually receive a solution heat treatment stage followed by one or more precipitation aging heat treatments. The solution heat treatment may be above or below the γ' solvus temperature depending on a number of factors, including intended grain size, whether strengthening from warm working is to be retained, the desired γ' morphology, and considerations of carbide precipitation. These microstructural goals are determined by the property requirements. Aging heat treatments are designed to precipitate γ' and control its volume fraction, size, morphology, and distribution. The aging heat treatments may also precipitate and stabilize various carbide phases and control their morphologies. The temperatures and times of aging heat treatments depend on the alloy composition and on the specific property goals.

The simplest heat treatment, for wrought alloys with relatively low alloying contents and low γ' volume fractions, is a high-temperature solution treatment followed by air or more rapid cooling, and then low-temperature aging. The solution heat treatment temperature is above the γ' solvus (thus dissolving γ' and possibly carbides, depending on the alloy) and causes recrystallization and grain growth to a desired size. The aging precipitates γ' homogeneously and $M_{23}C_6$ typically at grain boundaries. An example of this basic method for Nimonic 80A or Nimonic 90 is as follows:

- Solution heat treatment at 1080 °C (1975 °F) for 8 h and air cool
- Aging at 700 °C (1290 °F) for 16 h and air cool

The hardness changes as a result of aging Nimonic 80A at various temperatures after a solution exposure of 1080 °C (1975 °F) for h and water quenching are shown in Fig. 7. The curves exhibit normal precipitation hardening characteristics; the lower temperatures and longer aging times provide the highest hardnesses.

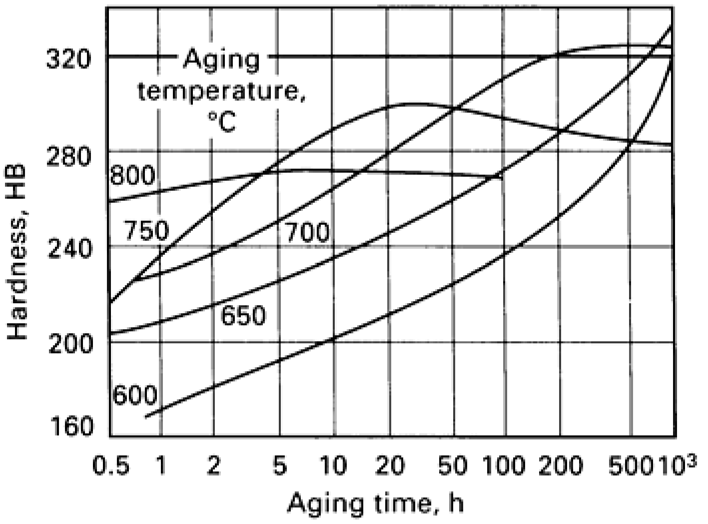

Fig. 7 Hardness changes on aging Nimonic 80A at various temperatures. Prior treatment: solution 1080 °C (1975 °F) for 8 h, water quenched. Source Ref 13

Heat treatment affects the types and morphologies of carbides and also the γ' morphology in more highly alloyed superalloys with higher γ' volume fractions. Consideration of these effects has led to modification of the above two-step (solution treat-and-age)treatments. In Nimonic 80A, the above two-step heat treatment yielded good tensile and short-time rupture properties, but did not stabilize the microstructure sufficiently to produce optimized properties for long-term elevated-temperature service. For a stabilized microstructure, a higher-temperature aging cycle of 850 °C (1560 °F) for 24 h (air cooling) was added before the final 700 °C (1290 °F) aging. The purpose of the stabilization treatment is to force the development of grain boundary $M_{23}C_6$ carbides by a reaction in which MC carbides react with matrix constituents to form $M_{23}C_6$ carbides and γ'. Thus, the stabilization aging heat treatment results in grain boundaries with coarse discrete $M_{23}C_6$ carbides surrounded by a layer of γ'. The stabilization of the grain boundary carbides led to better long-time (low stress, high temperature) stress-rupture properties as shown in Fig. 8.

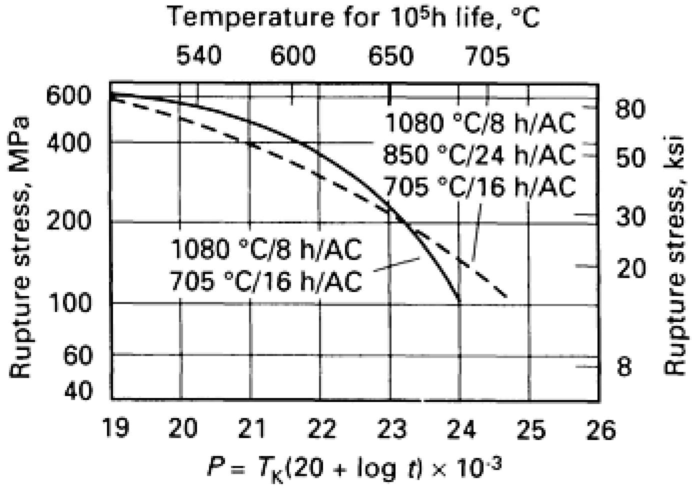

Fig. 8 Effect of increasing intermediate aging on rupture properties of wrought Nimonic 80A. AC, air cooled. Source: Ref 14

Carbide distributions can also be controlled by modifying the temperature for solution treatment. For example, a solution treatment of René 41 at 1175 °C (2150 °F) leads to precipitation of a grain-boundary film of $M_{23}C_6$, with deleterious effects on mechanical properties. Therefore, a lower solution treatment temperature (about 1075 °C, or 1970 °F) is used to

preserve the fine-grain as-worked structure with well-dispersed M_6C (Ref 15). With exposures of about 1075 to 1095 °C (1970 to 2000 °F) for 8 to 10 h, M_6C remains stable but γ' goes into solution (Fig. 9).

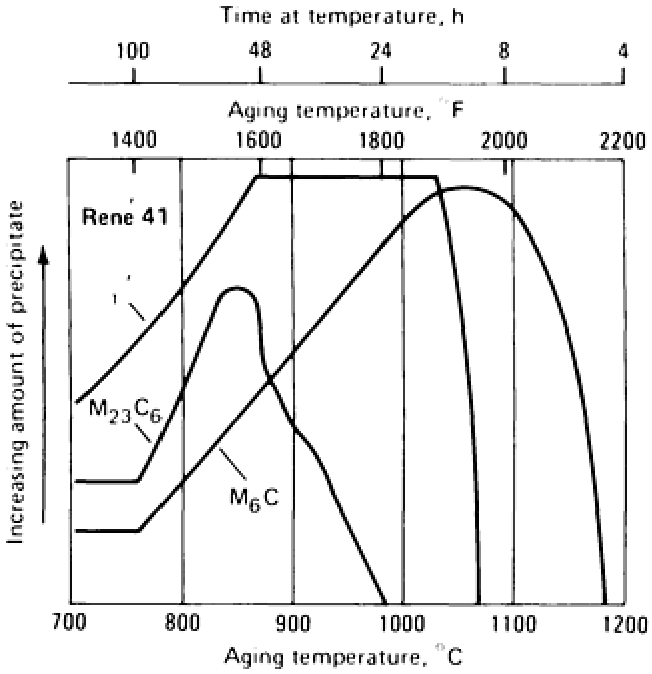

Fig. 9 Relative amounts of precipitates resulting from aging René 41 at various times and temperatures after solution treating at 1205 °C (2200 °F) and water quenching

Udimet 500 is typical of wrought precipitation-hardened superalloys that contain MC and $M_{23}C_6$ carbides and are strengthened by γ'. For a good balance of tensile strength and stress-rupture life, the alloy is given a stabilization treatment before final aging (see Example 2 in this article). If high room-temperature tensile properties are desired and stress-rupture requirements are less important, a two-step heat treatment consisting of just the 1080 °C (1975 °F) solution treatment and the 760 °C (1400 °F) age treatment may be utilized. Table 21 shows how the room-temperature tensile ductility and ultimate strength in Udimet 500 were improved by eliminating the 845 °C (1550 °F) stabilization treatment.

Table 21 Effect of eliminating intermediate aging on typical room-temperature mechanical properties of Udimet 500

	Ultimate tensile strength		**Yield strength (0.2% offset)**		**Elongation in 50 mm (2 in.), %**	Reduction in area, %
	MPa	**ksi**	**MPa**	**ksi**		
Specified min	1030	150	690	100	10	**15**
Obtained with intermediate aging[(a)]						
Test 1	1030	149	830	120	7	**11**
Test 2	970	141	810	118	4	**5**

Obtained without intermediate aging[(b)]						
Test 1	1170	170	800	116	14.5	**17**
Test 2	**1230**	**179**	**850**	**123**	**14**	**16**

(a) Heat treatment: 4 h at 1080 °C (1975 °F), air cool; 24 h at 845 °C (1550 °F), air cool (intermediate aging); 16 h at 760 °C (1400 °F), air cool.

(b) Same as (a), but without intermediate aging

For optimum creep strength, an initial high-temperature solution treatment may be added to develop a coarser grain size. For Udimet 500, a four-step heat treatment includes an initial solution treatment at 1175 °C (2150 °F) for 2 h (with air cooling) followed by the three-step heat treatment described in Example 2 of this article.

Waspaloy is a widely used superalloy for which the heat treatment approach is similar to that for Udimet 500. The heat treatment temperatures and times vary according to working temperatures and microstructural goals. For applications (such as turbine disks) requiring fine grain structures for optimum tensile, stress rupture, and cyclic properties, a typical heat treatment is:

- Partial solution treatment below the γ' solvus at 995 to 1040 °C (1825 to 1900 °F) for 4 h with air cooling (or faster)
- Stabilization at 845 °C (1550 °F) for 4 h with air cooling
- Aging at 760 °C (1400 °F) for 16 h with air cooling

Before requirements for finer grain sizes led to the use of lower solution temperatures, higher solution temperatures and longer stabilization treatments were used. This was because the higher solution temperature more effectively dissolved carbides, and because a longer stabilization (for example, 845 °C, or 1550 °F for 24 h with air cooling) was required in order to restore sufficient ductility by spheroidizing the reprecipitating grain-boundary carbides. Now, the lower-temperature solution treatment starts the carbide precipitation process, and a shorter stabilization can be used.

The Waspaloy heat treatment for applications (such as turbine blades) requiring better creep resistance (and therefore a coarser grain size) involves a higher solution temperature above the γ' solvus and a longer stabilization exposure. For turbine blade applications, Waspaloy typically receives:

- 1080 °C (1975 °F) for 4 h with air cooling (or faster)
- 845 °C (1550 °F) for 24 h with air cooling
- 760 °C (1400 °F) for 16 h with air cooling

Figure 10 illustrates the effect of the different heat treatments on the tensile and stress-rupture properties of Waspaloy. A disk heat treatment yields better tensile and rupture properties at lower temperatures. The blade heat treatment results in better rupture strength at higher temperatures.

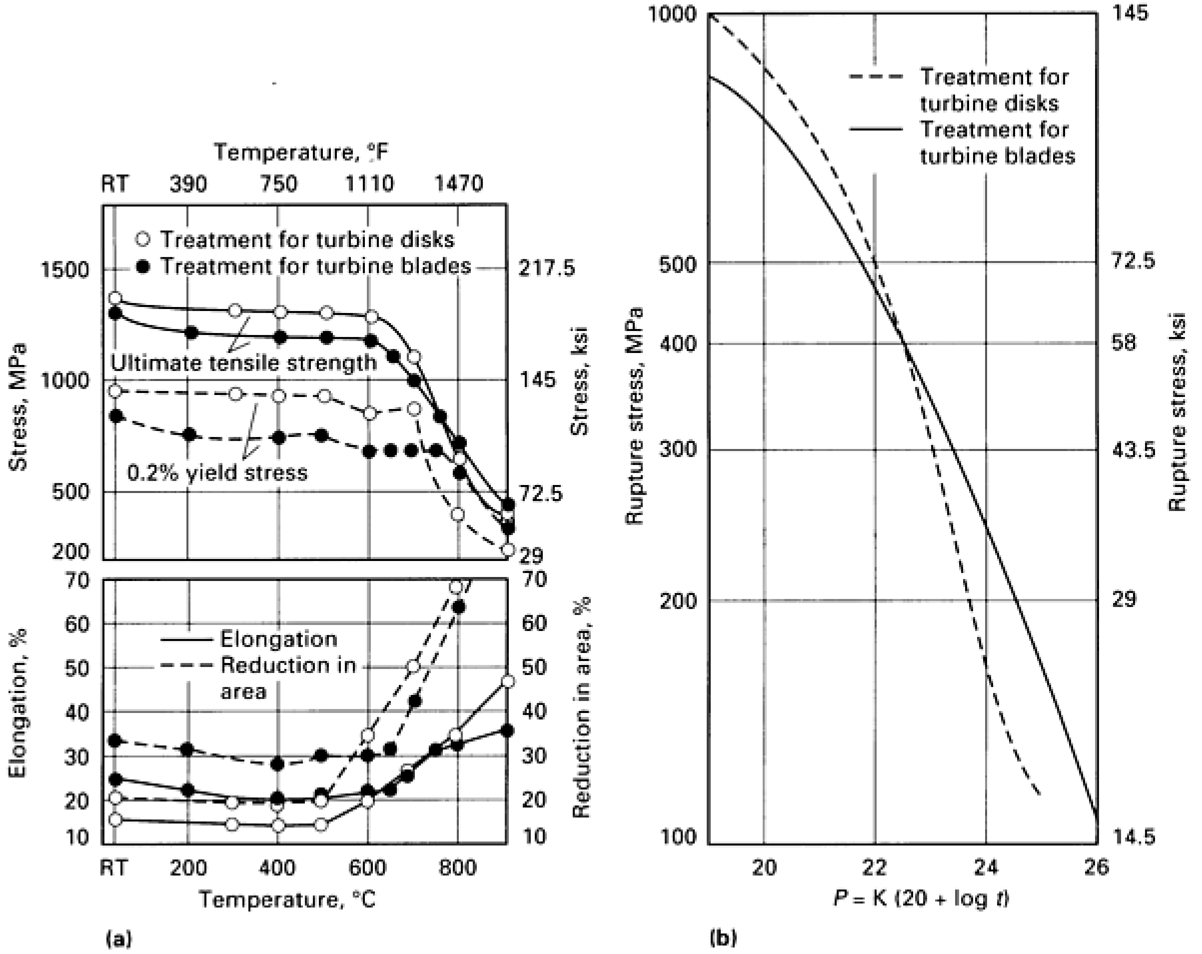

Fig. 10 Influence of different treatments on (a) the tensile properties of Waspaloy and (b) the Larson-Miller plot of Waspaloy. Source: Ref 16

Udimet 700 (or Astroloy, which is very similar) and Udimet 710 are examples of more highly alloyed wrought superalloys with a relatively high μ' volume fraction of about 40%. Different heat treatments are administered depending on whether a coarse-grained microstructure for turbine bucket and vane applications is desired, or a fine-grained microstructure for disk applications. For a coarse-grained microstructure the following heat treatment is typical:

- 1175 °C (2150 °F) for 4 h with air cooling
- 1080 °C (1975 °F) for 4 h with air cooling
- 845 °C (1550 °F) for 24 h with air cooling
- 760 °C (1400 °F) for 16 h with air cooling

The 1175 °C (2150 °F) annealing is a full-solution treatment above the γ' solvus that dissolves the precipitate and allows the grains to coarsen. During the 1080 °C (1975 °F) aging exposure, about half of the γ' that is ultimately formed precipitates and forms a coarse dispersion of particles 0.2 to 0.6 μm in diameter. The two subsequent aging heat treatments build precipitates of fine γ' between the coarser γ' particles, and also precipitate $M_{23}C_6$ at grain boundaries. This heat treatment yields an average grain size of about 225 μm with γ' volume fraction of about 45%. The coarse-grained structure is tailored for good creep-rupture strength.

For a fine-grained microstructure the heat treatment is of the following form:

- 1105 °C (2020 °F) for 4 h with air cooling (or faster)
- 870 °C (1600 °F) for 8 h with air cooling

- 980 °C (1800 °F) for 4 h with air cooling
- 650 °C (1200 °F) for 24 h with air cooling
- 760 °C (1400 °F) for 8 h with air cooling

The 1105 °C (2020 °F) anneal is a partial solution treatment below the γ' solvus that retains some of the γ' to limit grain growth. The subsequent treatments precipitate carbides and γ'. The two-step exposures of first 870 °C (1600 °F) and then 980 °C (1800 °F) are designed to maximize first the nucleation of precipitates and then the rate of growth of the precipitates. The average grain size of the structure produced is about 11 μm with a γ' volume fraction of about 35%. The fine-grained structure has better mechanical properties at turbine disk application temperatures than that from coarse-grained heat treatment, which is designed for higher-temperature applications.

The effect of the amount of cold working on the recrystallization and grain growth during subsequent solution treating of the nickel-base superalloy Nimonic 90 is shown in Fig. 11. The effect is similar to the behavior shown for A-286 in Fig. 1. The critical amount of deformation that leads to abnormally large grains is in the range of 2 to 10% reduction in thickness, and the grain growth accelerates rapidly at temperatures above 1100 °C (2010 °F).

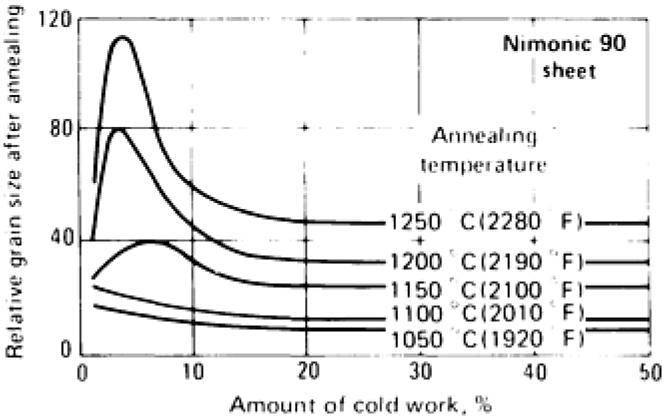

Fig. 11 Effect of cold work and annealing on grain size for Nimonic 90 sheet cold rolled in steps from 1.8 to 0.9 mm (0.072 to 0.036 in.) thick and annealed at five temperatures

The precipitation-hardened superalloys that undergo extensive deformation processing, as in sheet forming, usually require in-process annealing to maintain temperatures, relieve forming stresses, and enhance microstructural changes. The annealing practice can also have a marked effect on response to solution treating and aging. This is illustrated by the following two examples for René 41. Like solution-treatment temperatures (Fig. 9), high annealing temperatures can dissolve M_6C carbides, which are useful in preventing formation of $M_{23}C_6$ grain boundary films during aging.

Example 4: Effect of Annealing Temperature on the Grain-Boundary Carbides and Ductility of René 41 Sheet.

In one case, parts formed from René 41 sheet showed strain age cracking after solution treatment at 1080 °C (1975 °F) for $\frac{1}{2}$ h, air cooling, and then aging at 760 °C (1400 °F) for 16 h. Cracking has been attributed to a carbide network in the grain boundaries. Cause of the carbide network was traced to in-process annealing at 1180 °C (2150 °F). At 1180 °C (2150 °F) the M_6C carbide was dissolved. Subsequent exposure to temperatures between 760 and 870 °C (1400 and 1600 °F) produced an $M_{23}C_6$ carbide network in the grain boundaries that reduced ductility to an unacceptable level. If the annealing temperature is kept below 1095 °C (2000 °F), M_6C does not dissolve (Fig. 9) and ductility can be improved. A similar effect can occur in weldments of nickel-base alloys if they are annealed at temperatures above 1095 °C (2000 °F).

Example 5: Effect of Thermomechanical Processing on the Grain-Boundary Carbides and Ductility of René 41 Bar Stock.

A problem similar to that described in the preceding example occurred in René 41 bar stock. Grain-boundary carbide network reduced ductility and caused difficulty (sometimes cracking) during forming and welding. Investigation of the cause of the grain-boundary network indicated that the bar stock was produced with a final rolling temperature of 1180 °C (2150 °F). Light reductions were taken during final rolling to ensure proper size for the finished bar stock and to eliminate the possibility of surface tearing. This high rolling temperature, coupled with relatively light reductions (in the range of 2 to 3%), produced grain-boundary network because:

- The M_6C carbides were dissolved at the rolling temperature
- Slow cooling through the range of 870 to 760 °C (1600 to 1400 °F) produced $M_{23}C_6$ in an unfavorable morphology (grain-boundary carbide film)

Rolling temperatures of 1150 °C (2100 °F) maximum, coupled with a final reduction in rolling of at least 10 to 15%, eliminated the grain-boundary carbide film and produced bars that could be welded and formed.

Solid-Solution-Strengthened Iron-, Nickel- and Cobalt-Base Superalloys

Solid-solution-strengthened iron-, nickel-, and cobalt-base superalloys are generally distinguishable from the precipitation-strengthened superalloys by their relatively low content of precipitate-forming elements such as aluminum, titanium, or niobium. There are, of course, some exceptions to this, particularly as regards niobium content. Typical compositions for precipitation-strengthened and solid-solution-strengthened superalloys are given in Table 1.

As their classification implies, these alloys derive a significant proportion of their strength from solution strengthening, most typically associated with a high content of refractory metals, such as molybdenum or tungsten. Not to be overlooked, however, is the equally significant contribution of carbon, which serves both as a potent solution-strengthening element, and as a source of both primary and secondary carbide strengthening. Primary carbides, carried over from final melting operations, serve to control grain structure and thus contribute somewhat to alloy strength; however, the formation of secondary carbides, which is critical to developing the best strength, is also the key issue in formulating and performing alloy heat treatments.

Solid-solution-strengthened superalloys are usually supplied in the solution-heat-treated condition, where virtually all of the secondary carbides are dissolved, or "in solution." Microstructures generally consist of primary carbides dispersed in a single-phase matrix, the grain boundaries of which are reasonably clean. This is the optimum condition for good elevated-temperature strength and generally best room-temperature fabricability. When the carbon is mostly in solution, exposure at elevated temperatures below the solution temperature will result in secondary carbide precipitation. In service, where the alloy component is subjected to operating stresses, this carbide precipitation will occur both on grain boundaries and intragranularly on areas of high dislocation density. It is the latter that provides for increased strength in service. When exposure to temperatures below the solution temperature occurs during component heat-treating cycles, the result is usually to precipitate secondary carbides only on grain boundaries. This is not normally beneficial for subsequent fabrication, and it reduces the capability of the alloy to develop in-service strengthening by depleting carbon from solution.

Generally speaking, then, solid-solution-strengthened alloy components will exhibit highest strength when placed in service in the fully solution-heat-treated condition; however, the reality of modern complex component designs dictates what can and cannot be done in terms of final heat treatments. Quite often the compromise between component manufacturability and performance will mean something less than optimal alloy structure.

Annealing and Stress Relieving. In the case of solid-solution-strengthened superalloys, heat treatments performed at temperatures below the secondary carbide solvus or solutioning temperature range are classified as mill annealing or stress-relief treatments. Mill annealing treatments are generally employed for restoring formed, partially fabricated, or otherwise as-worked alloy material properties to a point where continued manufacturing operations can be performed. Such treatments may also be used in finished raw materials to produce structures that are optimum for specific forming operations, such as fine grain size structure for deep drawing applications.

Mill-annealed products may also be used in preference to solution heat treatments for final components where properties other than creep and stress-rupture strength are vital. For example, where low-cycle fatigue properties are important, mill annealing may be used to produce a finer grain size. A finer grain size from mill annealing may also be useful in applications where yield strength instead of creep strength is the limiting design criterion. Finally, mill annealing may be

selected in preference to solution annealing because of external constraints, such as avoidance of component distortion at full solution annealing temperatures, or limits to temperature imposed by the melting point of component braze joints.

Because mill annealing is performed below the secondary carbide solvus temperature, some decoration of grain boundaries can be expected in the microstructure. Depending upon the annealing temperature, the particular alloy, and the nature of the secondary carbide involved, this decoration may take the form of either discrete, globular particles or a more continuous film-like morphology. Cooling rates will markedly influence the appearance of this carbide precipitation, as most alloys of this type exhibit the most significant amount of precipitation in the temperature range from about 650 to 870 °C (1200 to 1600 °F). It is always recommended that components be cooled as rapidly as is feasible through this range, within the constraints of equipment used and with due consideration to avoiding component distortion from thermal stresses.

Typical minimum mill annealing temperatures for various alloys are given in Table 22. These temperatures vary significantly from alloy to alloy. They are based principally upon the ability of the treatment to develop a recrystallized grain structure starting from a cold-worked or warm-worked condition and to produce low enough yield strength and high enough ductility for subsequent cold forming operations. Grain size would be expected to increase somewhat, although perhaps not markedly, when higher mill annealing temperatures are used.

Table 22 Minimum mill annealing temperatures for solid-solution-strengthened alloys

Alloy	Approximate minimum temperature for mill annealing	
	°C	°F
Hastelloy X	1010	**1850**
Hastelloy S	955	**1750**
Alloy 625	925	**1700**
RA 333	1035	**1900**
Inconel 617	1035	**1900**
Haynes 230	1120	**2050**
Haynes 188	1120	**2050**
Alloy L-605	1120	**2050**
Alloy N-155	1035	**1900**

The same basic temperatures would apply for mill annealing hot-worked material, although solution annealing is more common. Hot-worked material is usually dynamically recrystallized during the hot-working operation, and the main effect of mill annealing is to promote uniformity of the structure throughout the piece.

Times at temperature required for mill annealing are governed by several factors. Sufficient furnace time should be allowed to ensure that all parts of the piece are at temperature for the requisite time. The requisite time should be long enough to ensure that structure changes, such as recovery, recrystallization, and carbide dissolution (if any), are essentially complete. Generally, about 5 to 20 min at temperature is sufficient, particularly in thin sections. In continuous thin-strip annealing operations, as little as 1 to 2 min will often suffice. Excessive time at temperature for mill annealing is not necessarily deleterious, but is most often not beneficial. Use of a thermocouple on the actual piece undergoing annealing is always appropriate.

Stress Relief. Unlike mill annealing, stress-relief treatments for solid-solution-strengthened superalloys are not well defined. Dependent upon the particular circumstances, stress relief may be achieved with relatively low-temperature annealing, or may require the equivalent of mill or even solution annealing. In any case, such treatments represent a major compromise between the effectiveness of stress relief and the harm done to the structure or dimensional stability of the component.

Strictly speaking, stress-relief annealing should be considered only if the material is not recrystallized by the treatment. If the intent is to relieve stresses in a piece or component that would otherwise be mill annealed or solution treated, then the first choice is the equivalent of a solution heat treatment or mill annealing to accomplish the required stress relief. Temperatures below the mill annealing temperature range, particularly in the range of 650 to 870 °C (1200 to 1600 °F), will likely result in significant carbide precipitation, or other phase formation in some alloys, which may significantly impair alloy performance. Treatments below 650 °C (1200 °F) may be less deleterious, but are likely to be less effective in relieving residual stresses.

To relieve stresses in a partially cold- or warm-worked piece or component (that is, a finish-formed component that cannot be mill- or solution-annealed), then the stress-relief treatment should be restricted to a temperature less than that which will induce recrystallization. In this class of material, that temperature will vary with the particular alloy and degree of cold or warm work, but will generally be less than about 815 °C (1500 °F). In some materials (such as Inconel 625 and Haynes alloy 214), age-hardening reactions occurring at these lower temperatures must be considered in addition to the more general carbide precipitation encountered in other alloys.

Times at temperature required to effect a significant amount of stress relief are equally ill-defined. For the equivalent to mill and solution annealing, similar times should be used. For lower-temperature stress-relief treatments, no specific guidelines are offered, but excessive times should be avoided for obvious reasons.

Solution heat treating is the most common form of finishing operation applied to solid-solution-strengthened superalloys. As mentioned earlier, a solution treatment places virtually all the secondary carbides into solution. The temperatures at which all secondary carbides are dissolved vary somewhat what from alloy to alloy, and can differ as a function of the type of secondary carbide involved and the carbon content.

Typical solution treatment temperatures for various alloys are given in Table 23. For some alloys the temperature range is broader than others; in most cases, such as Haynes 230, this is related to desired flexibility in controlling the grain size in the solution-treated piece. In Haynes 230, for example, an 1175 °C (2150 °F) solution treatment might produce an ASTM grain size between 7 and 9, while a solution treatment at 1230 °C (2250 °F) could be expected to yield a grain size of ASTM 4 to 6, assuming starting material in a sufficiently cold-reduced condition.

Table 23 Typical solution annealing temperatures for solid-solution-strengthened alloys

Alloy	Typical solution annealing temperatures	
	°C	°F
Hastelloy X	1165-1190	**2125-2175**
Hastelloy S	1050-1135	**1925-2075**

Alloy 625	1095-1205	**2000-2200**
RA 333	1175-1205	**2150-2200**
Inconel 617	1165-1190	**2125-2175**
Haynes 230	1165-1245	**2125-2275**
Haynes 188	1165-1190	**2125-2175**
Alloy L-605	1175-1230	**2150-2250**
Alloy N-155	1165-1190	**2125-2175**
Haynes 556	**1165-1190**	2125-2175

Recrystallization and Grain Size. A major function of the solution annealing treatment is to recrystallize warm- or cold-worked structure fully and to develop the required grain size. Aspects such as heating rate and time at temperature are important considerations. Rapid heating to temperature is usually desirable to help minimize carbide precipitation and to preserve the stored energy from cold or warm work required to provide recrystallization and/or grain growth during the solution treatment itself. For much the same reason that re-solution-treating an already annealed piece often does not coarsen grain size without increasing the temperature, slow heating of a cold- or warm-worked material to the solution-treating temperature can produce a finer grain size than may be desired or required.

Time at temperature considerations for solution heat treatments are similar to those for mill annealing, although slightly longer exposures are generally indicated to ensure full dissolution of secondary carbides. For minimum temperature solution treatments, heavier sections should generally be exposed at temperature for about 10 to 30 min, thinner sections for somewhat shorter times. Solution treatments at the high end of the prescribed temperature range can be shorter, similar to mill annealing. Although very massive parts, such as forgings, may benefit from somewhat longer times at temperature, in no case should any component be exposed to solution treatment temperatures for excessive periods (such as overnight). Long exposures at solution treatment temperatures can result in partial dissolution of primary carbides, with consequent grain growth or other adverse effects.

The effects of cooling rate upon alloy properties following solution heat treatment can be much more pronounced than those related to mill annealing. Because the solution treatment places the alloy in a state of greater supersaturation relative to carbon, the propensity for carbide precipitation upon cooling is significantly increased over that for mill annealing. It is therefore even more important to cool from the solution treatment temperature as fast as possible, bearing in mind the constraints of the equipment, and the need to avoid component distortion due to thermal stresses. The sensitivity of individual alloys to property loss from slower cooling down to about 650 °C (1200 °F) varies, but most alloys will suffer at least some property degradation as a result of secondary carbide precipitation. This is shown by the data in Table 24, in which the effects of various cooling practices on the low-strain creep properties of three alloys are described.

Table 24 Cooling rate effects on time to 0.5% creep at 870 °C (1600 °F) with 48 MPa (7 ksi) load

Solution treat at 1175 °C (2150 °F) and cool at the rate indicated	Time to 0.5% creep, h		
	Hastelloy X	**Haynes 188**	lnconel 617

Water quench	8	148	**302**
Air cool	7	97	**15**
Furnace cool to 650 °C (1200 °F) and then air cool	**6**	**48**	**9**

Solution Treating Combined with Brazing. Unlike mill annealing, which is usually performed as a manufacturing step itself, solution treating may sometimes be combined with another operation, which imposes significant constraints upon both heating and cooling practices. A good example of this is vacuum brazing. Often performed as the final manufacturing step in the fabrication of components, such a process precludes subsequent solution treatment by virtue of the limits imposed by the melting point of the brazing compound. Therefore, the actual brazing temperatures are sometimes adjusted to allow simultaneous solution heat treating of the component. Unfortunately, the nature of vacuum brazing furnace equipment specifically, and vacuum furnace equipment in general, is such that relatively slow heating and cooling rates are a given. In these circumstances, even with the benefit of advanced forced gas cooling equipment, the structure and properties of alloy components are likely to be less optimal than those achievable with solution treatments performed in other types of equipment.

Relationship of Processing History to Heat Treatment. As for most other alloy materials, the response of solid-solution-strengthened superalloys to heat treatment is very much dependent upon the initial material condition. Generally speaking, when the material is not in the cold- or warm-worked condition, the principal response to heat treatment is a change in the amount and morphology of secondary carbide phases present. Relief of minor residual stresses, or relaxation of internal strains, either of which may influence alloy properties to some degree, may also occur. Grain structure, however, may often be substantially unaltered by heat treatment when cold or warm work is absent.

Hot-worked products, in particular those produced at high finishing temperatures, undergo recovery, recrystallization, and grain growth during the working operation itself. If finish working temperatures are too high relative to the final mill-annealing or solution-treatment temperatures, a significant degree of control over the structure resides in the working operation, rather than in the heat treatment. Similarly, if the final hot-working reductions are small, the piece to be heat treated often is initially nonuniform and responds nonuniformly to heat treatment. Material finished at a very high temperature may be best heat treated at temperatures near the high end of the allowable range, and almost always at a temperature above the finish hot-working temperature. For cases with small finish reductions, temperatures at the low end of the range would probably be advisable to minimize the nonuniformity in structure. This last approach might be particularly advisable for pieces with very heavy section thickness, such as large forgings, large-size bars, and thick plates.

Fortunately, solid-solution-strengthened superalloys as a group exhibit relatively wide hot-working ranges, which allow finishing temperatures low enough to produce a warm-worked condition. They are also readily manufactured using cold working processes. In the warm-worked or cold-worked condition, grain structure control resides basically in the heat treatment, but results can be significantly influenced by the amount of work in the piece. As an example of this, the data presented in Table 25 show the influence of initial cold work on the grain size of final heat-treated Haynes 556 sheet.

Table 25 Effect of cold reduction and annealing temperature on grain size of 556 alloy

Cold reduction, %	**5-min subsequent annealing temperature**		**Degree of recrystallization**	ASTM grain size
	°C	**°F**		
0	None	None	. . .	**5.0-6.0**

10	1010	1850	Incomplete	**. . .**
20	1010	1850	Incomplete	**. . .**
30	1010	1850	Partial	**. . .**
40	1010	1850	Partial	**7.5-9.5**
50	1010	1850	Full	**9.0-10.0**
10	1065	1950	Incomplete	**. . .**
20	1065	1950	Incomplete	**. . .**
30	1065	1950	Full	**7.5-9.5**
40	1065	1950	Full	**8.0-9.5**
50	1065	1950	Full	**8.5-10.0**
10	1120	2050	Full	**5.0-5.5**
20	1120	2050	Full	**7.5-8.5**
30	1120	2050	Full	**7.0-7.5**
40	1120	2050	Full	**7.5-9.0**
50	1120	2050	Full	**8.0-9.5**
10	1175	2150	Full	**5.0-5.5**
20	1175	2150	Full	**6.0-6.5**
30	1175	2150	Full	**4.5-6.5**
40	1175	2150	Full	**4.5-6.5**
50	**1175**	**2150**	**Full**	**5.5-6.0**

The particular sequence of cold-work/annealing cycles used in multistep material manufacturing or component fabrication can also affect the structure and properties of these alloys. One general guideline is to keep the temperatures used for intermediate annealing steps at or below the final annealing temperature. Intermediate annealing at temperatures above the final annealing temperature can reduce the degree of structure control possible in the alloy.

The minimum level of cold work shown in Table 25, 10%, is an important rough dividing line between normal recrystailization behavior and possible abnormal grain growth in these alloys. Introduction of small amounts of cold or warm work prior to solution heat treating should be avoided where possible to minimize the potential for abnormal grain growth phenomena. The effects of very small amounts of cold work on the grain size response to annealing for Hastelloy X are shown in Table 26. The samples used to generate these data were carefully strained tensile test specimens, subsequently exposed to the annealing temperatures shown. Strains from 1 to 8% produced little effect for mill annealing temperatures up to 1120 °C (2050 °F); however, for solution annealing at 1175 °C (2150 °F), abnormal grain growth was observed for strains of 1 to 5%.

Table 26 Effect of small strains on abnormal grain growth of Hastelloy X

Prior cold work,%	**5-min subsequent annealing temperature**		ASTM grain size
	°C	**°F**	
0	None	None	**4.5-6.5**
1	1120	2050	**4.5-6.5**
2	1120	2050	**4.0-6.5**
3	1120	2050	**4.0-6.0**
4	1120	2050	**3.5-6.0**
5	1120	2050	**3.5-6.0**
8	1120	2050	**3.5-6.0**
1	1175	2150	**5.0 + 0 at surface**
2	1175	2150	**5.0-5.5 + 0 at surface**
3	1175	2150	**00-4.5**
4	1175	2150	**4.5-5.0 + 1.0-1.5**
5	1175	2150	**3.0-3.5 + 1.0-1.5 4.5-5.0**

8	**1175**	**2150**	**(recrystallized)**

Unfortunately, in everyday fabrication of complex components, it is difficult if not impossible to avoid situations where such low levels of cold work or strain are present. Some alloys are more tolerant of this than others, but virtually all will exhibit abnormal grain growth under some conditions. Procedures that may be effective for minimizing the problem are:

- Solution treating at the low end of allowable temperature ranges
- Mill annealing in preference to solution annealing for intermediate heat treatments during component fabrication
- Stress-relief annealing directly prior to final solution annealing

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Cast Superalloy Heat Treatment

Heat treatment of cast superalloys in the traditional sense was not employed until the mid-1960s. Before the use of shell molds, the heavy-walled investment mold dictated a slow cooling rate with its associated aging effect on the casting. As faster cooling rates with shell molds developed, the aging response varied with section size and the many possible casting variables. These factors, coupled with significant γ' alloying additions, provided the opportunity to minimize property

scatter by heat treatment. The combination of hot isostatic pressing (HIP) plus heat treatment has also greatly enhanced properties.

Generally, heat treating cast superalloys involves homogenization and solution heat treatments or aging heat treatments. A stress-relief heat treatment may also be performed to reduce residual casting, welding, or machining stresses. Cobalt-base alloy heat treatments may be done in an air atmosphere unless unusually high-temperature treatments are required, in which case vacuum or inert gas environments are used. Conversely, nickel-base alloys are always heat treated in a vacuum or in an inert gas medium. Detailed information can be found in Ref 17.

Like wrought superalloys, the solution heat-treating procedures of cast superalloys must be optimized to stabilize the carbide morphology. High-temperature exposure may cause extensive carbide degeneration, resulting in grain-boundary carbide overload and compromised mechanical properties. Unlike wrought superalloys, however, many polycrystalline materials are used in the as-cast plus aged condition without any specific solution step. Cast cobalt-base superalloys, for example, are not usually solution treated (although they may be given stress-relief and/or aging treatments). When required, cast cobalt-base superalloys are generally aged at 760 °C (1400 °F) to promote formation of discrete $Cr_{23}C_6$ particles. Higher-temperature aging can result in acicular and/or lamellar precipitates.

Precipitation-strengthened nickel- or iron/nickel-base superalloys are cast using the investment casting process. The resultant casting comprises a large number of grains and is referred to as a polycrystalline or conventional casting. If the casting is solidified under a thermal gradient, a columnargrained directionally solidified casting will result. Directionally solidified (DS) airfoil castings are used in the turbine sections of gas turbine engines to enhance durability and performance. Additional benefits can be achieved using directional-solidification investment casting to cast turbine airfoils as single crystals. Precipitation-strengthened nickel-base superalloys are primarily utilized for turbine airfoils, while iron-nickel alloys are employed as large investment-cast structural castings.

Superalloys are heat treated to control the morphology of the precipitating phases (γ', γ'', carbides, and δ) that are responsible for the mechanical properties of the alloy. Three basic heat treatment steps are used:

- Solution
- Stabilization
- Aging

Representative heat treatments for several alloys are listed in Table 27.

Table 27 Typical heat treatments for precipitation-strengthened cast superalloys

Alloy	Heat treatment (temperature/duration in h/cooling)(a)
Polycrystalline (conventional) castings	
B-1900/B-1900+Hf	**1080 °C (1975 °F)/4/AC + 900 °C (1650 °F)/10/AC**
IN-100	**1080 °C (1975 °F)/4/AC + 870 °C (1600 °F)/12/AC**
IN-713	**as-cast**
IN-718	**1095 °C (2000 °F)/1/AC + 955 °C (1750 °F)/1/AC + 720 °C (1325 °F)/8/FC + 620 °C (1150 °F)/8/AC**
IN-718 with HIP	**1150 °C (2100 °F)/4/FC + 1190 °C (2175 °F)/4/15 ksi (HIP) + 870 °C (1600 °F)/10/AC + 955 °C (1750 °F)/1/AC + 730 °C (1350 °F)/8/FC + 665 °C (1225 °F)/8/AC**

IN-738	**1120 °C (2050 °F)/2/AC + 845 °C (1550 °F)/24/AC**
IN-792	**1120 °C (2050 °F)/4/RAC + 1080 °C (1975 °F)/4/AC + 845 °C (1550 °F)/24/AC**
IN-939	**1160 °C (2120 °F)/4/RAC + 1000 °C (1830 °F)/6/RAC + 900 °C (1650 °F)/24/AC + 700 °C (1290 °F)/16/AC**
MAR-M246+Hf	**1220 °C (2230 °F)/2/AC + 870 °C (1600 °F)/24/AC**
MAR-M 247	**1080 °C (1975 °F)/4/AC + 870 °C (1600 °F)/20/AC**
René 41	**1065 °C (1950 °F)/3/AC + 1120 °C (2050 °F)/0.5/AC + 900 °C (1650 °F)/4/AC**
René 77	**1163 °C (2125 °F)/4/AC + 1080 °C (1975 °F)/4/AC + 925 °C (1700 °F)/24/AC + 760 °C (1400 °F)/16/AC**
René 80	**1220 °C (2225 °F)/2/GFQ + 1095 °C (2000 °F)/4/GFQ + 1050 °C (1925 °F)/4/AC + 845 °C (1550 °F)/16/AC**
Udimet 500	**1150 °C (2100 °F)/4/AC + 1080 °C (1975 °F)/4/AC + 760 °C (1400 °F)/16/AC**
Udimet 700	**1175 °C (2150 °F)/4/AC + 1080 °C (1975 °F)/4/AC + 845 °C (1550 °F)/24/AC + 760 °C (1400 °F)/16/AC**
Waspaloy	**1080 °C (1975 °F)/4/AC + 845 °C (1550 °F)/4/AC + 760 °C (1400 °F)/16/AC**
Directionally-solidified (DS) castings	
DS MAR-M 247	**1230 °C (2250 °F)/2/GFQ + 980 °C (1800 °F)/5/AC + 870 °C (1600 °F)/20/AC**
DS MAR-M200+Hf	**1230 °C (2250 °F)/4/GFQ + 1080 °C (1975 °F)/4/AC + 870 °C (1600 °F)/32/AC**
DS René 80H	**1190 °C (2175 °F)/2/GFQ + 1080 °C (1975 °F)/4/AC + 870 °C (1600 °F)/16/AC**
Single-crystal castings	
CMSX-2	**1315 °C (2400 °F)/3/GFQ + 980 °C (1800 °F)/5/AC + 870 °C (1600 °F)/20/AC**
PWA 1480	**1290 °C (2350 °F)/4/GFQ + 1080 °C (1975 °F)/4/AC + 870 °C (1600 °F)/32/AC**
René N4	**1270 °C (2320 °F)/2/GFQ + 1080 °C (1975 °F)/4/AC + 900 °C (1650 °F)/16/AC**

(a) AC, air cooling; FC, furnace cooling; GFQ, gas furnace quench; RAC, rapid air cooling

Solution Treating. Polycrystalline cast nickel-base superalloys may or may not be given solution treatment. Because alloys respond differently to γ' solution treatment, some are only given an aging treatment. For those that do respond to partial solution treatment, the treatment is performed at a temperature safely below the incipient melting point of the alloy for times ranging from 2 to 6 h at temperature. The solution heat treatment is employed to dissolve the phases in the as-cast microstructure, in the ideal case returning the alloy microstructure to a single-phase γ(fcc) solid solution, and to homogenize the segregated as-cast microstructure.

The solution treatment is performed at a temperature above or near the γ' solvus temperature. A protective atmosphere, such as vacuum, argon, helium, or hydrogen, can be used to prevent oxidation of the casting. When a vacuum furnace is employed a partial pressure of an inert gas, such as argon, is used rather than a hard vacuum to prevent surface depletion of chromium and aluminum from the castings. When the solution heat treatment temperature is very close to the incipient melting temperature of the alloy, varied heating rates are used to homogenize the castings during the time taken to reach the solution temperature. This is done to prevent incipient melting, which might occur if a segregated casting were heated very rapidly. Many conventionally cast (polycrystalline) nickel-base alloys are not solution heat treated, but all directionally solidified alloys, either columnar-grained or single-crystal castings, are solution treated.

Gamma prime and other phases precipitate as the casting is cooled below the γ' solvus. In nickel-base superalloys, such as those used for turbine airfoils, growth of the fine γ' precipitate phase is very rapid at a few hundred degrees Fahrenheit below the high temperature involved in solution heat treatment. Therefore, it is necessary to cool the casting as rapidly as possible to prevent coarsening of the γ' during the cooling cycle, which can degrade the mechanical properties of the casting. Rapid cooling rates are achieved in a vacuum furnace by introducing additional cold inert gas and circulating the gas in the furnace. This is sometimes referred to as a gas furnace quench (GFQ). A retort, which contains the castings in a protective gas environment, is employed when a conventional furnace (not vacuum) is used for solution heat treatment. Removing the retort from the furnace and passing cold gas through it provides the desired rapid cooling rate. With iron-nickel-base alloys, the solution heat treatment homogenizes the casting and dissolves the δ and γ" phases, which facilitates weld repair of the casting. For these alloys a rapid cooling rate from the solution temperature is not required.

The stabilization heat treatment is employed to enhance creep-rupture properties. A temperature between the solution and aging temperature is used. The purpose of this heat treatment is to optimize the γ' size and morphology and to assist decomposition of the coarse, as-cast MC carbides into fine, grain-boundary carbides. With nickel-base alloys used for turbine airfoils, the stabilization heat treatment is often combined with the heat treatment used to bond or diffuse a coating onto the alloy substrate. In iron-nickel-base alloys a stabilization heat treatment can be used to precipitate δ phase at the grain boundaries for good notch rupture properties. Like solution heat treatment, the stabilization heat treatment is carried out in a protective atmosphere, such as argon, helium, hydrogen, or vacuum, to prevent excessive oxidation of the casting. Retorts and conventional furnaces are used to provide the stabilization heat treatment under a protective atmosphere.

Cooling rates equivalent to air cooling or faster are normally used. As the stabilization heat treatment temperature is normally several hundred degrees Fahrenheit lower than the solution temperature, coarsening of the γ' or other strengthening precipitate phases will be much slower and a rapid cooling rate is not as critical. For iron-nickel-base alloy castings, which are commonly weld repaired in the solution-treated condition, the stabilization heat treatment also serves as a stress relief.

The aging heat treatment is employed to precipitate additional γ' as very fine precipitates. This is important to achieve tensile and lower-temperature creep-rupture properties. With iron-nickel-base superalloys, γ" also precipitates during the aging heat treatment. Cooling from the aging temperature is not critical, but rates equivalent to air cooling or greater are often used. Protective atmospheres are less critical at the lower temperatures employed for aging, but they are usually used. Equipment similar to that employed for the stabilization heat treatment is used for the aging heat treatment.

Hot isostatic pressing (HIP) is a process wherein hydrostatic pressure and elevated temperature are applied concurrently. It is utilized on superalloy castings to eliminate casting porosity. HIP is usually conducted at or near the solution temperature. Use of an inert gas such as argon under high pressure as the pressure transfer medium precludes achieving a rapid cooling rate upon completion of the cycle. As a result, castings receiving a HIP cycle that require a rapid cool from the HIP temperature are given a subsequent heat treatment at atmospheric pressure so that the castings can be rapidly cooled. A pre-HIP homogenization cycle is used for some large iron-nickel alloy castings to increase the local melting temperature by homogenization of the local alloy composition.

Stress-relief heat treatments are performed following welding or other processing on the casting that increases residual stress. They are usually carried out between the stabilization and aging temperatures in a protective atmosphere.

The directionally solidified nickel-base alloys, with their higher γ' solvus temperatures, require higher stress-relief temperatures than the iron-nickel-base alloys. Stress-relief temperatures of 870 to 1080 °C (1600 to 1975 °F) are employed to stress relieve precipitation-strengthened superalloy castings.

Solid-Solution-Strengthened Iron/Nickel-,Nickel-, and Cobalt-Base Alloys. Nonprecipitation-strengthened or solid-solution-strengthened high-temperature superalloy castings are generally distinguishable from the precipitation-strengthened cast super-alloys by their relatively low content of precipitate-forming elements such as aluminum, titanium, or niobium. These iron-nickel-, nickel-, and cobalt-base high-temperature alloys are heat treated to homogenize the casting and relieve any stresses in the casting as a result of either the casting process or welding. These alloys primarily derive their strength from solid solution strengthening, with carbides being the only other phases present. With no phase reactions to control enhancement of mechanical properties by heat treatment, many of these alloys do not require any heat treatment and are often used in the as-cast condition. Representative heat treatments for several alloys are listed in Table 28.

Table 28 Typical heat treatments for solid-solution-strengthened cast superalloys

Alloy	Heat treatment
Hastelloy C	**1220 °C (2225 °F)/0.5 h/air cool**
Hastelloy S	**1050 °C (1925 °F)/1 h, air cool**
Hastelloy X	**As-cast**
Inconel 600	**As-cast**
lnconel 625	**1190 °C (2175 °F)/1 h/air cool**
FSX-414	**1150 °C (2100 °F)/4/h furnace cool + 980 °C (1800 °F)/4 h/furnace cool**
MAR-M509	**As-cast**
WI-52	**As-cast**
X-40	**As-cast**

Subsequent processing following casting, such as application of a surface coating, welding, or brazing, may impose additional heat treatment requirements. Heat treatments to bond coatings to a cast superalloy substrate are usually performed at temperatures of 980 to 1090 °C (1800 to 2000 °F). Stress relief, following joining or for other purposes, can be carried out over a broad range of temperatures. The particular temperature represents a compromise between the effectiveness of stress relief and the damage to the structure or dimensional stability of the casting. Although not truly a stress relief, some stress-relief heat treatments are conducted at temperatures sufficiently high to cause recrystallization. In a cast component local recrystallization does not normally have significant detrimental effects on the mechanical properties of the casting and is usually tolerated.

The annealing or stress-relieving heat treatments that are given to this class of nonprecipitating high-temperature alloys are normally done in a protective atmosphere to prevent oxidation or surface contamination of the casting. Heat treatment is usually conducted in a batch-type furnace; the high-temperature superalloy castings are loaded into a retort that contains a protective atmosphere such as argon or hydrogen. Vacuum can also be used. Rapid cooling rates are not usually required.

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Heat Treating of Refractory Metals and Alloys

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Introduction

THE TERM REFRACTORY METAL can be used to describe a large number of metals. The discussion in this article is limited to the alloys of the four "classical" refractory metals: molybdenum, tungsten, niobium (columbium), and tantalum. Most commercially available alloys of these metals derive their strength from either cold working or solution hardening. Certain alloys employ dispersions of second phases to retard the recrystallization of a wrought structure, but, unlike nickel-base superalloys, no commercial refractory metal alloys use precipitation as a primary strengthening mechanism. Consequently, stress-relief and recrystallization annealing are the commonly employed heat treatments for the refractory metals.

Acknowledgements

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General Description of Annealing Treatments

Molybdenum and tungsten alloys are normally cold worked plus stress relieved to develop their best mechanical properties such as low ductile-brittle transition temperatures. Recrystallization destroys the strengthening developed by cold working and raises the ductile-brittle transition temperature to relatively high levels. Figure 1 shows the effect of recrystallization on the ductile-brittle transition in bending for unalloyed molybdenum sheet. Stress-relief annealing reduces the level of residual stress in components and restores some of the ductility exhausted by the heavy cold reductions used in making mill products, thereby permitting further fabrication with less danger of cracking and delamination. Stress-relief annealing is mandatory after welding these materials and may also be employed after extensive machining operations. Normally, a stress-relief temperature is chosen to produce a small amount (<10%) of recrystallization in the microstructure. This treatment produces optimum ductility without significant loss of strength. It also allows annealing to be confirmed by either simple hardness testing or metallographic observation. Stress-relief annealing of material to be further worked is usually performed at lower temperatures to avoid a partially recrystallized microstructure. Working of mixed microstructures can lead to variable properties and ductility problems in the finished product. Prior processing parameters, such as the amount of reduction prior to annealing and the temperature at which deformation takes place, markedly affect the recrystallization of molybdenum and tungsten and therefore also have a strong effect on the choice of stress-relief conditions. The effect of degree of working is shown in Fig. 2 for molybdenum rolled at 1200 °C (2200 °F).

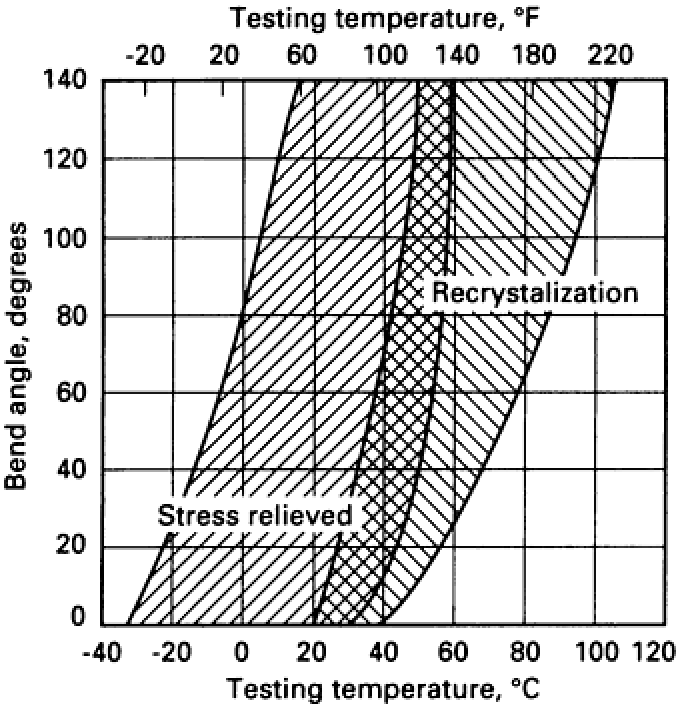

Fig. 1 Effect of annealing practice on the bend transition temperature of 1.6 mm ($\frac{1}{16}$ in.) molybdenum sheet. Courtesy of Climax Specialty Metals

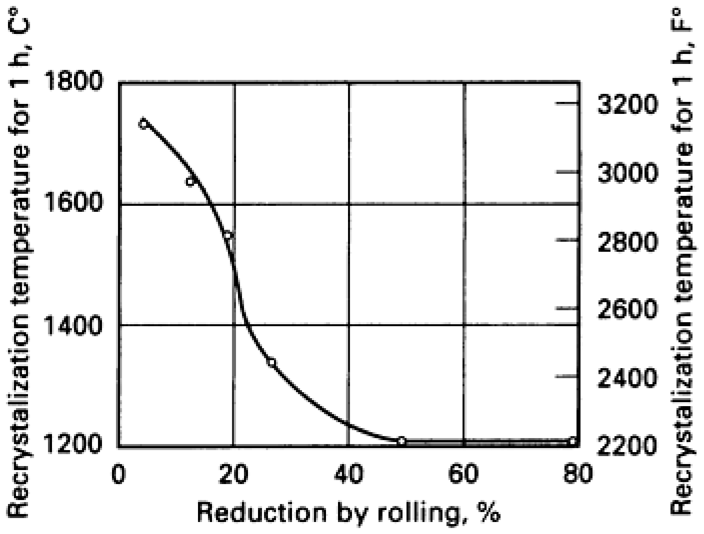

Fig. 2 Effect of degree of cold working on the minimum temperature for complete recrystallization of unalloyed arc-cast molybdenum. Courtesy of Climax Specialty Metals

A variety of proprietary stress-relief annealing practices are used by the manufacturers of molybdenum and tungsten mill products. These practices are designed to optimize fabrication properties such as the capability for hot spinning, drawing, and stamping. Typically they involve annealing to obtain a controlled amount of recrystallization in the microstructure. It is strongly recommended that users consult with a primary producer of molybdenum and tungsten to specify the appropriate product for a particular application or to optimize a specific property. Producers are also a valuable resource for advice on the heat treatment of fabricated molybdenum and tungsten products.

Table 1 lists the common commercial alloys of molybdenum and tungsten, along with typical temperature ranges for stress-relief and recrystallization annealing. It may be noted that the table does not include the lamp wire (doped tungsten) and thermocouple (W-5, 25, and 26 Re) alloys. The thermocouple alloys are not normally fabricated, other than by minimal bending and welding to form junctions, and processing parameters used in the wire and lamp manufacturing industries are highly proprietary. A more detailed discussion of annealing practice for mill products is included later in the section "Molybdenum and Tungsten Annealing Practice."

Table 1 Annealing temperatures for molybdenum and tungsten and their commercial alloys

Annealing designation	**Nominal alloy additions, wt%**	Annealing temperatures			
		Stress-relief		Recrystallization	
		°C	**°F**	**°C**	°F
Molybdenum alloys					
Mo[(a)]	None	850-950	1560-1740	1000-1200	**1830-2190**
Mo-TZM[(a)]	0.5 Ti, 0.1 Zr, 0.03 C	1100-1300	2010-2370	1350-1475	**2460-2690**
Mo-MHC[(a)]	1 Hf, 0.05 C	1100-1350	2010-2460	1400-1600	**2550-2910**
Mo-30W[(a)]	30 W	1150-1200	2100-2190	1300-1450	**2370-2640**
Doped Mo	0.07 Si, 0.05 K	1250-1350	2280-2460	1400-1600	**2550-2910**
Tungsten alloys					

(a) Arc-cast or powder metallurgy; all other compositions powder metallurgy

Tantalum and niobium differ greatly from molybdenum and tungsten in that these metals are ductile in the recrystallized condition. For this reason, they and their alloys are most frequently recrystallized prior to fabrication or use. In the as-rolled condition, the alloys are susceptible to cracking during forming. For less severe forming operations such as stamping, a stress-relief treatment of the as-rolled product at about 55 °C (100 °F) below the start of recrystallization suffices. However, full recrystallization annealing should precede more severe operations such as spinning, flow turning, and deep drawing. Because these alloys derive their strengthening primarily from solution hardening, the recrystallization practice depends on the alloy content of the material under consideration (including impurities such as oxygen and nitrogen), as well as the degree of cold work prior to annealing. An example of recrystallization behavior for commercial alloy C103 in sheet form is shown in Fig. 3.

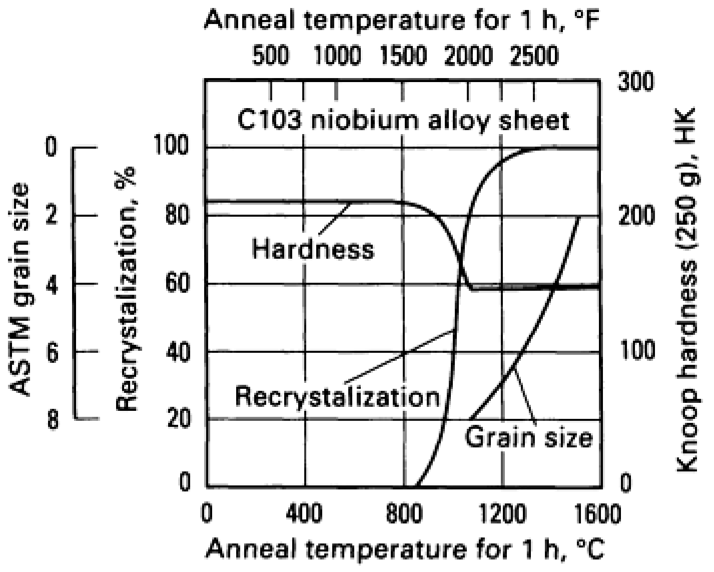

Fig. 3 Recrystallization behavior of alloy C103 for 1-h anneals in vacuum. Courtesy of Teledyne Wah Chang Corporation

Stress-relief treatments are typically used after welding to reduce residual thermal stresses and after forming operations to eliminate residual forming stresses. If components are coated after welding or forming to provide oxidation resistance, the thermal treatment involved in the coating process itself usually provides sufficient stress relief.

The common commercial alloys of tantalum and niobium are listed in Table 2, along with typical stress-relief and recrystallization annealing temperatures. The reader must bear in mind that the specific temperature required will depend on the degree of cold work and the processing history of the alloy. Annealing temperatures are not given for the niobium-hafnium-nickel-zirconium alloy in Table 2. The major application for this material is in fine, composite, superconducting wire. In this application, annealing practice during the manufacture of the composite wire has a major effect on the properties of the finished wire. Appropriate annealing practice is also a function of the other processing parameters used in wire drawing, such as drawing reductions and temperatures. For these reasons, annealing schedules for superconducting composite wire are highly proprietary and application specific. The other major application for this alloy is in aircraft rivets, where the material is purchased in the appropriate microstructural condition directly from the manufacturer. More details about annealing practice for tantalum and niobium is provided in the section "Tantalum and Niobium Annealing Practice" in this article.

Table 2 Annealing temperatures for tantalum and niobium and their commercial alloys

Annealing designation	**Nominal alloy additions, wt%**	Annealing temperature			
		Stress-relief		Recrystallization	
		°C	**°F**	**°C**	°F
Tantalum alloys					
Ta	None	850	1560	1000-1250	**1830-2280**
Ta	None[(a)]	1000	1830	1200-1350	**2190-2460**

FS63	2.5 W, 0.15 Nb	1000	1830	1200-1300	**2190-2370**
FS61 (KBI-6)	7.5 W [(a)]			1400-1550	**2550-2820**
Ta-10W (FS60, KBI-10)	10 W	1100	2010	1300-1600	**2370-2910**
T111	8 W, 2 Hf	1100	2010	1400-1650	**2550-3000**
T222	9 W, 2.4 Hf, 0.01 C	1100	2010	1400-1650	**2550-3000**
Niobium alloys					
Nb	None	800	1470	900-1200	**1650-2190**
Nb-1Zr (FS80, WC 1Zr, KBI-1)	1 Zr	875-1150	1610-2100	1150-1250	**2100-2280**
SNb 291, WC 291	10 Ta, 10 W	1000	1830	1150-1200	**2100-2190**
Nb 752	10 W, 2.5 Zr			1300-1400	**2370-2550**
C 129Y	10 W, 10 Hf, 0.1 Y	900	1650	1150-1250	**2100-2280**
FS85	28Ta, 11 W, 0.8 Zr	1150	2100	1300-1400	**2370-2550**
C103	**10 Hf, 1 Ti, 0.7 Zr**			**1250-1375**	**2280-2510**

(a) Powder metallurgy; all other compositions arc-cast

Molybdenum and Tungsten Annealing Practice

Furnace atmosphere considerations are important when chosing heat-treating equipment for molybdenum and tungsten because both metals form carbides and volatile oxides. Figure 4 shows the recession of molybdenum in a variety of oxygen-containing atmospheres, while Table 3 summarizes the qualitative behavior of molybdenum and its alloys in various gas atmospheres. Tungsten would be expected to behave in a similar manner. The tendency to form brittle surface carbides and the phenomenon of volatile oxide evaporation indicate that carbon- and oxygen-containing atmospheres are to be avoided, especially for thin products such as sheet and foil. Thick-section products such as rod, bar, and plate can frequently tolerate surface recession due to oxidation and are sometimes annealed in air-atmosphere furnaces. Both hydrogen and nitrogen may be considered inert to pure molybdenum and tungsten, but internal nitriding can occur in alloys containing titanium, zirconium, and hafnium. High-purity dry hydrogen is the preferred atmosphere for annealing molybdenum and tungsten because of its compatibility with the metals and because it improves surface cleanliness by reducing surface oxides during annealing. High-quality vacuum systems may also be used to anneal these materials. Surface decarburization can occur in atmospheres containing oxygen, and this may be a problem for alloys that depend on carbide formation to stabilize the microstructure against recrystallization. Adding zirconium and titanium to the alloy can also cause the formation of undesirable oxide, carbide, and nitride phases when annealing is performed in atmospheres contaminated with oxygen, carbon, or nitrogen. If the products to be annealed are to be further machined, furnace atmosphere is less critical, and less stringent guidelines can be followed.

Table 3 Qualitative high-temperature behavior of molybdenum and its alloys in various gas atmospheres

Atmosphere	**Molybdenum behavior**	Alloy behavior
Oxygen	At higher pressures, formation of solid and liquid oxides; evaporation of volatile oxides resulting in weight losses. At low pressures, no surface oxide scales; evaporation of volatile oxides, resulting in steady states with temperature- and pressure-dependent weight losses. C-containing Mo is degassed by CO formation	**Complex oxidation behavior showing weight gains and weight losses**
		Formation of volatile oxides, possible selective evaporating; internal oxidation
Water vapor	At high pressures, oxidation and evaporation of volatile oxides and Mo-O-H compounds. At low pressures, formation of gaseous H_2 and evaporation of volatile oxides; no surface scales, steady states with temperature- and pressure-dependent weight losses	**Similar to oxygen**
Nitrogen	At high temperatures, pressure-temperature-concentration equilibriums with low N concentrations even at high pressures. At low temperatures, no reaction	**Pressure-temperature-concentration equilibriums, internal nitriding**
Ammonia	At high temperatures, NH_3 is dissociated into H_2 and N_2 with solid solution formation; at low temperatures, nitride formation	**At high temperatures, NH_3 dissociation, formation of solid solutions, and/or internal nitriding. At lower temperatures, external and/or internal nitriding**
Carbon monoxide	Solution of C and O; carbide formation; oxide evaporation	**Solution of C and O; external and/or internal carbide and oxide formation, oxide evaporation**
Hydrogen	Formation of solid solution, low H concentration even at high H_2 pressures; at high H_2O/H_2 ratios, possible oxygen degassing; at high H_2/CH_4 ratio, possible carbon degassing	**Formation of solid solution and/or internal hydride formation**
Hydrocarbons	Carbon solution and carbide formation with H_2 desorption	**Carbon solution and external and/or internal carbide formation**
Inert gas	Reduction of metal evaporation; in case of oxygen-containing impurities, formation of volatile oxides resulting in additional metal losses	**Reduction of evaporation of base or alloying metals; in case of oxygen-containing impurities, oxidation processes**
Vacuum	**Degassing of H and N via H_2 and N_2 desorption, degassing of C and O via CO formation, degassing of O via oxide evaporation; at high residual pressures, contamination possible**	**Degassing processes, contamination**

Source: Ref 1

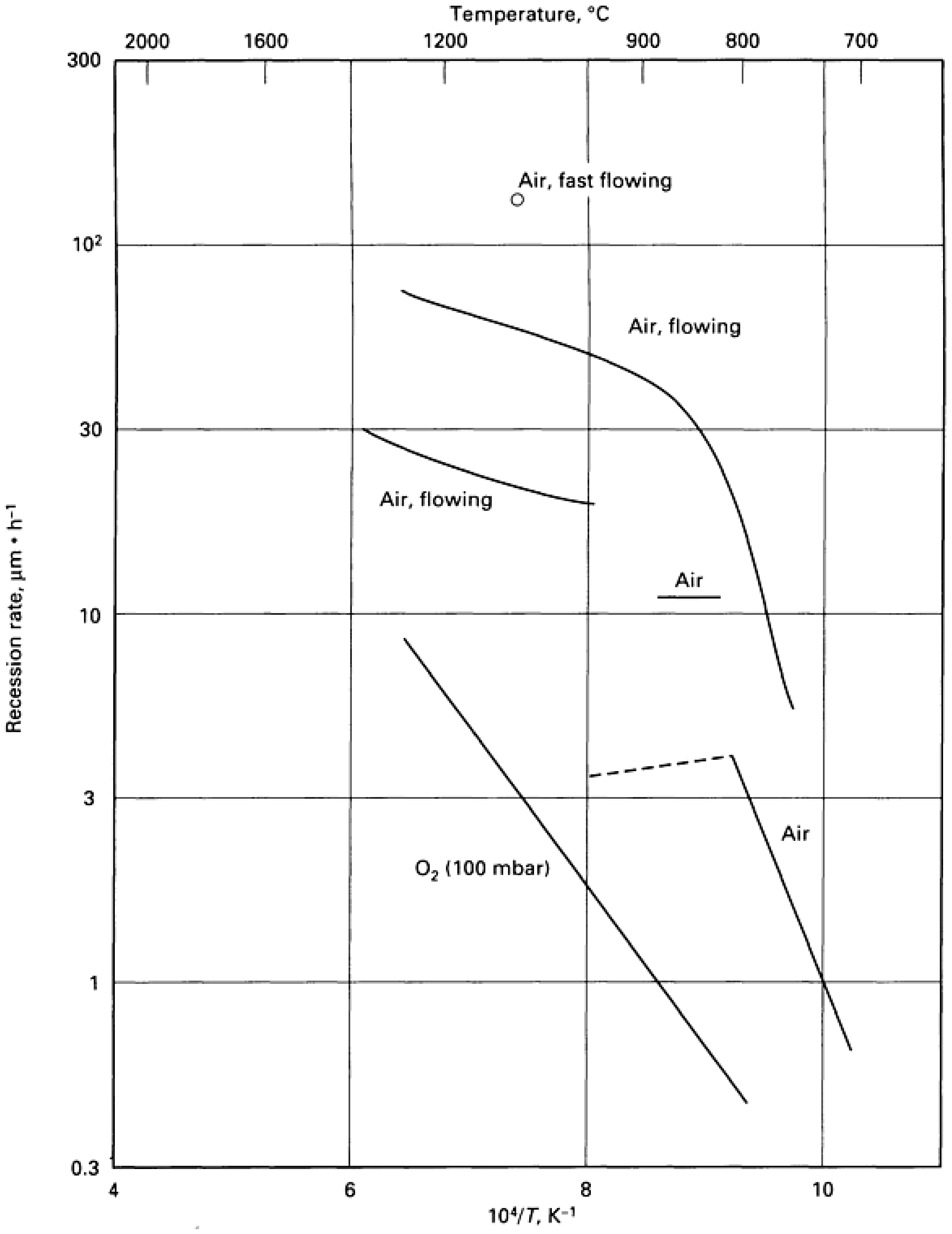

Fig. 4 Oxidation of molybdenum in pure oxygen and air. T, temperature. Source: Ref 1

Cleaning of molybdenum and tungsten is desirable to remove compounds that could cause carbon contamination during heat treatment. If components are heavily oxidized as a result of hot forming in air, it is wise to remove the oxide chemically prior to annealing in order to maintain furnace cleanliness. A variety of cleaning agents may be used to remove oils and hydrocarbons. Vapor degreasing and hand or automatic washing with detergent solutions both work well. For chemical cleaning, molten caustic (1.5 to 3% sodium nitrite in sodium hydroxide at 425 °C, or 800 °F) followed by hot water rinsing effectively removes heavy surface oxides.

Recrystallization behavior of molybdenum is shown in Fig. 5. The data for this figure were obtained on 1.6 mm ($\frac{1}{16}$ in.) vacuum arc-cast sheet, but are also useful for estimating the behavior of other gages. Thinner sections, having greater degrees of cold work, will have curves shifted to lower temperatures. Thicker sections will recrystallize at higher temperatures.

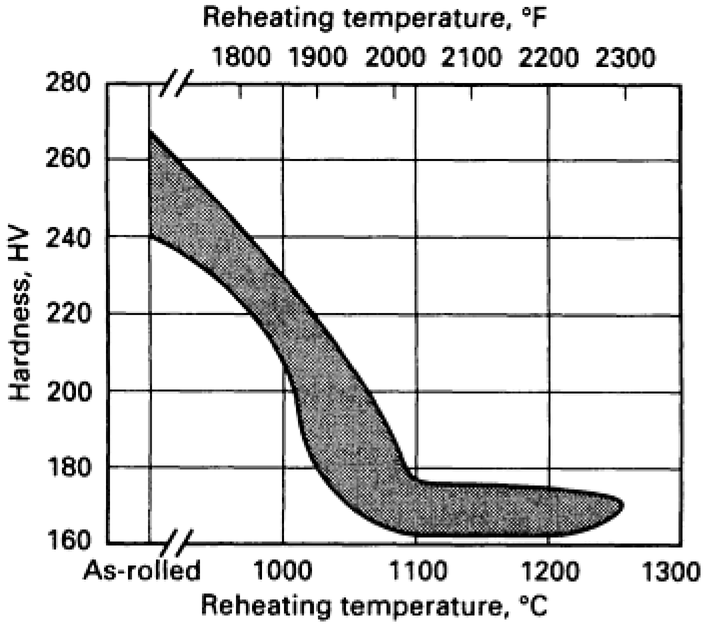

Fig. 5 Recrystallization behavior of 1.6 mm ($\frac{1}{16}$ in.) vacuum arc-cast molybdenum sheet, as reflected by room-temperature hardness after 1-h anneals at the indicated temperature. Courtesy of Climax Specialty Metals

Because molybdenum and tungsten suffer increases in their ductile-brittle transition temperature in the recrystallized condition, mill products are normally supplied in the stress-relieved condition. The exceptions to this rule are molybdenum and tungsten forging billets, which by definition require further working. For this reason, powder-metallurgy molybdenum and tungsten forging billets are normally supplied in the pressed and sintered condition and do not require thermal treatment prior to forging. Vacuum arc-cast molybdenum and tungsten forging billets are typically produced from extruded ingots and are supplied in the fully recrystallized condition. Because the ductile-brittle transition temperature of recrystallized molybdenum and tungsten is very sensitive to grain size, a recrystallization temperature is chosen that will produce the smallest grain size possible in the recrystallized product.

Figure 6 summarizes a range of data on the recrystallization behavior of arc-cast TZM molybdenum alloy (UNS R03630). This figure may be used to estimate the time required for recrystallization at a given temperature, or vice versa. Again, the figure shows clearly the effect of gage, with the thinner gages recrystallizing at smaller values of the exposure parameter than thicker gages. Figure 7 is a composite of recrystallization information on a variety of arc-cast TZM alloy mill products. It can be seen that the degree of cold work most strongly affects the temperature at which recrystallization begins and has less effect on the temperature for complete recrystallization.

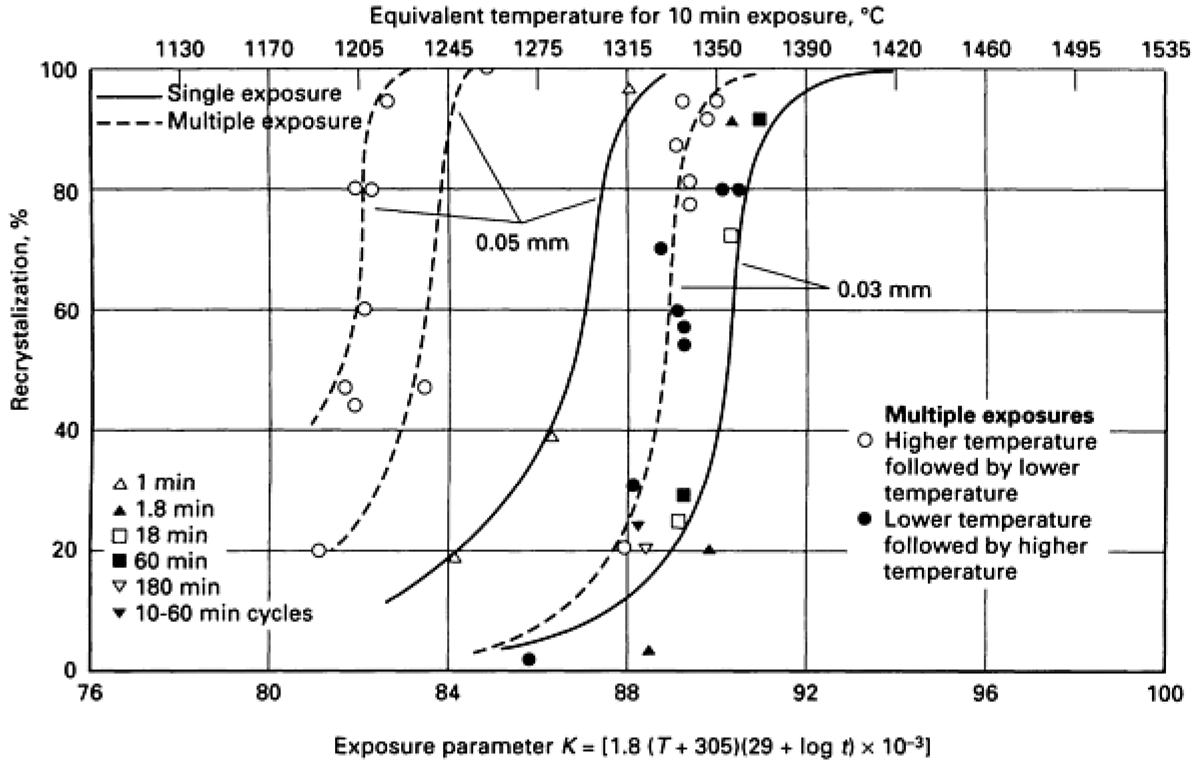

Fig. 6 Recrystallization behavior of arc-cast TZM alloy, as defined by a thermal exposure parameter (*K*) with temperature (*T*) in degrees Celsius and time (*t*) in minutes. Source: Ref 2

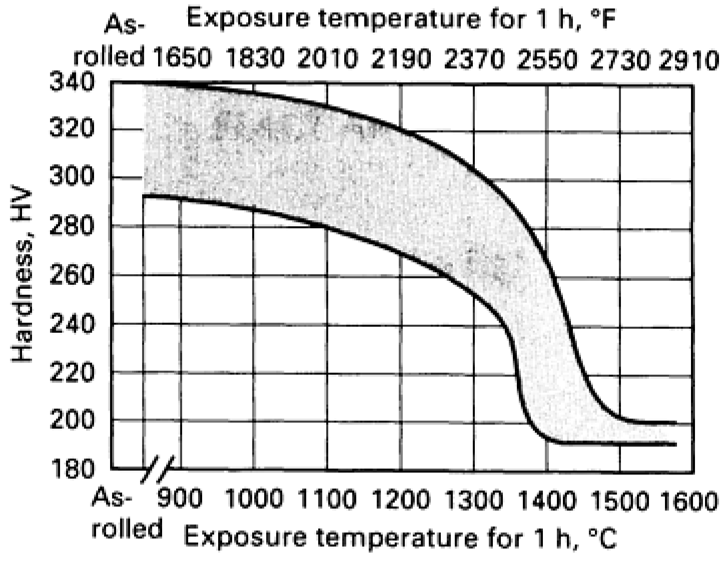

Fig. 7 Scatter band of room-temperature hardness versus 1-h exposure temperature for rolled arc-cast TZM bar and sheet products. Source: Ref 3

Stress-relief annealing of tungsten and molybdenum may be accomplished by annealing slightly below the temperature required to initiate recrystallization. The curves of Fig. 4, 5, and 6 may be used to estimate the temperature required for stress relief, or the recommendations of Table 1 may be followed. Pilot annealing on material from the same lot, using the table and figures as guidelines, can also be employed to custom-tailor the annealing practice for a particular application. As noted previously, normal practice is to select a final stress-relief temperature that results in a small amount (<10%) of recrystallization in the microstructure.

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Tantalum and Niobium Annealing Practice

Table 2 lists general recommendations for the annealing temperatures of tantalum and niobium materials. The trend toward bonding tantalum and niobium to other metals presents special problems that must be carefully reviewed from a metallurgical standpoint. The recommendations of Table 2 probably do not apply to most clad materials.

It is strongly suggested that users contact the supplier of the primary fabricated metal to review plans and procedures prior to any thermal treatment of tantalum, niobium, or their alloys. Numerous expensive failures have resulted from attempts to perform thermal treatment in air, in atmospheres with inadequate inert-gas protection, or in inadequate vacuum systems.

Furnace atmosphere control during the heat treatment of tantalum and niobium is even more important than it is for tungsten and molybdenum. These metals absorb oxygen, nitrogen, and hydrogen from the atmosphere as temperatures increase above 650 °C (1200 °F). The surface oxidation of both metals occurs in air above 300 °C (570 °F), and the oxidation rate increases with increasing temperature. Carbon can also be absorbed if the carbon potential of the furnace atmosphere is sufficient. Hydrogen embrittlement may occur in hydrogen-containing atmospheres. Hydrogen absorption in tantalum and niobium takes place at low temperatures but desorption occurs as temperatures increase from 200 to 1000 °C (400 to 1830 °F). Although this provides a method of hydrogen removal, cooling in the presence of hydrogen should be avoided.

The impurities picked up from furnace atmospheres form brittle surface layers that are detrimental to further forming and machining operations and to service performance. The heat treatment of materials with brittle surface layers will result in the diffusion of the embrittling species into the bulk of the material. Because the metals are readily embrittled by the addition of even a few hundred parts per million of oxygen, nitrogen, carbon, or hydrogen, this diffusion can render the entire cross section brittle. To prevent the pickup and diffusion of these interstitial elements during heat treating, appropriate surface-cleaning procedures, furnace maintenance, and operational practices are essential.

Furnace Selection. Because these alloys are easily contaminated during annealing, special care must be exercised in furnace selection, cleanliness of work, and annealing practice. Cold-wall radiant-heated furnaces with refractory metal heating elements, primary heat shields, permanent hearth materials, and support fixtures are normally used when heat treating niobium and tantalum. These furnaces operate at vacuums of 0.01 Pa (10^{-4} torr) or greater and have low leak rates. Hot-wall argon atmosphere furnaces have also been used to anneal tantalum and niobium, but adsorbed gases and metals on hot furnace walls are likely to cause contamination. Argon must be free of hydrogen and have a dew point below -50 °C (-60 °F).

Leak rate control is the key to the successful heat treating of tantalum and niobium alloys, especially with products having high surface-to-volume ratios, such as low-gage wire, tube, and strip. Leak rate must be measured in a stabilized system, that is, one that has pumped for a period of time and is no longer outgassing. It is defined as the pressure rise (typically in torr) per second, per liter of chamber volume. The example below illustrates the measurement of leak rate.

Assume that a 1200 l (42.4 ft^3) vacuum furnace chamber is isolated by closing the high-vacuum valve. The pressure rise is observed, and an increment of rise is timed by a stopwatch. Assuming the chamber pressure rises 0.25 Pa (2×10^{-3} torr) in 5 min, the leak rate would be calculated as:

$$\frac{\text{Pressure change . Chamber volume}}{\text{Time}} = \frac{2x10^{-3}.1200}{300} = 0.8\ x\ 10^{-2} torr.l/s$$

where pressure change is measured in torr, chamber volume in liters (l), and time in seconds (s). This rate is acceptable because it is below the suggested limit of 10^{-2} torr · l/s. The full calculation need not be carried out for every measurement because for a particular furnace the leak rate criterion implies a particular pressure rise rate. In the above example, the pressure rise would have to be less than $\frac{1}{3}$ Pa (2.5 × 10^{-3} torr) in 5 min for the furnace to satisfy the leak rate criterion.

Furnace Cleanliness. Furnaces must be clean and usually must not be used for other operations or other metals unless a given practice has been found to be satisfactory. Furnaces previously used to perform brazing operations should not be used. Good practice dictates that furnaces be heated to a temperature 100 °C (180 °F) above the annealing temperature in the empty condition to remove adsorbed gases. As further insurance, tantalum foil is frequently used as an outer wrapping on parts to react with impurities in the furnace.

If furnaces are refurbished for use with tantalum and niobium after being used with other materials, care must be taken to clean and decontaminate thoroughly all furnace components. Vacuum furnaces employing argon quenching and gas recycling will suffer deposition of volatile elements (braze alloys, chromium in nickel-base and stainless alloys) in the argon heat exchanger. If the heat exchanger is not thoroughly cleaned as part of the furnace refurbishment, argon quick cooling with tantalum and niobium loads can redeposit these elements on the refractory metal surfaces.

Furnace qualification is often a customer requirement and usually includes a limit on the amount of allowable contamination as measured by increased hardness or interstitial content. If there is any doubt regarding furnace quality, it would be prudent to overlap components in tantalum or niobium foil.

Cleaning of tantalum and niobium is a critical step in preparation for heat treatment. All surface contamination must be removed by machining or grinding and pickling before annealing because of the embrittlement mentioned previously. Cleaning and degreasing present no special problems. Conventional methods and materials may be used, although hot caustics must be avoided. First, thorough degreasing is carried out using a detergent or solvent. Degreasing is followed by chemical etching, typically with a mixture of 60% HNO_3, 20% HF, 20% H_2SO_4 (vol %); hot and cold water rinses in distilled water; and spot-free drying. The etching solution may be either strengthened by HF or weakened by water to achieve the amount of stock removal necessary to ensure the cleanliness of the metal surface. One company eliminates H_2SO_4 because some evidence indicates that it can contribute to weld embrittlement. Nitric acid should always be present, however, because it prevents hydrogen pickup during pickling. Further, elevated-temperature forgings will have an oxygen-contaminated outer layer, and this must be removed from all surfaces by machining or grinding before acid pickling.

Recrystallization annealing is the most common thermal treatment applied to tantalum and niobium alloys. The recrystallization temperature is so highly dependent on purity, amount of cold work, and prior history that current practice is to anneal pilot samples to ensure that the correct temperatures are used. Time at temperature is typically 1 h.

Table 2 can be used as a guide for choosing pilot temperatures. Materials given heavy fabrication reductions will recrystallize to finer grain sizes at lower temperatures than those given lighter fabrication reductions. The recrystallization annealing temperature is also somewhat dependent on interstitial purity. For example, pure tantalum containing 200 ppm O requires a higher recrystallization annealing temperature than does pure tantalum containing less than 50 ppm O.

A typical annealing sequence is:

- Visually verify material cleanliness
- Load, using tantalum, tantalum alloy, or molybdenum fixtures for support, or tantalum foil for protection, as required
- Pump down
- Check leak rate
- Turn on power to temperature
- Hold at temperature for required time
- Turn power off

- When temperature drops below 1000 °C (1830 °F), backfill to 2000 Pa (15 mm Hg) with industrial high-purity (99.995% min) argon or helium
- Before removing load from furnace, allow to cool to below 200 °C (390 °F), which can require from 3 to 5 h depending on furnace size and mass of load

This sequence is not intended to be a detailed procedure for annealing these materials but rather to create an awareness of the difficulties and risks of heat treating these materials to avoid the repetition of costly past errors. The major risk is loss of vacuum at a temperature that results in the extremely costly destruction by oxidation, not only of parts being heat treated, but also of the furnace shielding and heating elements.

Principles of Heat Treating of Nonferrous Alloys

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Introduction

THE PRINCIPLES which govern heat treatment of metals and alloys are applicable, of course, to both ferrous and nonferrous alloys. However, in practice there are sufficient differences to make it convenient to emphasize as separate topics the peculiarities of the alloys of each class in their response to heat treatment. For example, in nonferrous alloys, eutectoid transformations, which play such a prominent role in steels, are seldom encountered, so that the principles associated with time-temperature-transformation diagrams and with martensite formation are not emphasized in this article. On the other hand, the principles associated with chemical homogenization of cast structures are applicable to many alloys in both classes.

Examination of the heat treatment used for nonferrous alloys reveals that a wide variety of processes are employed. However, because the process of diffusion underlies nearly all heat treatments, the concepts of diffusion are summarized first in this article. Annealing after cold working is a very important heat treatment for nonferrous alloys, and this topic is discussed next. Then the subject of homogenization annealing is reviewed, because it is an important heat treatment for as-cast structures. The process of precipitation, and the hardening that accompanies it, are described next, because these phenomena are especially important in aluminum-base alloys (and also in some magnesium, copper and nickel-base alloys). Then, to illustrate the formation of structures in which two phases are present in comparable quantities (for example, titanium-base alloys, some copper brasses, and so on), the heat treatments of a specific type of Cu-Zn alloy are examined. Finally, references are listed which provide additional information on the principles of heat treatment of nonferrous alloys.

Diffusion in Metals and Alloys

In heat treatment of metals and alloys, the rate of structural changes is usually controlled by the rate at which the atoms in the lattice change position. Thus, when cold worked copper is annealed and softens, or an aluminum-base alloy is aged, we are interested in how the atoms move relative to each other so as to bring about the observed changes in properties. The movement of the atoms involved here is called diffusion, and it is this process of diffusion which is examined in this section.

Diffusion in Pure Metals (Self-Diffusion). Atoms in a lattice at finite temperatures are not static, but are vibrating in three dimensions around the normal atom position, usually the lattice site. Thus, consideration arises as to whether these atoms, by some mechanism, can exchange positions with each other and thereby move through the lattice. Such movement of the atoms of a pure metal is termed self-diffusion, and it is usually detected by experiments in which a thin layer of a radioactive atom is placed on the surface (for example, by plating) of the same metal which is not radioactive and then the sample is given an annealing treatment at sufficient temperature and for sufficient time to allow diffusion. Because the difference between the radioactive and nonradioactive atoms is in the nuclear structure, and not in the valence electrons which are related to bonding, it is assumed that the radioactive atoms move through the lattice by the same mechanism and at the same rate as do the nonradioactive atoms. Thus, the movement of the radioactive atoms, which can be followed by a suitable radioactivity detector, reflects the type of movement the atoms in the metal undergo.

Such an experiment is illustrated schematically in Fig. 1. The radioactive layer is depicted as only two atoms thick, whereas it will really be much thicker (for example, 1 mm). The sequence of time from 0 to t_3 shows increasing amounts of radioactive atoms (closed circles) moving into the lattice of the nonradioactive atoms (open circles), and simultaneously the lattice sites of the radioactive atoms are occupied by the nonradioactive atoms. The amount of radioactivity is measured as a function of depth into the sample from the surface, giving the profiles shown at the bottom of the figure. (Note that Fig. 1 does not show the intensity in the radioactive layer; it will decrease with time due to radioactive decay. This decay will also alter the intensity-depth curves, but this correction is not shown in the schematic curves in Fig. 1.)

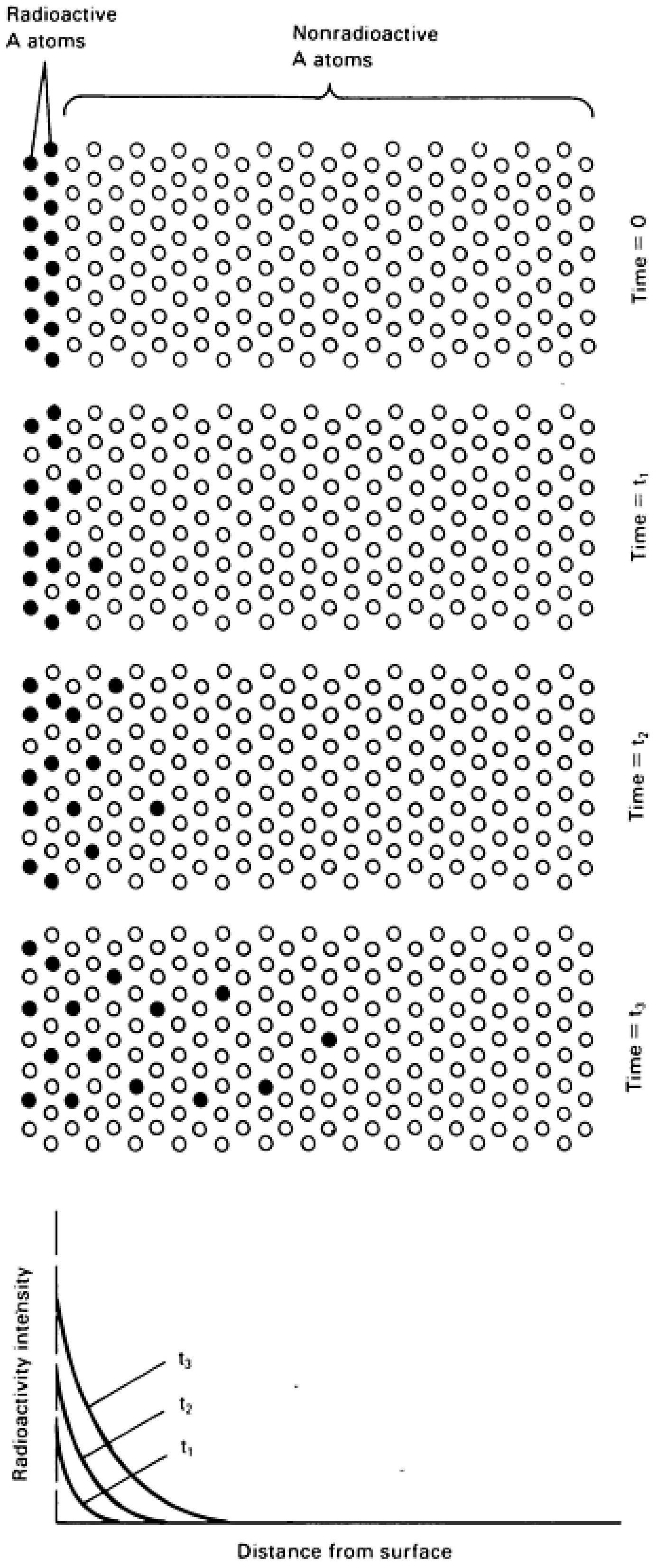

Fig. 1 Schematic diagram showing self-diffusion in a pure metal (radioactive atoms represented by solid circles)

Vacancies. The movement of atoms in the lattice, as depicted in Fig. 1, can be conceived to occur by several mechanisms. For example, at any instant in time, it is possible that the nearest two neighboring atoms have vibrated in

directions so that space is left around the two atoms, allowing them to exchange positions simultaneously. Such an event is depicted in Fig. 2(a). It is clear that the two atoms which exchange positions must move, to some extent, the neighboring atoms in order to pass each other during the exchange process. It may also be possible for four atoms to vibrate at some instant so that they move cooperatively in a ring, allowing all four to move simultaneously to new neighboring positions, as depicted in Fig. 2(b).

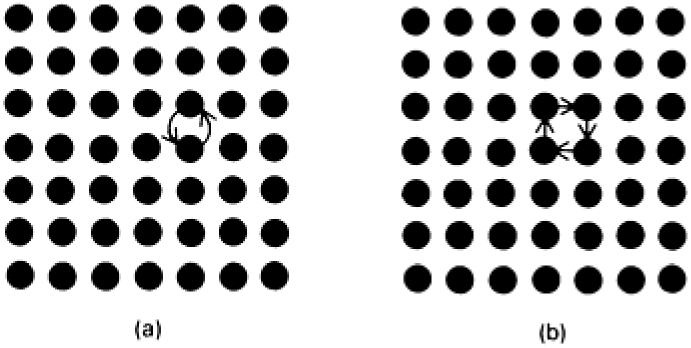

Fig. 2 Schematic representation of two possible diffusion mechanisms. (a) Two atoms move simultaneously to exchange positions. (b) Four atoms move cooperatively to rotate simultaneously to move to new positions.

Although mechanisms such as those just suggested probably occur in some alloys, in most metals and alloys diffusion occurs by vacancy movement. An unoccupied normal atom position in the crystal structure (usually a lattice site) is a vacancy. The presence of vacancies in a lattice at equilibrium is a consequence of a balance between the energy required to form the vacancies ΔH and the entropy ΔS created by their presence. Thus, there is an equilibrium concentration which minimizes the free energy change ($\Delta G = \Delta H - T\Delta S$).

If a vacancy exists in a lattice, then it requires much less energy for an atom to change positions than in the mechanisms depicted in Fig. 2. An atom has only to move into the vacancy, with much less energy. Such movement is shown in Fig. 3. It is to be noted that the diffusion occurs by rather random movement of the vacancies throughout the lattice.

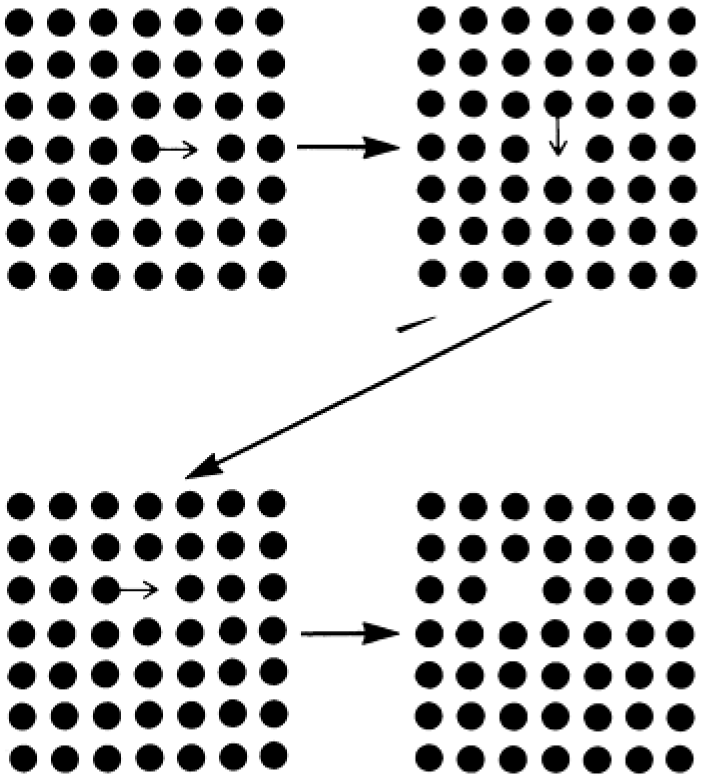

Fig. 3 Schematic depiction of diffusion by vacancy movement. The vacancy moves to the new positions with time as shown by the small arrows. The large arrows show the changes with time.

Diffusion in Alloys (Chemical Diffusion). When two metals (or alloys) are placed in contact, atoms will begin to migrate across the contacting interface. Such diffusion of unlike species is called chemical diffusion, and is illustrated schematically in Fig. 4. (For the process to occur as shown in Fig. 4, the metals have to be soluble in each other; otherwise, when sufficient amounts of one metal diffuse into the other to reach a concentration corresponding to the solubility limit, precipitation of a second phase occurs.) The chemical diffusion depicted in Fig. 4 actually occurs by vacancy diffusion.

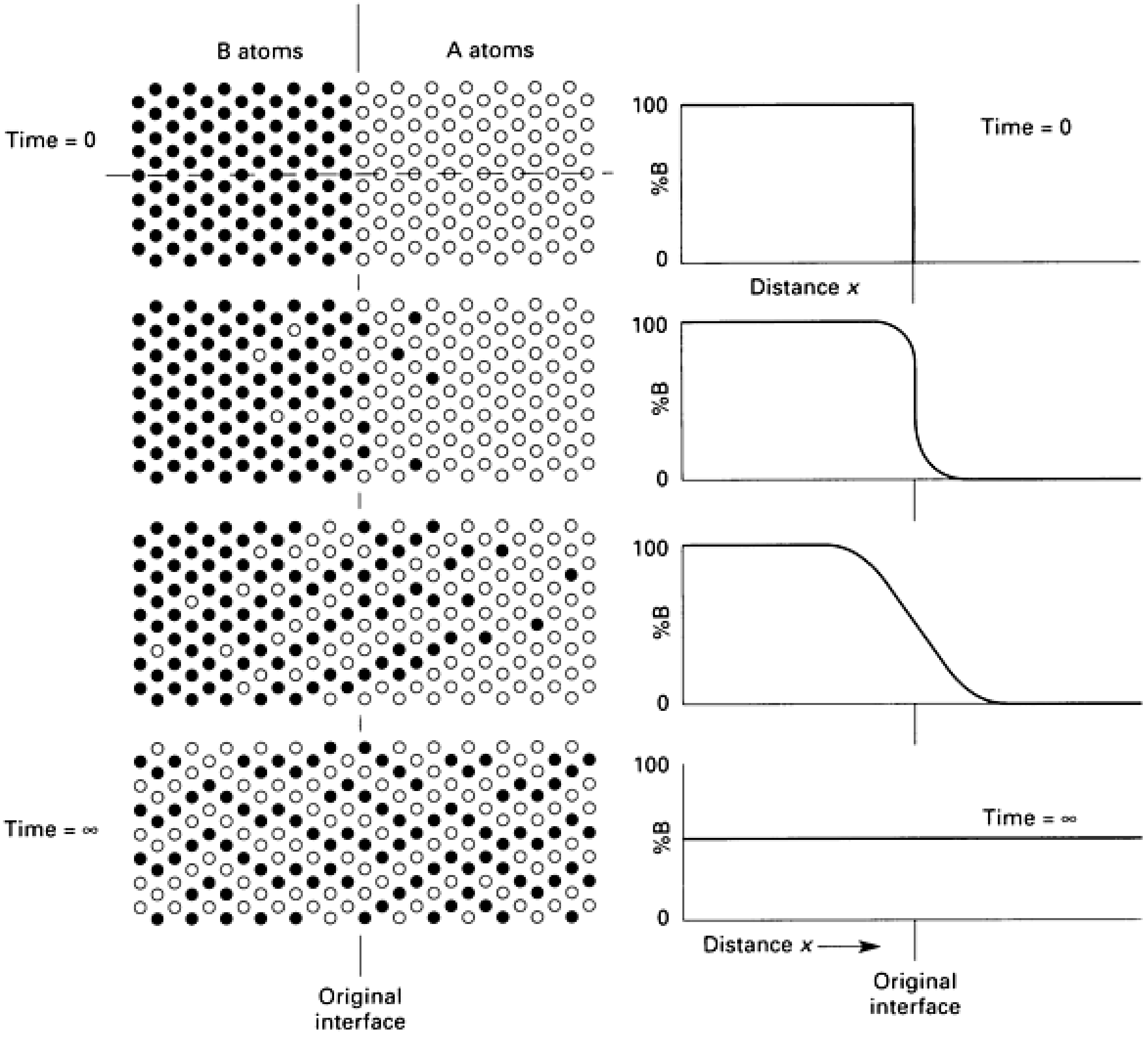

Fig. 4 Schematic illustration of chemical diffusion involving two different metals. The diffusion couple is made up of pure B (solid circles) and pure A (open circles). As time progresses, mixing on the two sides occurs. At infinite time, complete mixing has been achieved, with the chemical composition being identical on both sides.

Fick's Laws of Diffusion. The mathematical relation that connects the concentration of the diffusing species with distance is Fick's law, a phenomenological equation which fits well most diffusion data. Fick's first law states that the diffusion flux, J (in one-dimensional diffusion), is given by:

$$J = -D(dC/dx) \qquad \textbf{(Eq 1)}$$

where C is concentration and x is distance. D is a constant at a given temperature, but may be concentration-dependent; it is called the diffusivity or diffusion coefficient. Figure 5 illustrates the relation between these terms and the concentration profile associated with chemical diffusion, such as illustrated in Fig. 4. Figure 6 shows data typical of those obtained by machining thin layers from a diffusion couple and analyzing each for the amount of the metals present. The diffusion flux (if concentration is put in proper units) is defined as thenumber of atoms of the diffusing species which pass through a plane of unit area, which is normal to the diffusion direction, per unit time. Thus, the flux may be given in terms of number of atoms per square centimeter per second.

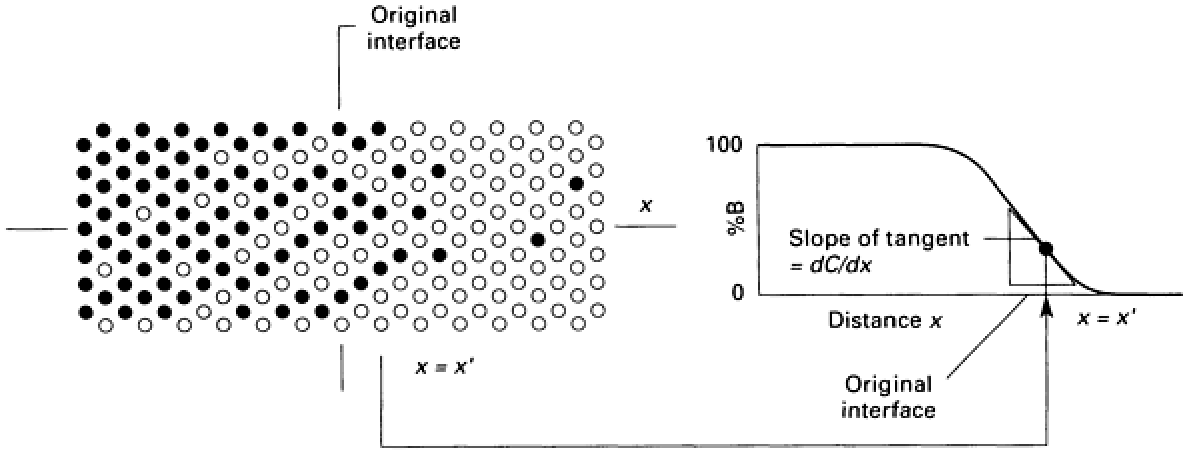

Fig. 5 Illustration of the meaning of the terms in Fick's first law of diffusion. Flux of atoms across the plane at $x = x'$ is the number of atoms crossing a plane 1 cm square per unit time (s) and is proportional to the gradient dC/dx at that location ($x = x'$): $J = -D(dC/dx)$. The proportionality constant is the diffusivity or diffusion coefficient. The negative sign is required to make the flux positive to be physically realistic, as the gradient dC/dx is negative.

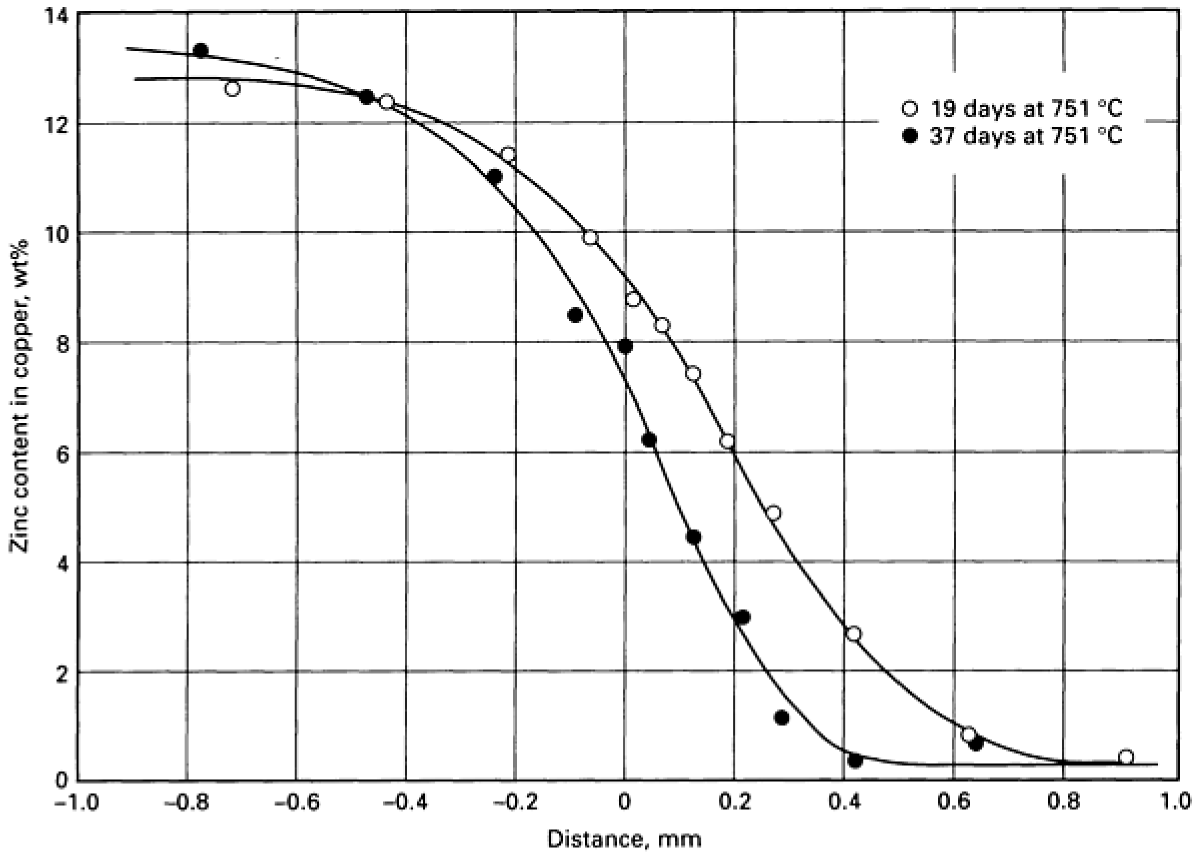

Fig. 6 Concentration profile data typical of metals obtained from a diffusion couple, which in this case was copper-zinc. Each point represents the chemical analysis of a thin layer machined from the sample. Adapted from Ref 1

The effect of time, *t*, on the flux is incorporated in Fick's second law (again, for one-dimensional diffusion):

$$dC/dt = D\frac{d}{dx}(dC/dx) = D\frac{d^2C}{dx^2} \qquad \textbf{(Eq 2)}$$

If the diffusion couple consists of two pure metals A and B that are completely soluble in each other, the solution to this equation is:

$$C_A = \frac{1}{2}\ [1 - f\ (x/2\sqrt{Dt})] \qquad \textbf{(Eq 3)}$$

where f is the Gauss error function and C_A is the concentration of A at distance *x* from the original interface. (Similar expressions are obtained for different starting conditions--for example, an alloy coupled against a pure metal, and so on. See Ref 2.) To extract *D*, then, for a given diffusion time *t* at a given distance *x*, the value of C_A is obtained (for example, read from Fig. 6). This allows a value of $f\ (x/2\sqrt{Dt})$ to be obtained. Then, error function tables are used to determine the argument of $f\ (x/2\sqrt{Dt})$--that is, to determine a value for $(x/2\sqrt{Dt})$. Then *D* is obtained.

Such a procedure should yield the same value of *D* no matter what value of *x* is chosen. However, it is found that *D* will usually vary, meaning that it is a function of composition. In this case, the equation to use is:

$$dC/dt = \frac{d}{dx}(DdC/dx) \qquad \textbf{(Eq 4)}$$

The solution is more complicated, but allows determination of the diffusion coefficient as a function of composition (see Ref 2).

An important practical relation evolves from the solution to Fick's second law--namely, that the time-distance relation for a given concentration *C* is $x^2 \cong Dt$. This means, for example, that during a homogenization treatment designed to remove the effects of dendritic segregation (coring), the time is proportional to x^2, where *x* is approximately the dendritic arm spacing. This expression is a conservative approximation, and more exact solutions are available in the text by Shewmon (Ref 2).

Temperature Dependence of the Rate of Diffusion. The dependency of the rate of diffusion on temperature is found to be exponential, which is not surprising, because many rate reactions obey such a dependency. Thus, *D* is given by:

$$D = D_0\ e^{-B/T} \qquad \textbf{(Eq 5)}$$

where D_0 and *B* are constants, and *T* is absolute temperature. Theoretical treatments show that this should be written as:

$$D = D_0 e^{-Q/RT} \qquad \textbf{(Eq 6)}$$

where *R* is the ideal gas constant and *Q* is the activation energy for the diffusion process. *Q* reflects the energy required to move an atom over a barrier from one lattice site to another; the barrier is associated with the requirement that the atom must vibrate with sufficient amplitude to break the nearest neighboring bonds in order to move to the new locations.

The values of D_0 and Q shown in Table 1 typify those found in metals. The equation above for the temperature dependency of D predicts that log D plotted versus $1/T$ should be a straight line, and Fig. 7 shows some typical linear results for metals and alloys.

Table 1 Values of the diffusion constant (D_0) and the activation energy (Q) for diffusion in various substitutional and interstitial solid solutions

Solute	**Solvent (host structure)**	**D_0, cm^2/s**	**Q, kcal/mole**
Substitutional diffusion			
Copper	Copper	0.78	50.50
Copper	Tin	0.11	45.00
Copper	Nickel	1.92	68.00
Nickel	Copper	1.1	53.80
Copper	Aluminum	0.647	32.27
Zinc	Copper	0.73	47.50
Lead	Lead	0.887	25.50
Titanium	Titanium	0.000358	31.20
Aluminum (4%)	Copper	0.0455	39.50
Zinc (24-29%)	Copper	0.095	35.00
Interstitial diffusion			
Hydrogen	Copper	10^{-2}	10.00
Oxygen	Copper	10^{-3}	46.00
Carbon	Titanium	0.00302	20.00
Oxygen	Titanium	1	40.00
Hydrogen	Tantalum	. . .	6.00

Carbon	Tantalum	0.0061	38.52
Nitrogen	Tantalum	0.0056	37.84
Oxygen	Tantalum	0.0044	25.45

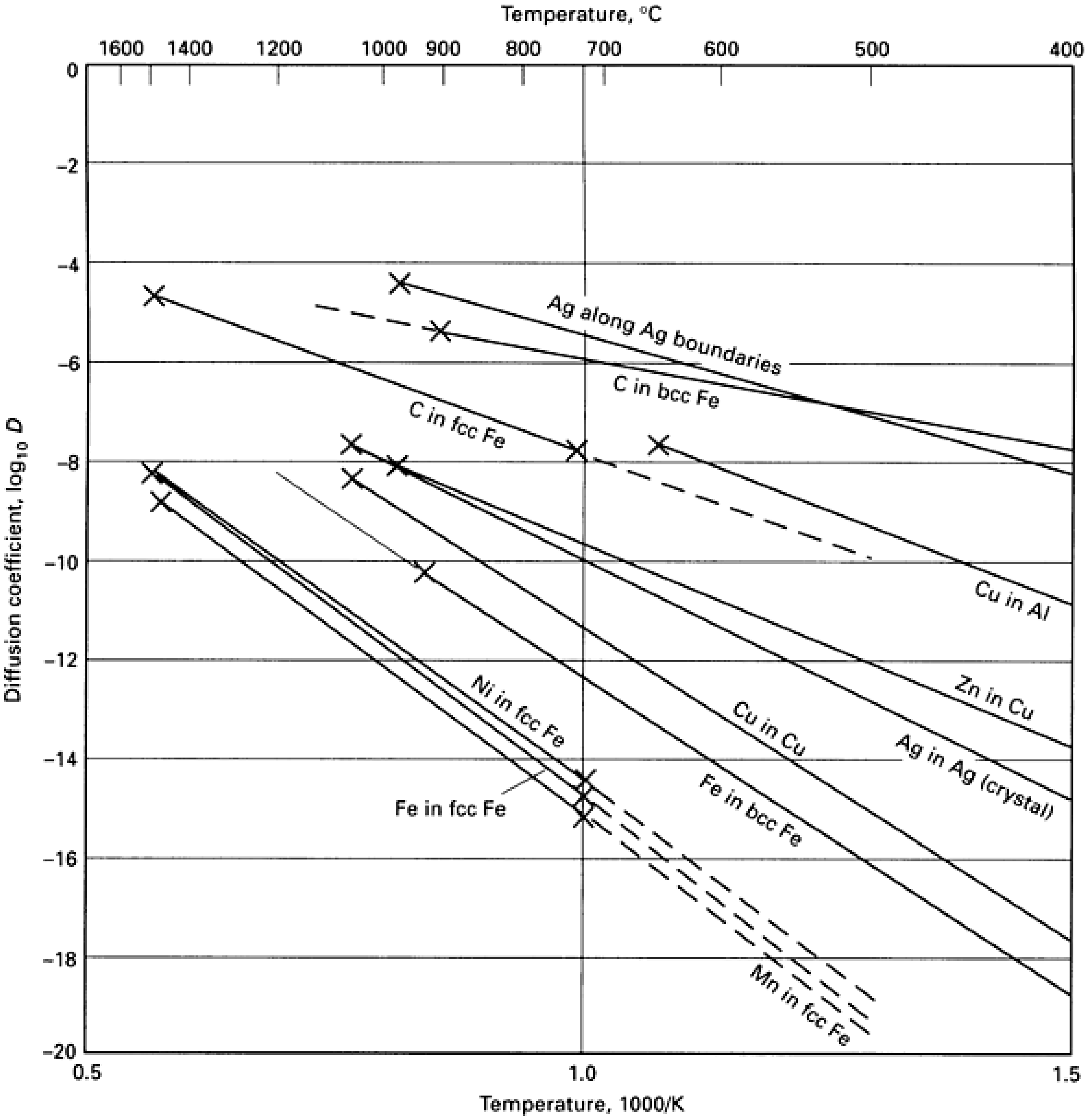

Fig. 7 Plots of diffusion coefficients and temperature (log *D* versus 1/*T*) for several metals. The straight lines are prominent and commonly found. Source: Ref 3

The exponential temperature dependence is important in heat treating. It shows that the rate of change in processes which are diffusion-controlled will increase greatly with an increase in temperature. Thus, an increase in temperature of 10 K will approximately double the rate of the process.

Intrinsic Diffusion Coefficients. If the original interface of the diffusion couple is identifiable, then experiments show that the location where half of the diffusing species will have moved from one side to the other does not coincide

with the original interface. This is sometimes referred to as the *Kirkendall effect*, and is taken as strong experimental evidence of the vacancy mechanism of diffusion in metals. Darken showed that the relation between the measured diffusion coefficient (as described above) and the intrinsic diffusion diffusivities of the individual atom species (for a binary system of atoms A and B) is:

$$D = C_A D_A + C_B D_B \qquad \textbf{(Eq 7)}$$

Here C_A and C_B are the mole fractions of A and B, respectively, and D_A and D_B are the intrinsic diffusivities of A and B, respectively. D_A and D_B are concentration-dependent.

Interstitial Diffusion. If the solute atom is sufficiently small, it will locate in an interstice between the larger solvent atoms, forming an interstitial solid solution. Diffusion of interstitial atoms occurs, not by a vacancy mechanism, but by the atoms jumping from one interstitial site to another. (Fick's laws still apply.) As the interstitial solute atom increases in size, the activation energy increases (Table 1), showing that it becomes more difficult for the atom to move between the solute solvent atoms to a neighboring interstitial site. In general, the activation energy for interstitial diffusion is less than that for substitutional diffusion.

Grain-Boundary Diffusion. Experimental studies have shown that diffusion along grain boundaries, along the core of dislocations and on free surfaces is considerably more rapid than diffusion through the interior of a crystal. Of particular interest here is grain-boundary diffusion, which influences precipitation and phase changes at the boundary. The data in Fig. 7 for self-diffusion in silver show that the grain-boundary diffusivity is several orders of magnitude greater than bulk diffusion. Also, as temperature decreases, bulk diffusion becomes slower and grain-boundary diffusion becomes more important.

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Annealing of Cold Worked Metals

Dislocations. Plastic deformation in metals and alloys occurs primarily by relative movement or slip of blocks of material on specific crystallographic planes (slip planes) and in certain directions (slip directions). (Plastic deformation in metals can also occur by twinning. However, in the brief treatment here, this mechanism will not be discussed.) This occurs not by movement of regions of the crystal as a whole, but by movement of successive dislocations. A dislocation is a lattice effect (either edge or screw) which is present in even well-annealed metals as a consequence of prior processing. Dislocations play a central role in plastic deformation because less energy is required to produce slip by movement of the dislocations than by movement of entire regions of a crystal past each other. This process is illustrated in Fig. 8 for an edge dislocation. Obviously, millions of dislocations must repeat this process in order to generate visually obvious shape changes. This is possible, however, because the dislocations, which are present in the metal prior to plastic deformation, create other dislocations by a multiplication mechanism during plastic deformation.

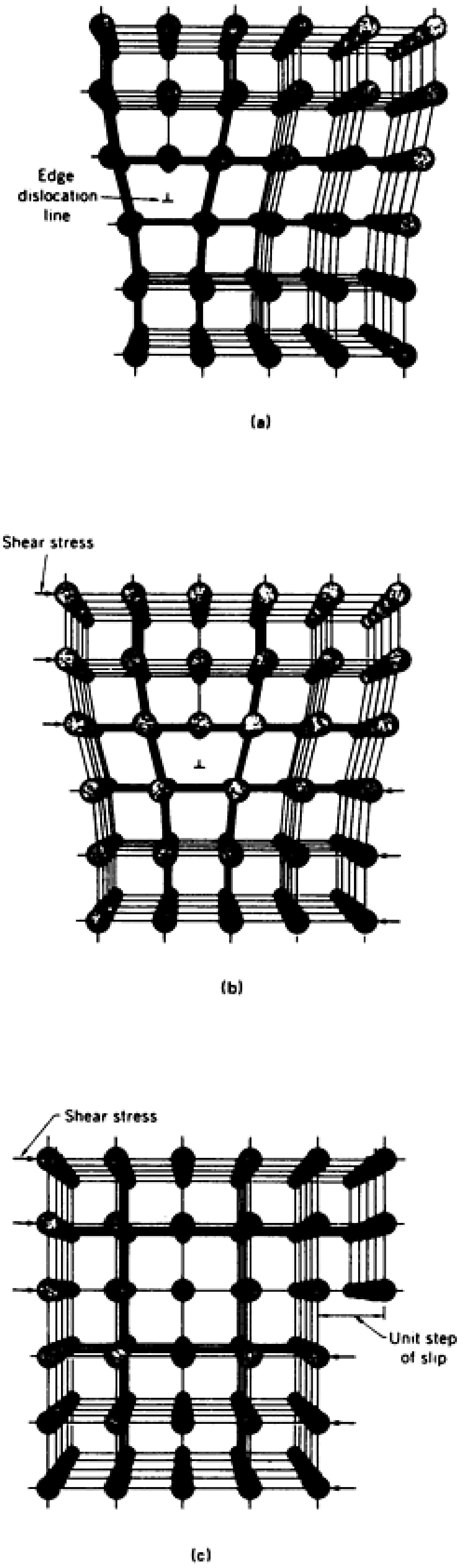

Fig. 8 The motion of an edge dislocation and the production of a unit step of slip at the surface of the crystal. (a) An edge dislocation in a crystal. (b) The dislocation has moved one lattice spacing due to the shearing force. (c) The dislocation has reached the edge crystal and produced unit slip. Adapted from Ref 4

In hexagonal close-packed crystals, the prominent slip plane is the close-packed (001) plane, and the slip directions in this plane are the close-packed directions, of which there are three nonparallel, identical choices. Thus, this crystal structure exhibits three slip systems. In the face-centered cubic structure, the slip plane is also the close-packed plane {111}. However, in this system there are four types of nonparallel {111} planes. In each plane there are three possible slip directions (<110> type), and hence 12 slip systems. In the body-centered cubic structure, the slip plane is of the {110} type (also the most closely packed plane in this system) of which there are six, and the slip directions are of the <111> type, of which there are two in each plane. Thus, the body-centered cubic structure also has 12 slip systems. The types of slip plane and slip direction are sensitive to temperature, and in some alloys other slip systems are activated when temperature changes.

Effect of Cold Working on Properties and Microstructure. The multiplication of dislocations on several slip systems upon plastic deformation leads to their interaction with each other, and this restricts their movement, so that further deformation requires an increase in external load. Thus, the material work (or strain) hardens. This effect is illustrated in Fig. 9, which shows the strengthening induced by deformation in rolling of pure copper, and of copper-zinc solid-solution alloys, at 25 °C (77 °F). Plastic deformation such that strengthening or hardening occurs is called *cold working*; plastic deformation such that work hardening does not occur is called *hot working*. (Alternative definitions are given below, under "Hot Working.") Note that these definitions have no particular attachment to room temperature.

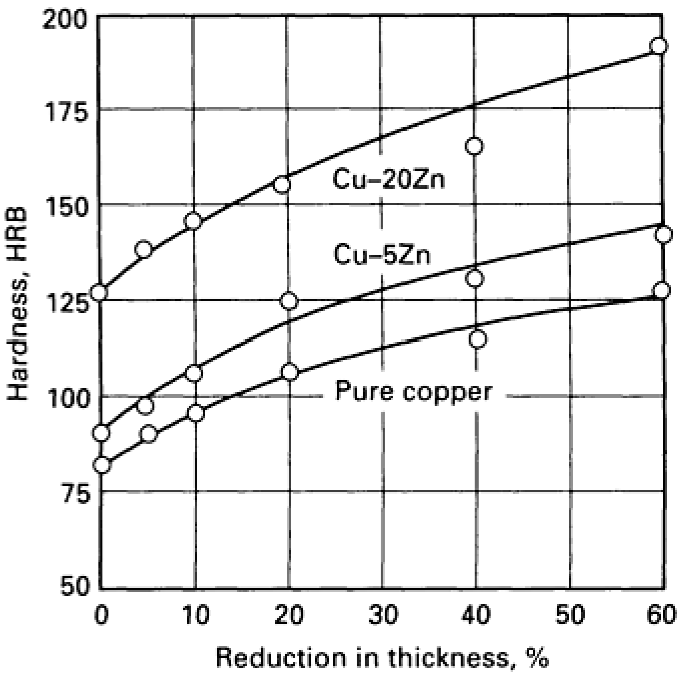

Fig. 9 The effect of plastic deformation (by rolling at 25 °C, or 77 °F) on hardness of pure copper and two Cu-Zn solid-solution alloys. Source: Ref 5

Cold working increases hardness, yield strength, and tensile strength, and lowers ductility. It also increases electrical resistivity because the increasing density of dislocations scatters the electrons. Figure 10 illustrates the effects of cold working on several properties.

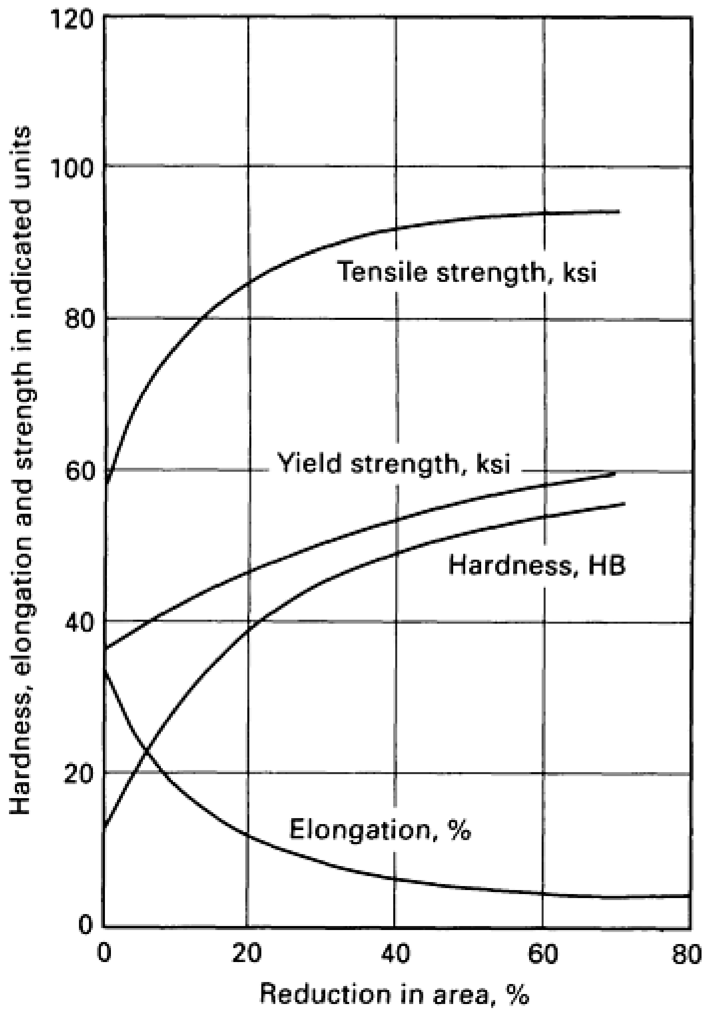

Fig. 10 The effect of cold working (by rolling at 25 °C, or 77 °F) on the tensile mechanical properties and hardness of oxygen-free, high-conductivity (OFHC) copper. Adapted from Ref 6

Cold working of a metal causes distortion of grains, and the specific nature of this distortion depends on the type of deformation (for example, rolling, swaging, and so on). If the plane of observation is parallel to the rolling direction, the grains will appear elongated in the rolling direction. Also observed in the microstructure are parallel striations within the grains, the density of which increases with the amount of deformation. These striations are actually rows of etch pits, or etched grooves, where the etchant has removed metal preferentially at surface locations at which the dislocations emerge. Such striations are sometimes called *deformation bands.* In metals and alloys which show annealing twins (mainly face-centered cubic metals, such as copper and brass), the twins, originally appearing as straight lines crossing (or nearly crossing) the grains, become bent, distorted, and fragmented. All of these microstructural features of cold worked metals are illustrated in Fig. 11.

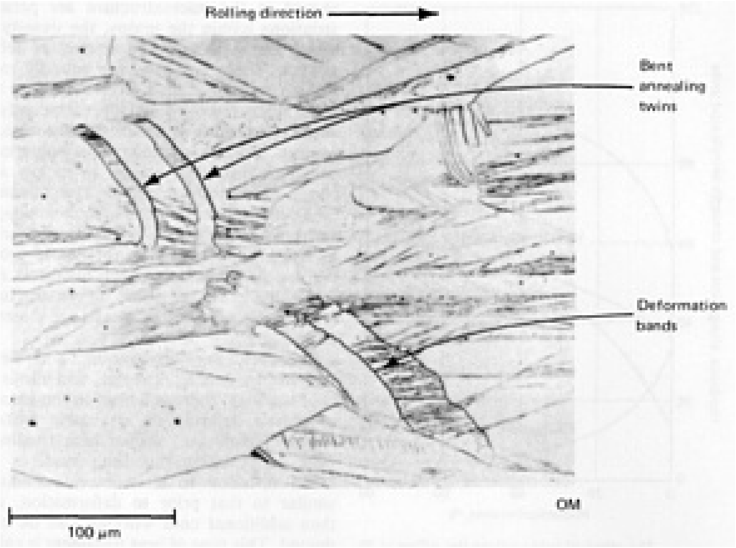

Fig. 11 The microstructure of a Cu-5Zn alloy cold rolled at 25 °C (77 °F) to a 40% reduction in thickness, showing deformation bands and bent annealing twins revealed by etching the polished surface. The features marked "Bent annealing twins" are not mechanical twins. Before cold working, straight annealing twins become bent and curved due to slip occurring across them, thus producing bent annealing twins. In this type of copper-base solid solution, mechanical twins are very difficult to form, requiring high deformation rates (for example, explosive forming). OM, optical micrograph. Source: Ref 5

Recovery, Recrystallization, and Grain Growth. In shaping of metals and alloys by cold working, there is a limit to the amount of plastic deformation attainable without fracture. However, proper heat treatment prior to reaching this limit restores the metal or alloy to a structural condition similar to that prior to deformation, and then additional cold working can be conducted. This type of heat treatment is called *annealing*, and in this section some of the principles involved and the effects which occur are summarized.

Because cold working produces an increasing concentration of lattice defects (for example, dislocations), the energy of the crystals is increased. Thus, there is a thermodynamic driving force for the metal to undergo changes which will return it to the original, low-energy condition. The rates of these changes depend on the mechanisms involved, and are sensitive functions of temperature and alloy.

The changes in strength that occur during annealing are illustrated by the hardness data in Fig. 12(a). The hardness (and the yield and tensile strengths) initially remains approximately constant (or increases slightly), then shows an abrupt decrease, followed by a continued, but gradual, decrease. The data shown in Fig. 12(a) are for a fixed temperature. A similar result is obtained by annealing samples for a fixed time at increasing temperatures, as shown in Fig. 12(b).

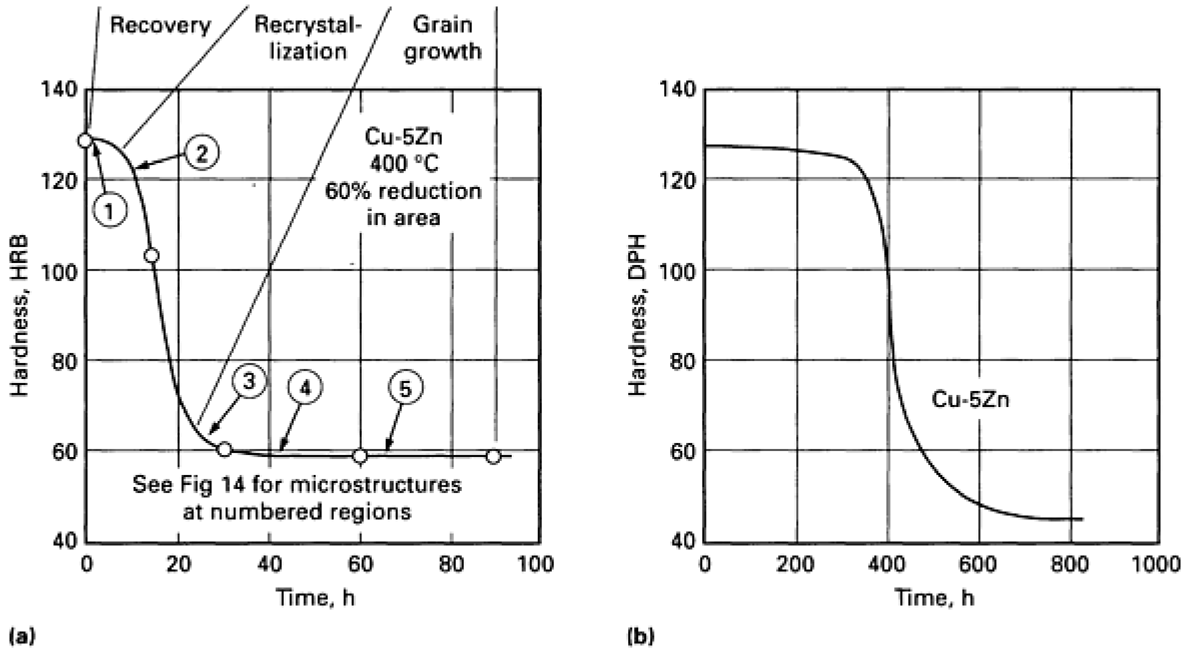

Fig. 12 (a) Effect of annealing time at fixed temperature (400 °C, or 750 °F) on hardness of a Cu-5Zn solid-solution alloy cold worked 60%. (b) Effect of annealing temperature at fixed time (15 min) on hardness of a Cu-5Zn solid-solution alloy cold worked 60%

The stage of annealing for short times or at low temperatures wherein the hardness remains constant, or increases slightly, is called the *recovery region*. Here the dislocations undergo movement by thermal activation, being rearranged into arrays somewhat more stable and more difficult to move than in the cold worked, unannealed condition, and hence cause a slight increase in hardness. In this period, such rearrangement allows some properties to attain their values prior to cold working, and hence is referred to as recovery. One such property is electrical resistivity, as illustrated in Fig. 13. The cellular arrangement of the dislocations, compared with that of the cold worked condition, increases the mean free path of the electrons and lowers the resistance.

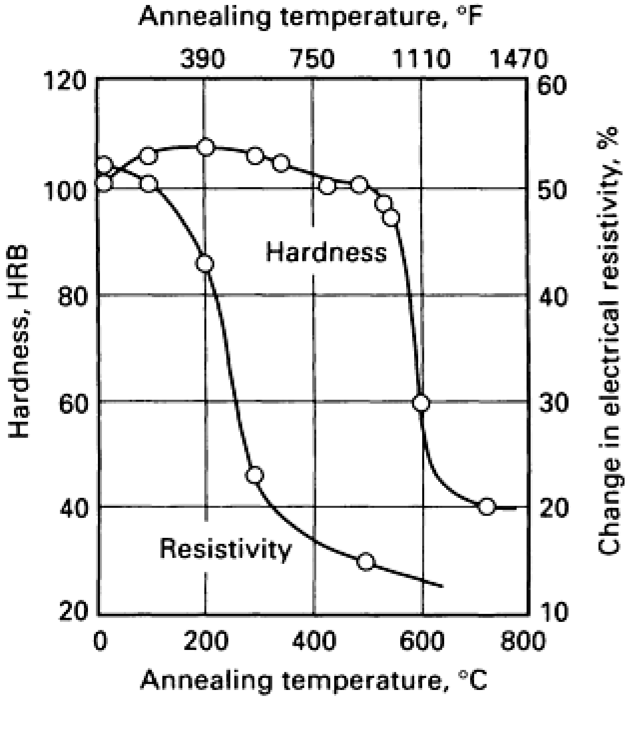

Fig. 13 Effect of annealing temperature on hardness and electrical resistivity of nickel. The metal has been cold worked at 25 °C (77 °F) almost to fracture. Annealing time, 1 h. Adapted from Ref 7

After longer times or at higher temperatures, the structure undergoes a more radical change. Small crystals appear which contain a low dislocation density (of magnitude similar to that prior to cold working) and hence are relatively soft. These crystals nucleate in regions of high dislocation density, and thus in the microstructure appear at or near deformation bands. With time, these nuclei grow, and more nuclei form in the remaining cold worked matrix. Eventually, these grains contact each other (at that time the original worked material has disappeared). The formation of these grains is referred to as *recrystallization.* During this recrystallization period, strength decreases drastically (Fig. 12 and 13).

Following recrystallization, the energy of the alloy is reduced further by a decrease in the grain-boundary area by grain growth. Thus, the long-time or high-temperature region of the annealing curve is referred to as grain growth. Because strength decreases as grain size increases, during this period the hardness decreases, although only gradually (Fig. 12a).

The microstructural changes which occur during annealing are illustrated in Fig. 14. During recovery, there is a decrease in the density of deformation bands, although this effect is not prominent. When crystallization commences, small, equiaxed grains begin to appear (see micrograph 2 in Fig. 14 and Fig. 15) in the structure. These continue to form and grow until the cold worked matrix is consumed, which marks the end of the recrystallization period and the beginning of grain growth. Further annealing causes only an increase in grain size (see micrographs 3, 4, and 5 in Fig. 14).

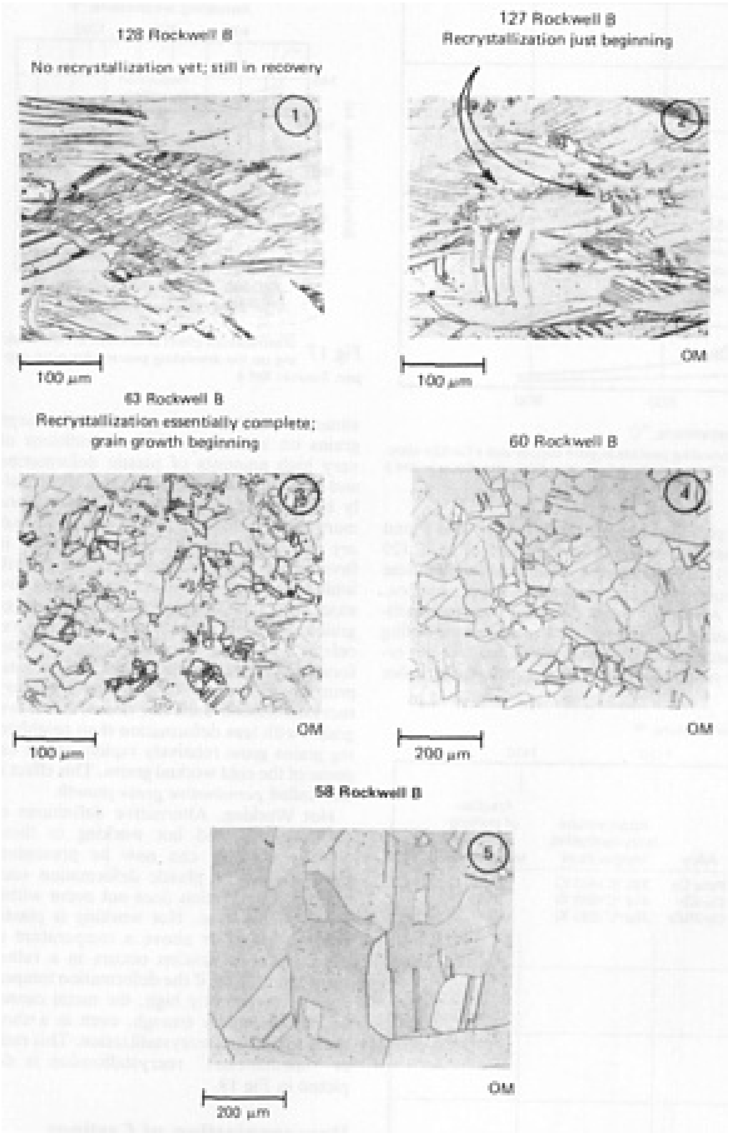

Fig. 14 Microstructure of a Cu-5Zn alloy, cold rolled to 60%, then annealed for different times at 400 °C (750 °F). The numbers refer to the different annealing times shown in Fig. 12(a). Source: Ref 5

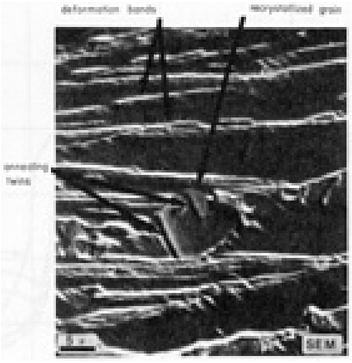

Fig. 15 High-magnification scanning electron micrograph showing a small recrystallized nucleus. Cu-5Zn alloy, cold worked by rolling 20 °C (68 °F) to reduction in thickness of 60%; annealed 60 min at 350 °C (660 °F). Source: Ref 5

Factors Affecting Recrystallization. Because annealing of cold worked metals is usually carried out to soften the material, the temperature and time required to complete recrystallization must be known in order to determine the proper heat treatment. It is common to refer to the recrystallization temperature as an indicator of the temperature at which the metal must be annealed for softening. (This temperature can be taken to be that which gives any specified amount of recrystallization.)

Several factors affect the value of the recrystallization temperature. Two of the most important are annealing time and amount of prior cold work. Figure 16 illustrates the effect of annealing time. The longer the time at a given temperature, the farther the metal progresses in the annealing process. Thus, if a metal just commences recrystallization at 200 °C (400 °F) in 15 min, then it may be completely recrystallized in 30 min.

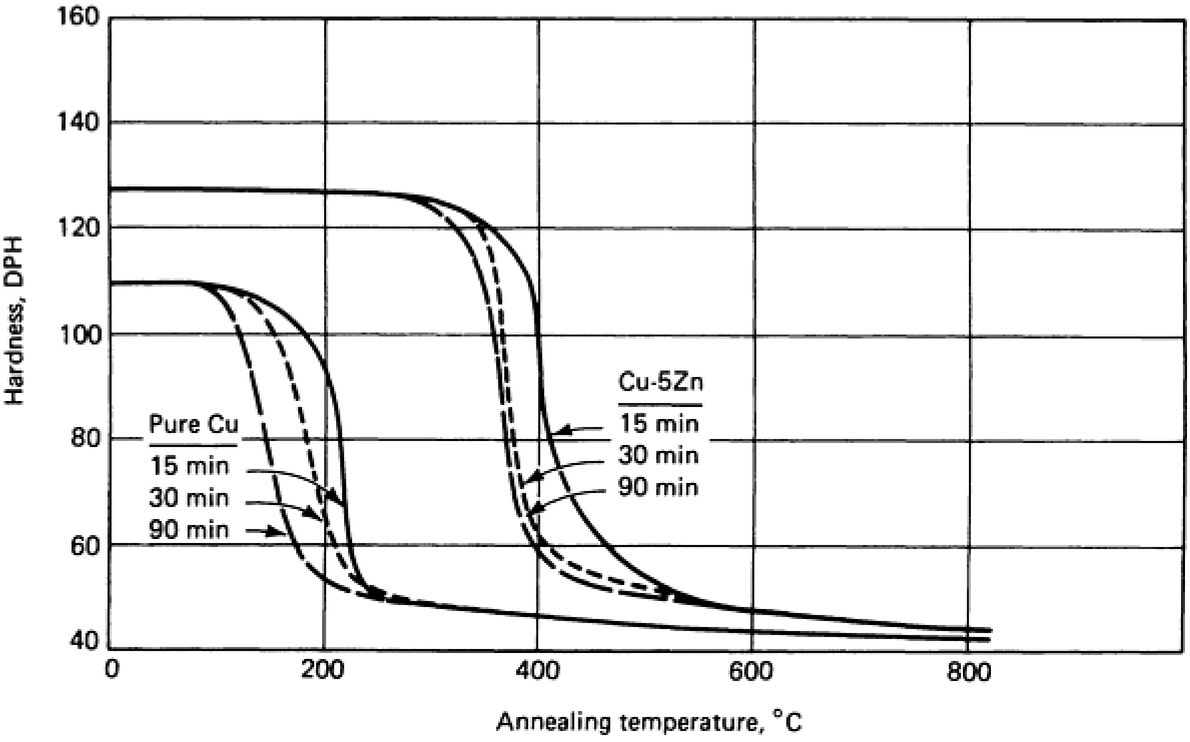

Fig. 16 Illustration of the effect of annealing time on the annealing process in pure copper and a Cu-5Zn alloy. Both materials were originally cold rolled at 25 °C (77 °F) to 60% reduction in thickness. Source: Ref 5

The effect of the amount of prior cold work is illustrated in Fig. 17. Increasing amounts of plastic deformation increase the concentration of lattice defects (for example, dislocations) and make the metal more thermodynamically unstable. Hence, recrystallization occurs at lower temperatures, or in shorter times, the greater the amount of cold work. Although this is the main effect, it is to be noted that the type of deformation, the rate of deformation, and the deformation temperature also affect the rate of recrystallization.

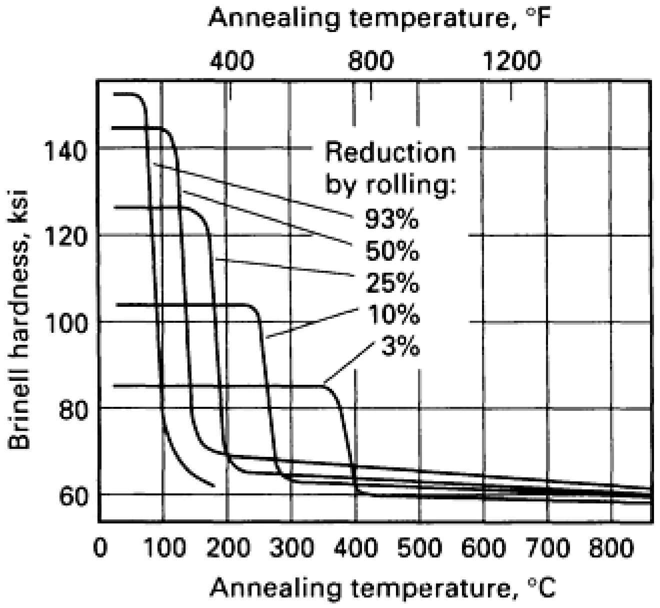

Fig. 17 Illustration of effect of amount of cold working on the annealing process for pure copper. Source: Ref 8

Chemical composition affects the recrystallization process, and here a distinction must be made between solid-solution alloys and multiphase alloys. In many alloys containing second-phase particles, the presence of such particles favors formation of recrystallization nuclei and thus lowers the recrystallization temperature. In solid-solution alloys, even quite small amounts of solute can have potent effects on the recrystallization temperature. For example, addition of 0.05% Ag to copper will increase the recrystallization temperature from about 140 °C (285 °F) to about 340 °C (645 °F). Thus, because silver only slightly lowers the electrical conductivity of copper, this alloy is used in applications which require the alloy to be cold worked for strength but in which slight heating may occur, and stress relaxation and recrystallization must be prevented.

If the solubility is sufficiently high to allow considerable solute concentration, the recrystallization temperature may decrease. This is illustrated in Fig. 18 for Cu-Zn alloys. This effect is expected to be related to the influence of zinc on the atom mobility in Cu-Zn alloys, and indeed the activation energy, Q, for diffusion in these alloys increases slightly with additions of up to 10% Zn, then decreases considerably with additions from 10 to 20% Zn.

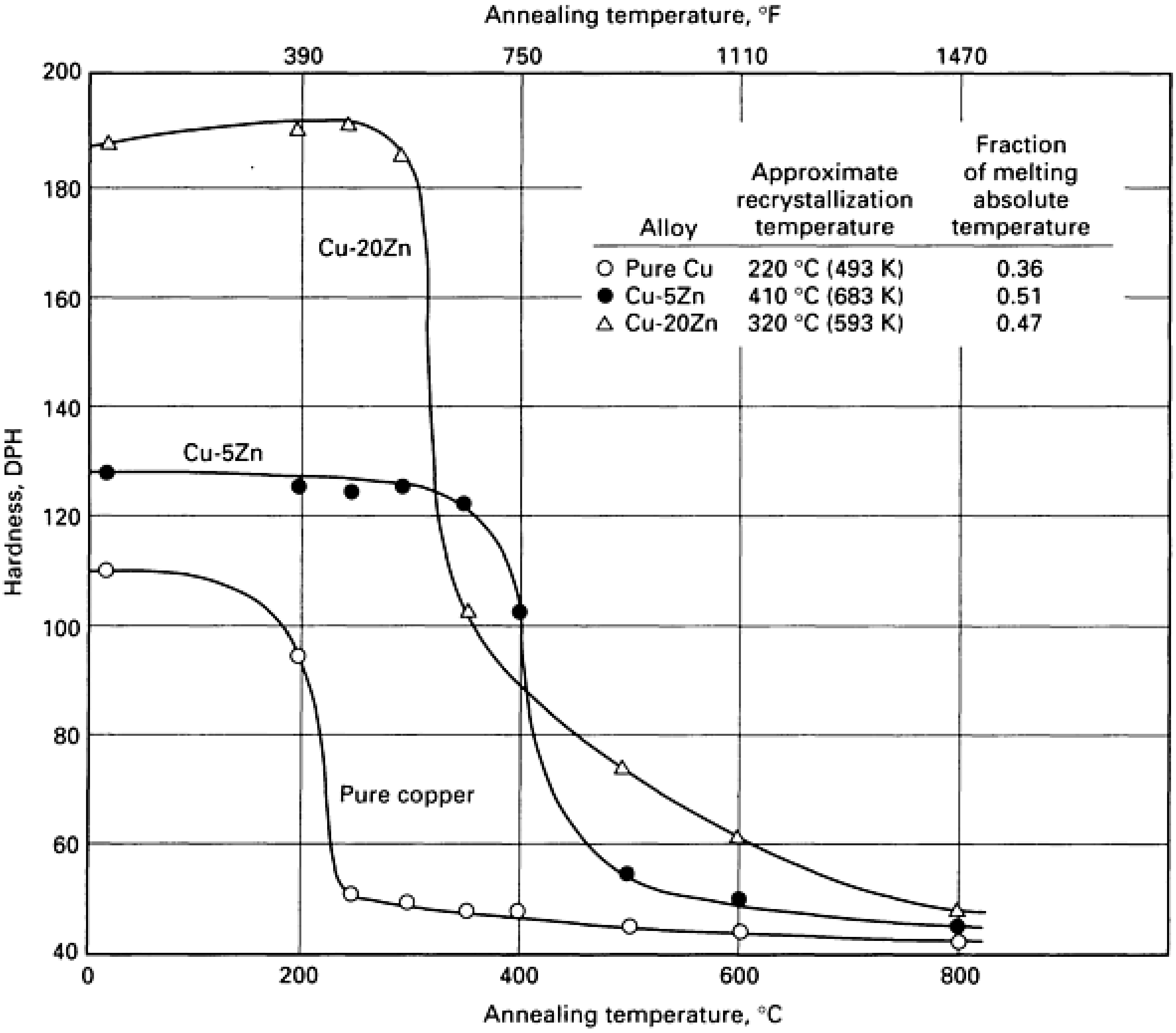

Fig. 18 Illustration of effect of zinc content of Cu-Zn solid-solution alloys on the annealing process. The alloys were originally cold rolled at 25 °C (77 °F) to 60% reduction in thickness. The recrystallization temperatures listed are based on the inflection point of each curve. Source: Ref 5

It is useful here to note a rule of thumb--that the recrystallization temperature is approximately 0.3 to 0.6 of the absolute melting point. In the case of Cu-Zn solid-solution alloys, addition of zinc to copper lowers the melting point, and thus the recrystallization temperature will decrease for high zinc contents (for example, 20 to 30%) (see Fig. 18).

Because recovery, recrystallization and grain-growth processes all involve atom movement, it is expected that the rates of these processes will depend on temperature in the same functional relation as does diffusion--that is, the rate is proportional to $e^{-Q/RT}$, where Q is the activation energy for the particular process. Thus, we may take as an approximation that the time required at a given temperature for recrystallization to commence (or for any given amount of recrystallization to be attained) will be inversely proportional to this exponential expression. Using as typical activation energies those given for diffusion, it is found that a decrease in temperature of 10 °C (20 °F) may increase by a factor of two the time required for recrystailization to commence.

Abnormal Grain Growth. The recrystallization process referred to in the preceding discussions is sometimes called *primary recrystallization*, to distinguish from other situations which lead to unusually large grains on annealing. Under conditions of very high amounts of plastic deformation and high annealing temperatures, abnormally large grains can develop following primary recrystallization: this is called *secondary recrystallization.* Such behavior is favored by the presence of grain-growth inhibitors, such as insoluble particles (for example, inclusions). Abnormally large grains can also form if the metal has received a critical, but small, amount of deformation (for example, about 10% or less) prior to annealing. In this case, primary recrystallization does not occur, but a few grains with less deformation than neighboring

grains grow relatively rapidly at the expense of the cold worked grains. This effect is also called *germinative grain growth.*

Hot Working. Alternative definitions of cold working and hot working to those given previously can now be presented. Cold working is plastic deformation such that recrystallization does not occur within a reasonable time. Hot working is plastic deformation at or above a temperature at which recrystallization occurs in a rather short time. Thus, if the deformation temperature is sufficiently high, the metal cannot be cooled rapidly enough, even in a short time, to prevent recrystallization. This rather "spontaneous" recrystallization is depicted in Fig. 19.

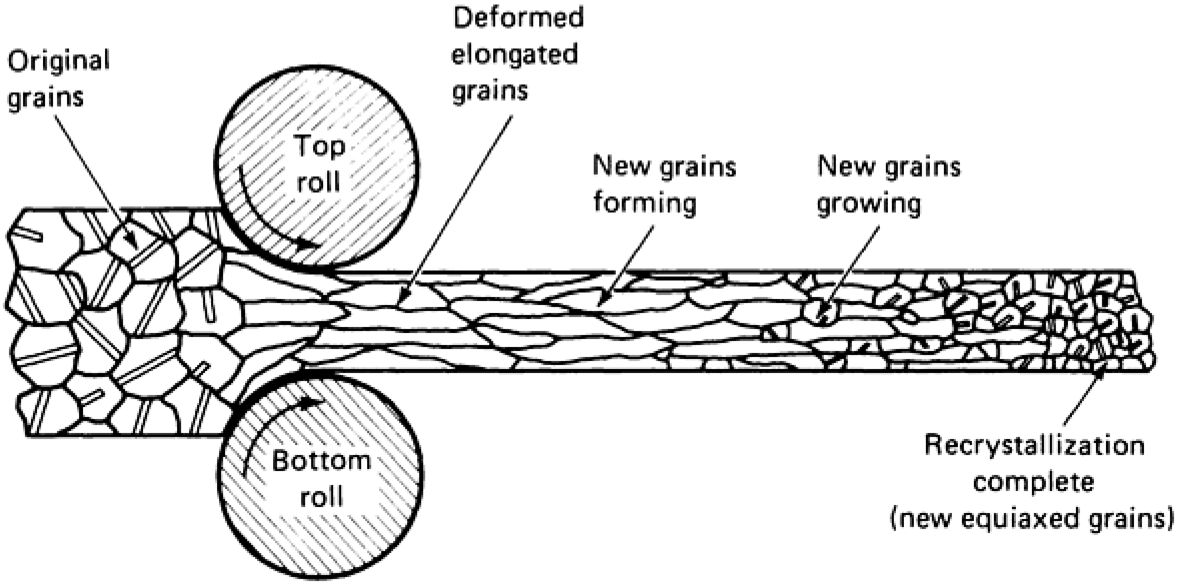

Fig. 19 Schematic illustration of the change in grain structure on hot rolling. Source: Ref 9

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Homogenization of Castings

One of the most important commercial heat treatments is homogenization of castings. Such a treatment is used prior to mechanical processing of the cast ingot, and it is often used even when an object is cast into essentially the final shape. The temperatures and times used depend on the diffusion rate and the starting structure (the latter dictates the concentration gradients and the diffusion path). To understand how this enters into the situation, it is important to know how solidification occurs in alloys, and especially how chemical segregation develops during solidification.

Dendrite Formation. In metals and alloys, the crystals which form in the liquid during freezing generally have a configuration consisting of a main branch with many appendages. A crystal of such a morphology is called a dendrite ("fern-like"), and its formation is illustrated schematically in Fig. 20. During freezing, many crystals form, usually on the cold sidewalls of the mold, but also in the center of the casting. As these dendritic crystals grow, they eventually become large enough so that impingement occurs. Then the remaining liquid freezes, with a boundary formed between the

differently oriented grains. The original dendritic pattern may not be apparent by observation of only the geometry of the grain boundaries outlining the grains.

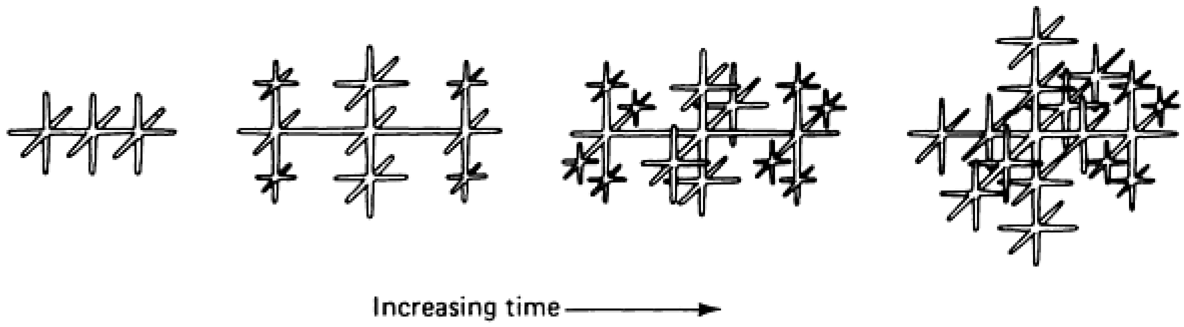

Fig. 20 Schematic illustration of a dendritic crystal forming in a liquid. Adapted from Ref 10

Coring. In solidification of most alloys, chemical segregation intrinsically accompanies dendrite formation. To see how this develops, consider a hypothetical alloy whose phase diagram is that shown in Fig. 21. On slow cooling of a liquid alloy containing 30% B, crystallization commences at temperature T_0. The chemical composition of this crystal will be 10% B. As cooling continues, the crystal grows in size (as a dendrite). The phase diagram shows that the equilibrium composition of the crystal must follow the solidus line (line abc in Fig. 21). Thus, the crystal continuously changes its chemical composition, approaching 30% B as the temperature approaches that of completion of freezing, T_2. At T_2, the metal consists of crystals each containing uniformly 30% B. Note that the center of each crystal corresponds to the original nucleus, which had only 10% B when freezing commenced. Thus, on cooling, as the dendrites increased in size, from each layer frozen onto the crystal some B atoms must move throughout the crystal, including some to the center, to maintain the chemical composition uniformly at the value given by the solidus at any given temperature.

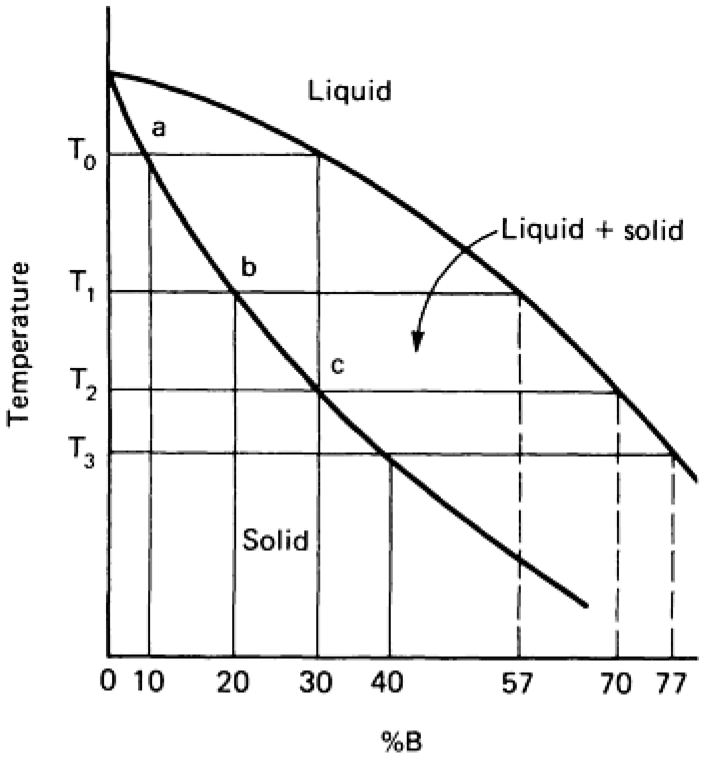

Fig. 21 Hypothetical phase diagram of system A-B, showing the composition of the solid as a 30% B alloy

freezes. Adapted from Ref 5

Clearly, such atom movements require finite time, and the question naturally arises as to what deviations from equilibrium will occur if the alloy is cooled rapidly from the liquid. A simplified picture of what occurs is as follows. On rapid cooling, the first crystals to form have a composition of 10% B. As these grow, the interface between the liquid and the solid crystals maintains the chemical composition given in the phase diagram. Thus, when the crystal has grown as the temperature has decreased from T_0 to T_1, the outside of the crystal will have a composition of 20% B. However, due to the rapid cooling, the center of the crystal will still be 10% B. Between the center and the outside, the composition varies smoothly between 10 and 20% B. The rapid cooling has not allowed sufficient time for significant diffusion to occur in this composition gradient. On slow cooling, freezing would be complete when the temperature reached T_2. However, at this temperature the outside of the crystal has a composition of 30% B, but the center only 10% B. Thus the average composition of the crystal is somewhere between 10 and 30% B. Freezing cannot be complete until the average composition reaches 30% B (because this is the composition of the alloy), and hence under-cooling occurs. Layers continue to add to the dendrite, until the sidearms impinge, and finally all of the dendrites impinge on each other, and freezing is complete. In the example used here, the last layer to freeze, when the sidearms make contact, contains 40% B (Fig. 21).

The frozen structure consists of dendrites in which the central regions of the main branch and of the sidearms contain about 10% B, and the regions where the sidearms met on completion of freezing contain about 40% B. If an etchant is used for which the rate of attack of the metal is sensitive to this compositional difference, then certain regions will be dissolved or attacked more readily than others. The surface then will consist of low and high regions, which reflect light differently, causing contrast in the appearance of the microstructure. An example is shown in Fig. 22 for a Ni-Cu alloy containing 30% Cu. Note that at low magnification the uneven etching has revealed the dendritic structure of the crystals.

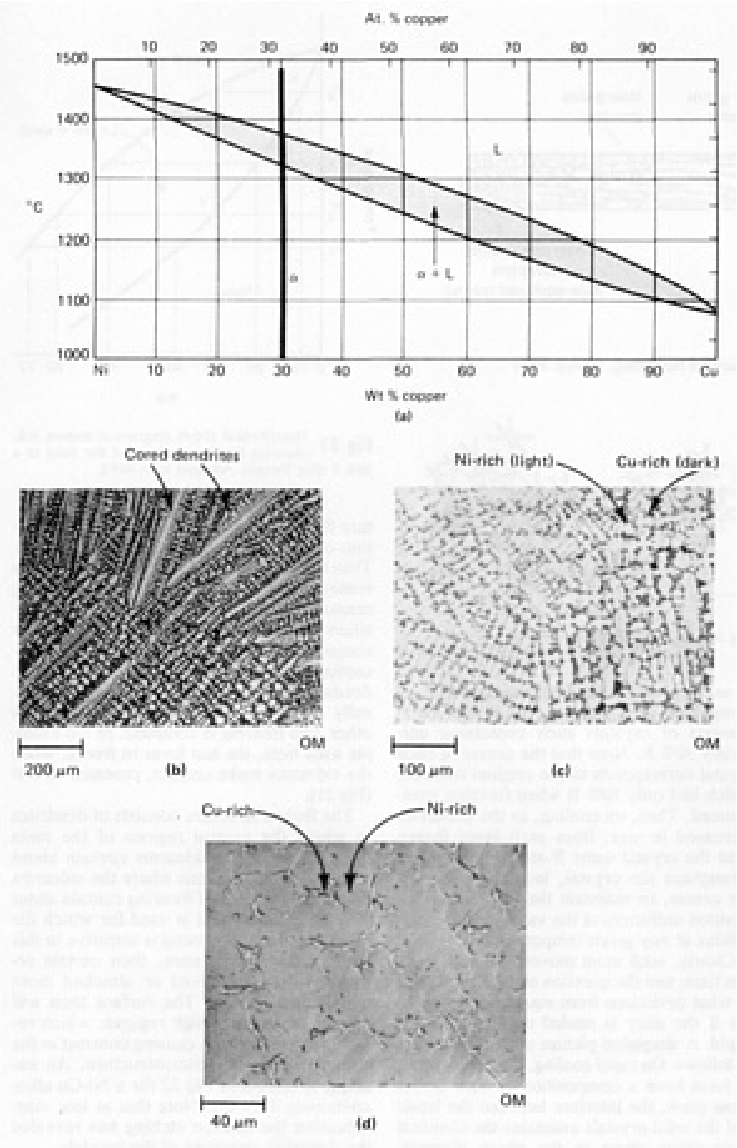

Fig. 22 The Ni-Cu phase diagram and the microstructure of a Ni-30Cu alloy that has been cooled rapidly from the liquid, developing a nonequilibrium cored structure. (a) Ni-Cu phase diagram. (b), (c), (d) The microstructure at increasingly higher magnifications. Note that the dendrite cells are approximately 40 μm across (d). Source: Ref 5

This chemically segregated, dendritic structure is referred to as cored, and the process of its formation is called coring.

Chemical Homogenization Annealing. The chemical gradients in a dendritically cored structure can be reduced to an acceptable level by annealing at a sufficiently high temperature for a sufficient time. The rate of diffusion is given by an appropriate solution to Fick's law. As a conservative approximation, the required time is $x^2 \cong Dt$, where x is the distance between the regions of low and of high concentration in the dendrite cell, which is one-half of the cell size. As an example, in Fig. 22(d) the cell size is approximately 40 μm, so x = 20 μm. Taking $D = 2 \times 10^{-10}$ cm^2/s at 1000 °C (1273 K) for a Ni-30Cu alloy, then the required homogenization time is about 6 h. At 1100 °C (1373 K), $D = 10^{-9}$, and the required time is 1 h. Obviously, higher temperatures lower considerably the required time, but other factors, such as excessive oxidation, must be considered.

If an ingot with a cored, cast structure, such as that shown in Fig. 22, is reduced in thickness 50% by rolling, then the dendritic cells will (on the average) be elongated in the rolling direction but reduced in thickness 50% in the through-thickness direction of the rolled plate. Thus the effective diffusion distance x becomes about 10 μm (0.4 mil). Then, at 1000 °C (1830 °F), the required homogenization annealing time becomes about 1 h, instead of the 6 h for the as-cast

structure. This points out the advantage in processing of coupling a homogenization anneal with plastic deformation to remove coring present in the as-cast structure.

In many alloy ingots, there also occurs gross, or ingot, segregation, where the chemical composition of the outside of the ingot may be different from that along its center-line. Here the final liquid freezes, and rejection of solute elements (frequently impurities) from the advancing front of the freezing crystals, in which they have a lower solubility, results in a region rich in these elements near the center. However, a calculation similar to that above shows that the diffusion distance in this type of chemical inhomogeneity is much too great to be reduced appreciably by homogenization annealing.

In many commercial nonferrous alloys, the as-cast structure will not only be cored, but also will contain nonequilibrium, second-phase particles. In such systems, on slow cooling, when freezing is complete a single-phase solid will be present (as described above). However, on rapid cooling in which coring occurs, the liquid composition may increase to the value of the eutectic before freezing is completed. Then this liquid freezes to a solid eutectic structure. The microstructure then consists of a dendritically cored matrix containing small regions of multiphase, eutectic solid. These regions will dissolve on proper solution heat treatment, and thus will be removed along with the coring.

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Precipitation Hardening Heat Treatments

In designing alloys for strength, an approach often taken is to develop an alloy in which the structure consists of particles which impede dislocation motion dispersed in a ductile matrix. The finer the dispersion, for the same amount of particles, the stronger the material.

Such a dispersion can be obtained by choosing an alloy which, at elevated temperature, is single phase, but which on cooling will precipitate another phase in the matrix. A heat treatment is then developed to give the desired distribution of the precipitate in the matrix. If hardening occurs from this structure, then the process is called precipitation hardening or age hardening. It is to be noted that not all alloys in which such a dispersion can be developed will harden.

The mechanism of strengthening by precipitation hardening involves the formation of coherent clusters of solute atoms (that is, the solute atoms have collected into a cluster but still have the same crystal structure as the solvent phase). This causes a great deal of strain because of mismatch in size between the solvent and solute atoms. The cluster stabilizes dislocations, because dislocations tend to reduce the strain, similar to the reduction in strain energy of a single solute atom by a dislocation. When dislocations are anchored or trapped by coherent solute clusters, the alloy is considerably strengthened and hardened.

However, if the precipitates are semicoherent (sharing a dislocation-containing interface with the matrix), incoherent (sharing a disordered interface, akin to a large-angle grain boundary, with the matrix), or are incapable of reducing strain behavior because they are too strong, a dislocation can circumvent the particles only by bowing into a roughly semicircular shape between them under the action of an applied shear stress. Consequently, the presence of the precipitate particles, and even more importantly the strain fields in the matrix surrounding the coherent particles, provide higher strength by obstructing and retarding the movement of dislocations. The characteristic that determines whether a precipitate phase is coherent or noncoherent is the closeness of match or degree of disregistry between the atomic spacings on the lattice of the matrix and on that of the precipitate.

Solution Heat Treatment. A prerequisite to precipitation hardening is the ability to heat the alloy to a temperature range wherein all of the solute is dissolved, so that a single-phase structure is attained. This is shown schematically in Fig. 23 for a 10% B alloy in a hypothetical system A-B. Heating above the solvus temperature T_2 for this alloy, and holding in the α range for sufficient time, will form the single phase α. This is the required solution heat treatment. This structure is then retained at ambient temperatures by cooling rapidly (for example, water quenching) from the α range to prevent the precipitate from forming. The structure is supersaturated with respect to the solute, and hence is unstable.

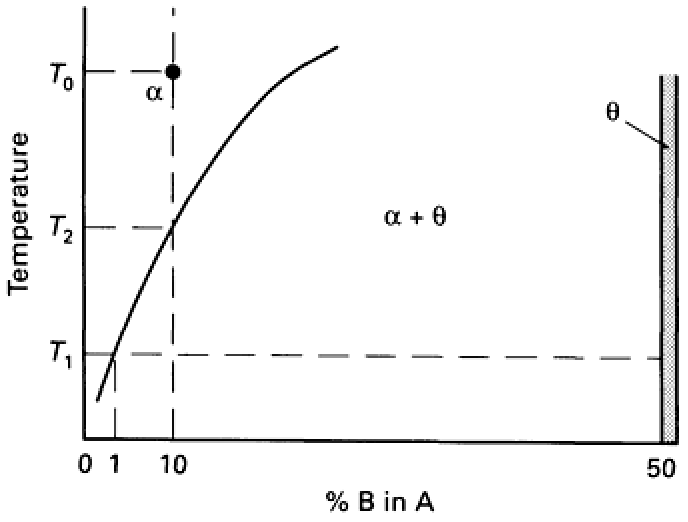

Fig. 23 Hypothetical phase diagram of system A-B. The decreasing solubility of B in α with decreasing temperature allows an alloy containing 10% B to be single-phase at high temperature (that is, above T_2) but two-phase at low temperature (T_1). Adapted from Ref 5

The Process of Precipitation. After quenching from the α region (Fig. 23), precipitation is achieved by reheating the alloy below the solvus (T_2 in Fig. 23) at a suitable temperature for a suitable time. During this time, at localized regions (for example, grain boundaries), the precipitates nucleate. Because these precipitates have a higher solute content than the matrix, the region in the matrix surrounding them is reduced in solute content. This forms a concentration gradient such that the solute atoms diffuse from the adjacent matrix toward the particles, allowing the precipitates to continue to grow. The rate of growth is diffusion-controlled and is given by an appropriate solution to Fick's law. The precipitation process is depicted schematically in Fig. 24. Here the precipitate contains 50% B (see Fig. 23).

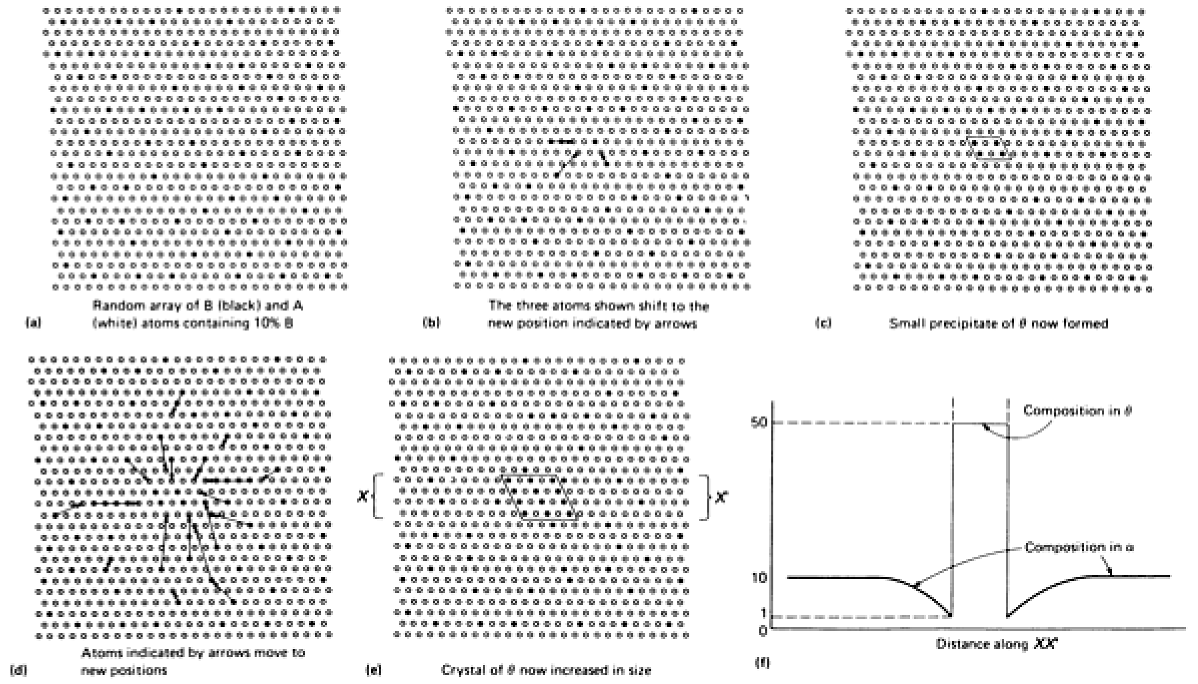

Fig. 24 Schematic illustration of formation of a precipitate in a supersaturated matrix. Time is increasing from (a) to (e), but at (e) equilibrium is not yet attained. (f) Concentration profile through the precipitate in (e). Source: Ref 5

The maximum amount of precipitate which can form is given by the equilibrium amount, which can be calculated from a mass balance (lever rule). Once this equilibrium amount of precipitate has been attained, then further change in the precipitates is caused by the tendency for the system to reduce the precipitate/matrix interfacial area. Thus, with time at a given aging temperature, the smaller precipitates dissolve, with the solute diffusing through the matrix to contribute to the growth of the larger particles. This results in a microstructure containing larger, but fewer, particles. An equivalent effect is obtained by using a high aging temperature for a given time. These changes are depicted schematically in Fig. 25.

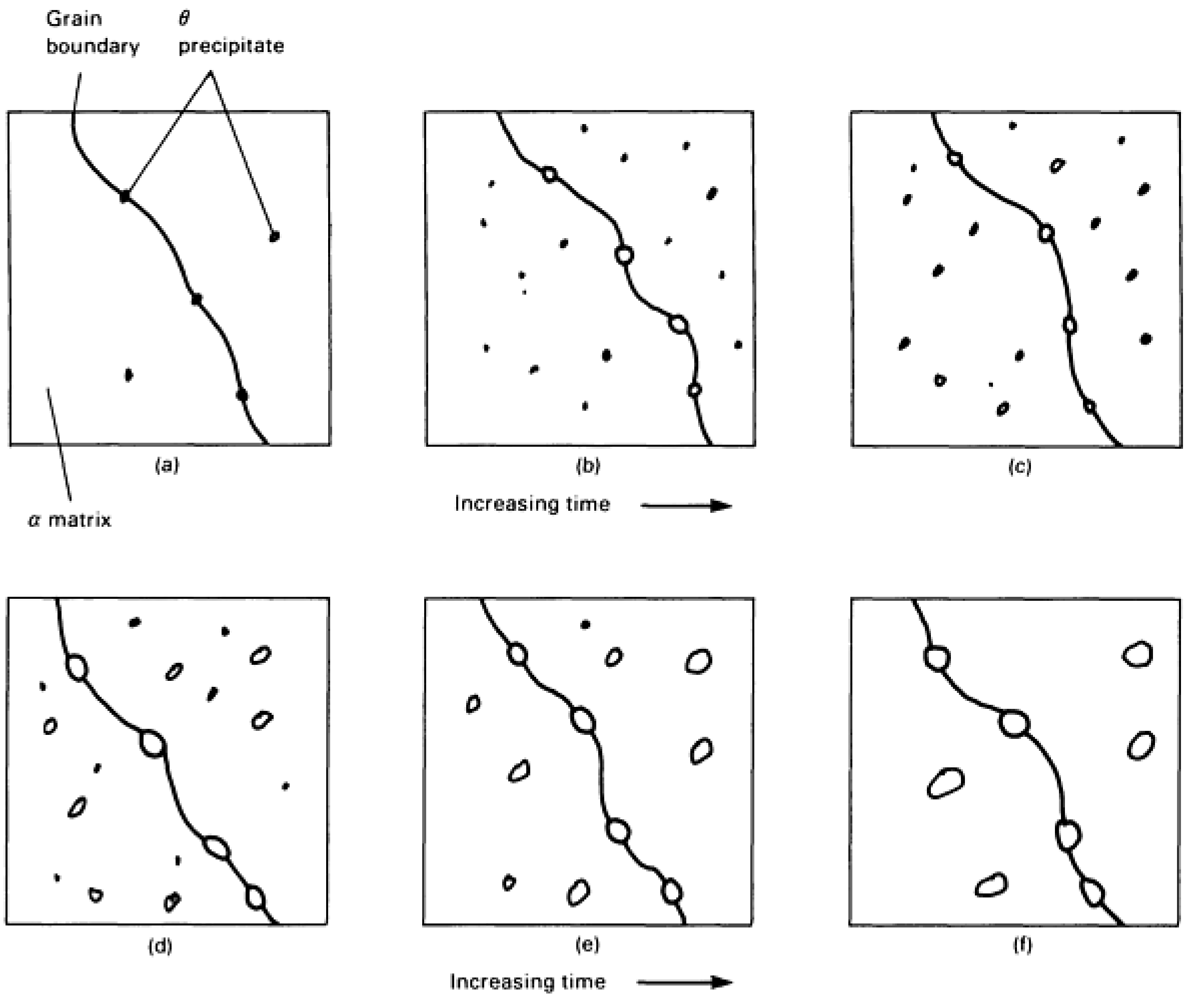

Fig. 25 Schematic illustration of formation of θ precipitates in the α matrix (a and b) and their coarsening (c to f)

Control of Precipitation through Heat Treatment. The precipitation heat treatment for the desired properties is determined empirically. Higher precipitation temperatures usually are associated with a lower nucleation rate and thus a coarser precipitate distribution. Also, as the precipitation temperature used approaches the solvus, the amount of precipitate decreases (vanishing at the solvus).

The microstructural effects will be demonstrated by referring to the aging of an Al-5Cu alloy. Figure 26 shows that this alloy must be solution heat treated at temperatures between 530 °C (986 °F) (solvus) and 560 °C (1040 °F) (solidus). If this alloy is quenched from 545 °C (1015 °F) (after 1 week), then aged for 12 h at 400 °C (750 °F), the structure obtained will be that shown in Fig. 27(a). The precipitates are fine and evenly distributed, and are about 1 μm in size. If an aging temperature of 300 °C (570 °F) is used (for 12 h), then the structure in Fig. 27(b) is obtained. It can be seen that this higher aging temperature produced a somewhat coarser distribution of θ than that at 300 °C (570 °F).

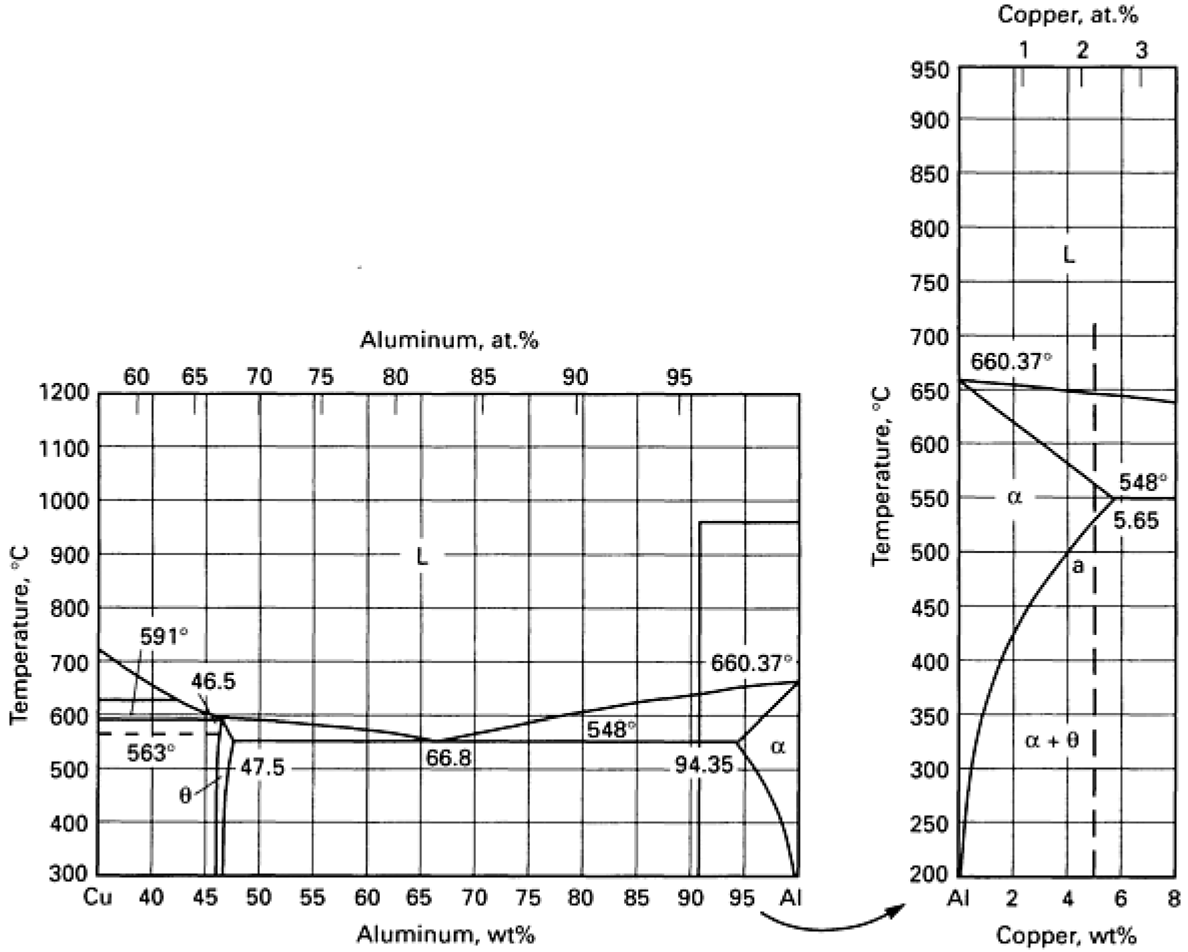

Fig. 26 The aluminum-rich end of the Al-Cu phase diagram, showing the 5% Cu line

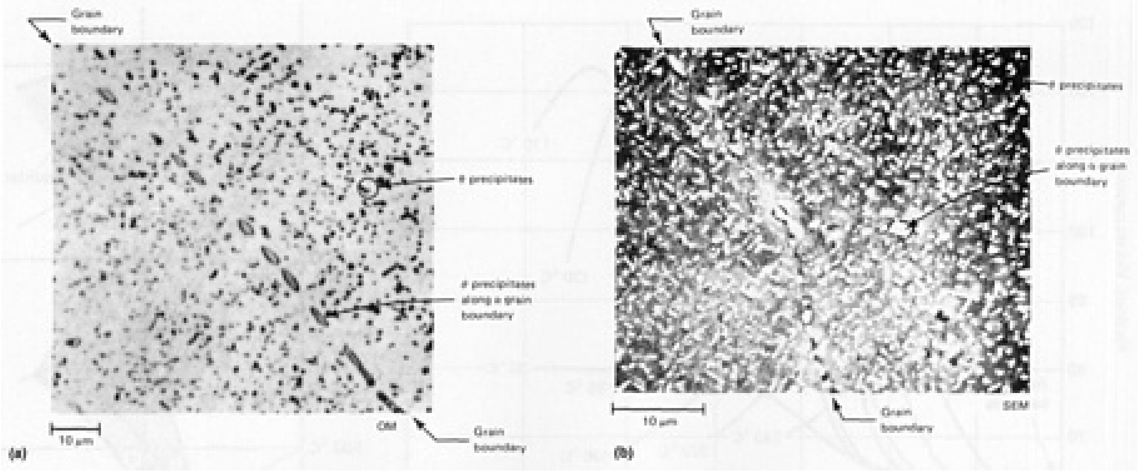

Fig. 27 Microstructure of Al-5Cu alloy heated for 1 week at 545 °C (1015 °F), cooled rapidly to 25 °C (77 °F), then held 12 h at (a) 400 °C (750 °F) and (b) 300 °C (570 °F). (a) Optical micrograph (OM). (b) Scanning electron micrograph (SEM). Source: Ref 5

In the Al-5Cu alloy (and in most other precipitation-hardenable alloys), the precipitation process is not as simple as that depicted schematically in Fig. 24. Instead, formation of the equilibrium precipitate (θ in the Al-Cu alloy) is preceded by formation of one or more nonequilibrium configurations or precipitates. For an Al-4.6Cu alloy, this is shown in Fig. 28.

In the earliest stage, Cu-rich zones form (called *Guinier-Preston Zones*), followed by two metastable precipitates (θ" and θ'), before the equilibrium θ" appears. Note how fine these metastable phases are. In Fig. 28, the θ" particles are approximately 0.01 μm in size, corresponding to particles about 50 atoms in size.

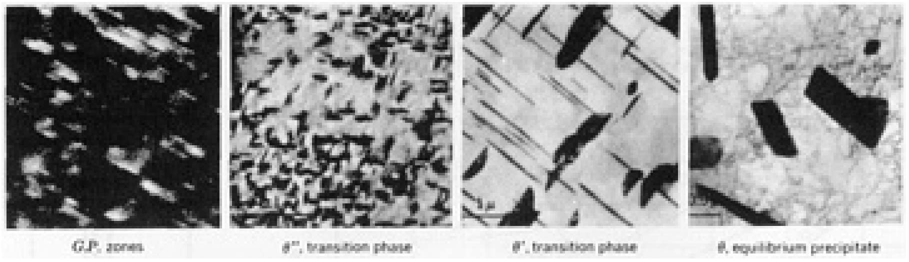

Fig. 28 Transmission electron micrographs of precipitates formed in an Al-4.6Cu alloy with increasing aging time (left to right). The micrograph at far right shows θ precipitates similar in size to those shown in Fig. 27(b). Adapted from Ref 11

Precipitation Hardening. The high strength is produced by the finely dispersed precipitates that form during precipitation treatments (which may include either natural, room-temperature aging, or artificial aging at elevated temperatures). The strengthening which occurs during aging of an Al-4Cu alloy is illustrated in Fig. 29. Note that the maximum hardness is about double that in the as-quenched (supersaturated α) condition. Also note that the maximum hardness does not correspond to formation of the equilibrium θ phase, but to the metastable, transition phases, which form in a considerably finer distribution than does θ(compare Fig. 28 and 27).

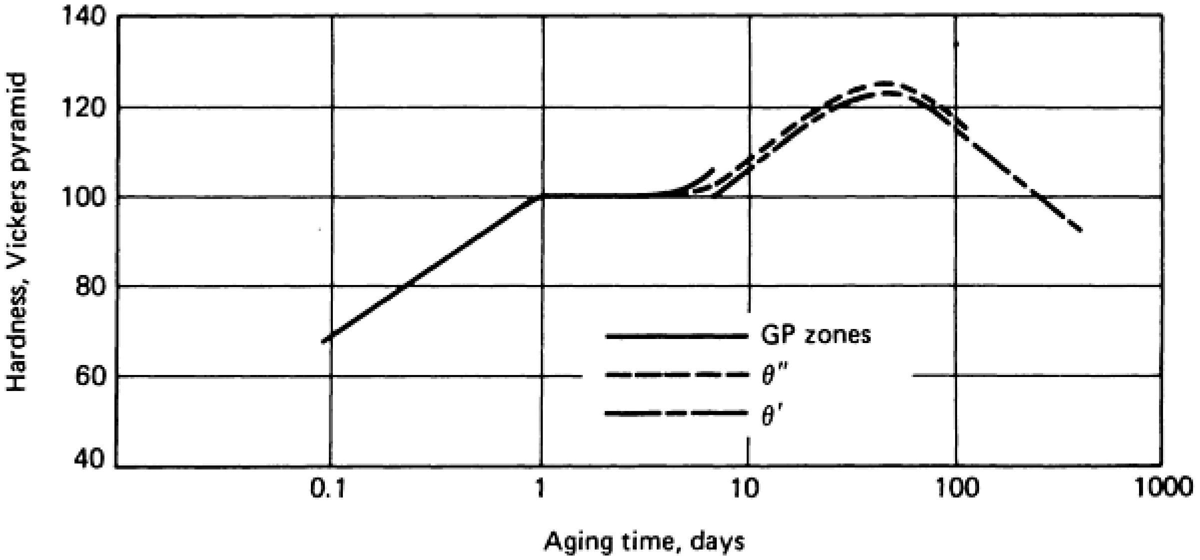

Fig. 29 Hardness curve for an Al-4Cu alloy showing the relationship between the various precipitates formed and the hardness on aging at 130 °C (265 °F). Compare this curve to the structures shown in Fig. 28. Source: Ref 5

The effect of temperature and time on aging is illustrated by the data in Fig. 30. As pointed out previously, the higher the precipitation temperature, the lower the maximum hardness, because less precipitate forms as the solvus temperature is approached. However, the higher the temperature, the higher the rate of precipitation, and hence the maximum hardness is attained in less time.

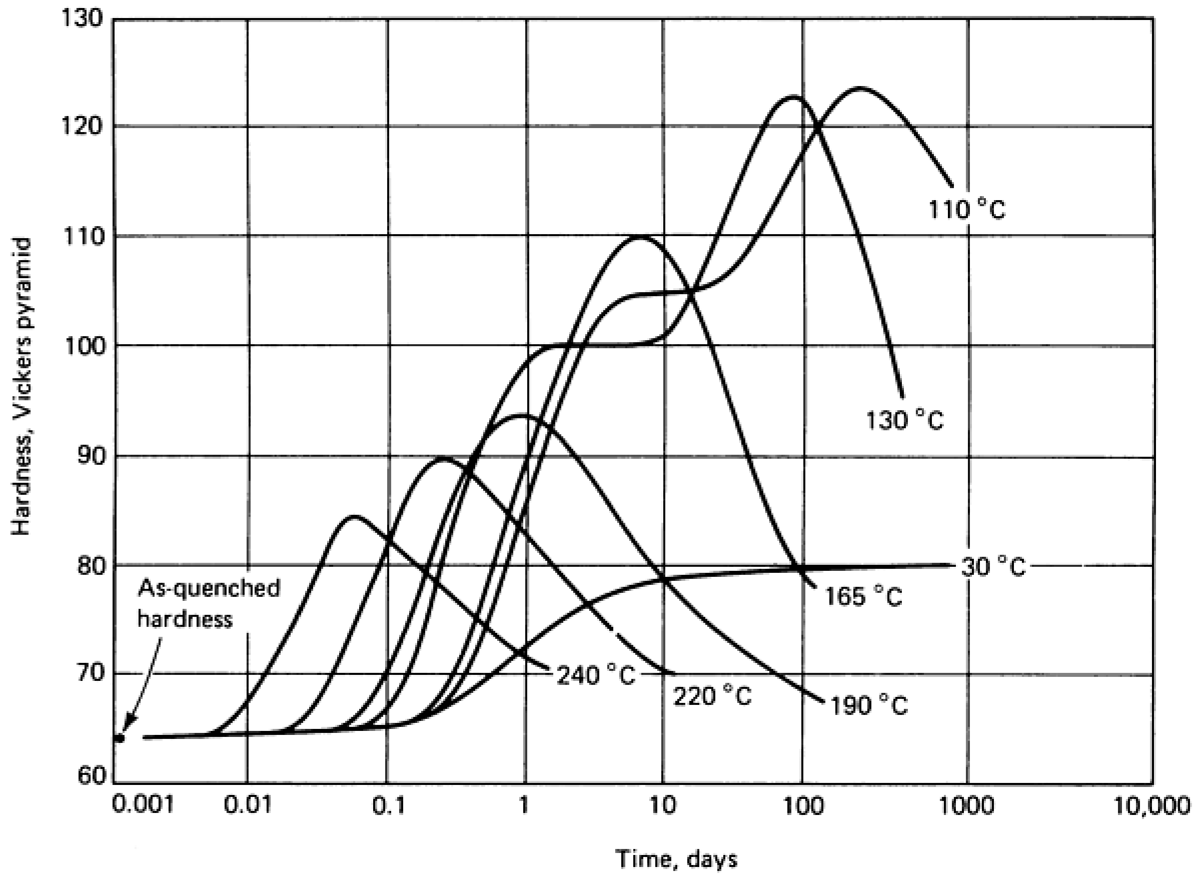

Fig. 30 Hardness as a function of aging time for an Al-4Cu alloy. The alloy was solution annealed for at least 48 h at 520 °C (970 °F), then cooled quickly (water quenched) to 25 °C (77 °F). Adapted from Ref 12

In most commercial precipitation-hardenable alloys, the rate of precipitation is low at ambient temperature, although sufficiently rapid to bring about measurable hardness changes in a reasonable time, as shown in Fig. 30 for aging at 30 °C (85 °F). If hardening occurs at or near ambient temperature, it is termed *age hardening*; aging at other temperatures is called *precipitation hardening.*

Commercial alloys usually contain multiple elements, so that the required heat treating temperatures cannot always be deduced from an examination of related binary-phase diagrams. In many alloys which contain mainly two alloying additions, the ternary phase diagram can be used as a guide for establishing the required heat treatments. For example, consider the aluminum-base alloy 2024. It contains approximately 4% Cu and 1% Mg, with lesser amounts of manganese, silicon, iron, chromium, and zinc. Considering the alloy to be an Al-Cu-Mg ternary alloy, and using 4% Cu and 1% Mg to represent the average concentrations of these elements, then the aluminum-rich end of the ternary phase diagram can be used to illustrate the required heat treatments. This is shown in Fig. 31. The liquidus is about 650 °C (1200 °F), the solidus 570 °C (1060 °F), and the solvus 500 °C (930 °F). Thus, the solution annealing temperature must be between 500 and 570 °C (930 and 1060 °F). When consideration is given to the allowable range of the amounts of copper and magnesium in the 2024 alloy, then the solution annealing range is narrowed. Avoiding heating above the liquidus is of particular importance, because this will allow formation of small regions of liquid in the structure, which on cooling form compounds, and can lead to problems in achieving desired properties. The specification for the solution annealing temperature for alloy 2024 is 488 to 499 °C (910 to 930 °F), only an 11 °C (20 °F) spread. Thus, if 494 °C (921 °F) is used, only a deviation of about ±5 °C (±9 °F) is allowed.

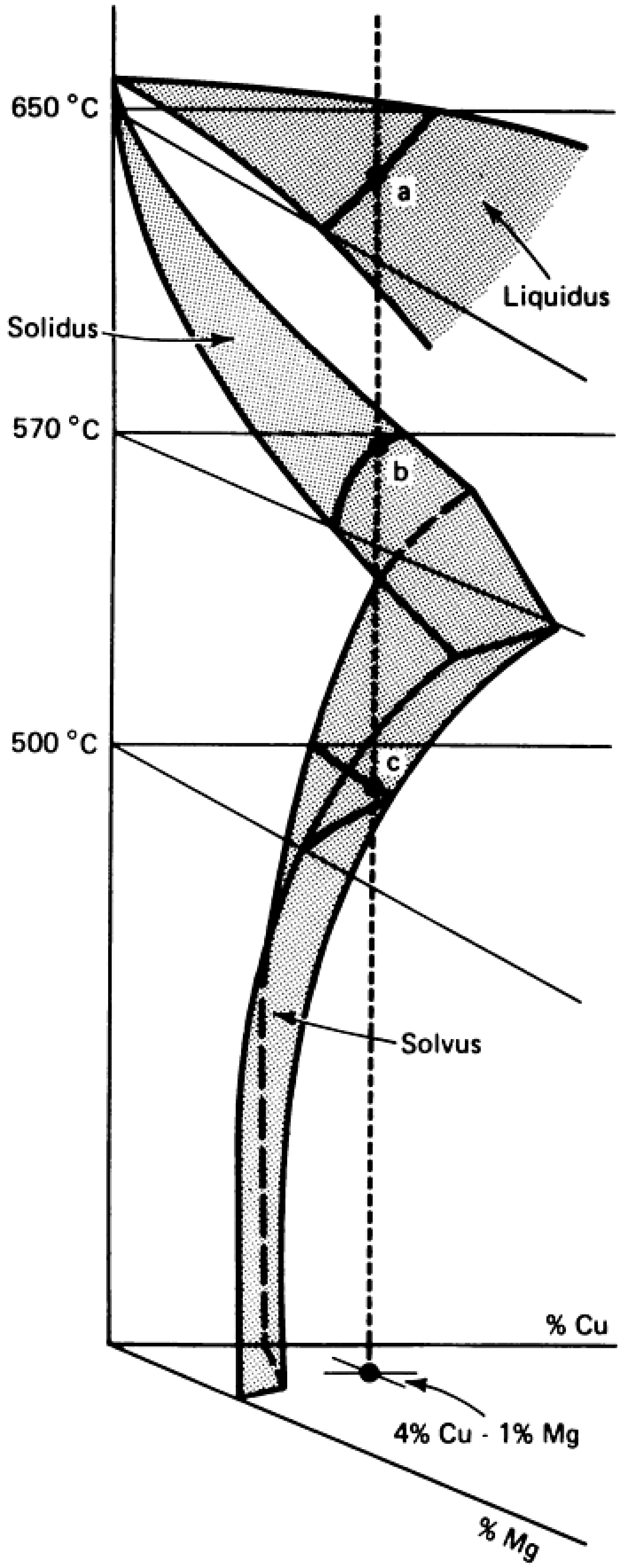

Fig. 31 Schematic illustration of the aluminum-rich end of the Al-Cu-Mg phase diagram, with the liquidus, solidus, and solvus shown for 4Cu-1Mg alloy

Aging of alloy 2024 must be carried out below the solvus, about 500 °C (930 °F). The response to aging for this alloy is typified by the data in Fig. 32. Note that there is a range of combinations of temperature and time which will give about the same optimum mechanical properties.

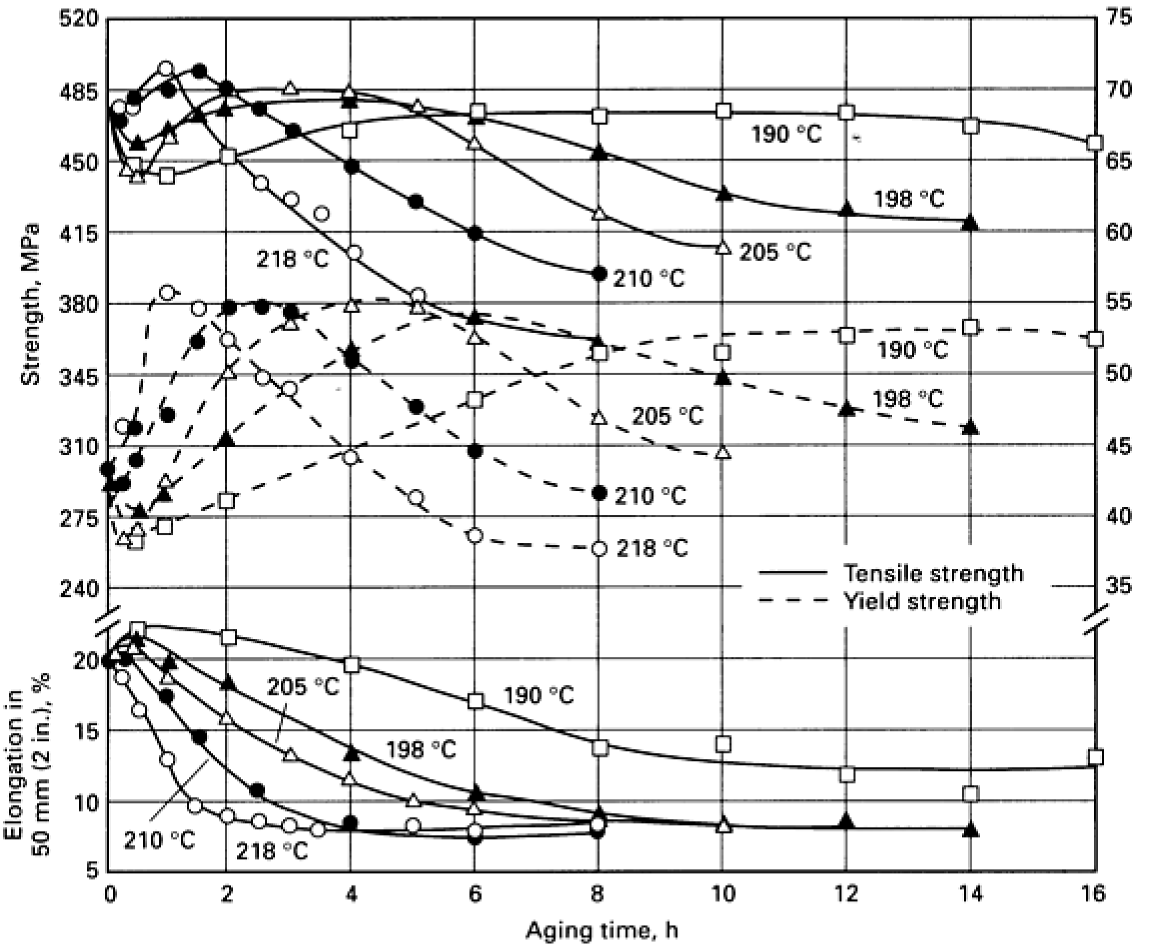

Fig. 32 Effect of aging time and temperature on mechanical properties of aluminum-base alloy 2024. The initial condition was the natural aged state (temper T4). Source: Ref 13

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Development of Two-Phase Structures

In some nonferrous alloys (for example, titanium-base alloys and high-zinc Cu-Zn alloys), the desired structure consists of a mixture of two phases of comparable quantity (unlike the two-phase structures developed in precipitation hardening, where the precipitate is in the minority). The morphology and amount of each are varied by control of the high temperature used and the cooling rate from that temperature. The preferred microstructure can be quite complex, and the required treatment differs considerably for different systems, so that a systematic treatment of the principles involved is difficult. Instead, in this section a specific alloy will be used to illustrate the types of treatments involved.

In the Cu-Zn system, alloys containing about 40% Zn serve as the basis for some commercial alloys (for example, Muntz metal and naval brass). The Cu-Zn phase diagram (Fig. 33) shows that the alloys of interest are in the region of α and β phase stability. The β phase is body-centered cubic, with the copper and zinc atoms located at random on the lattice sites.

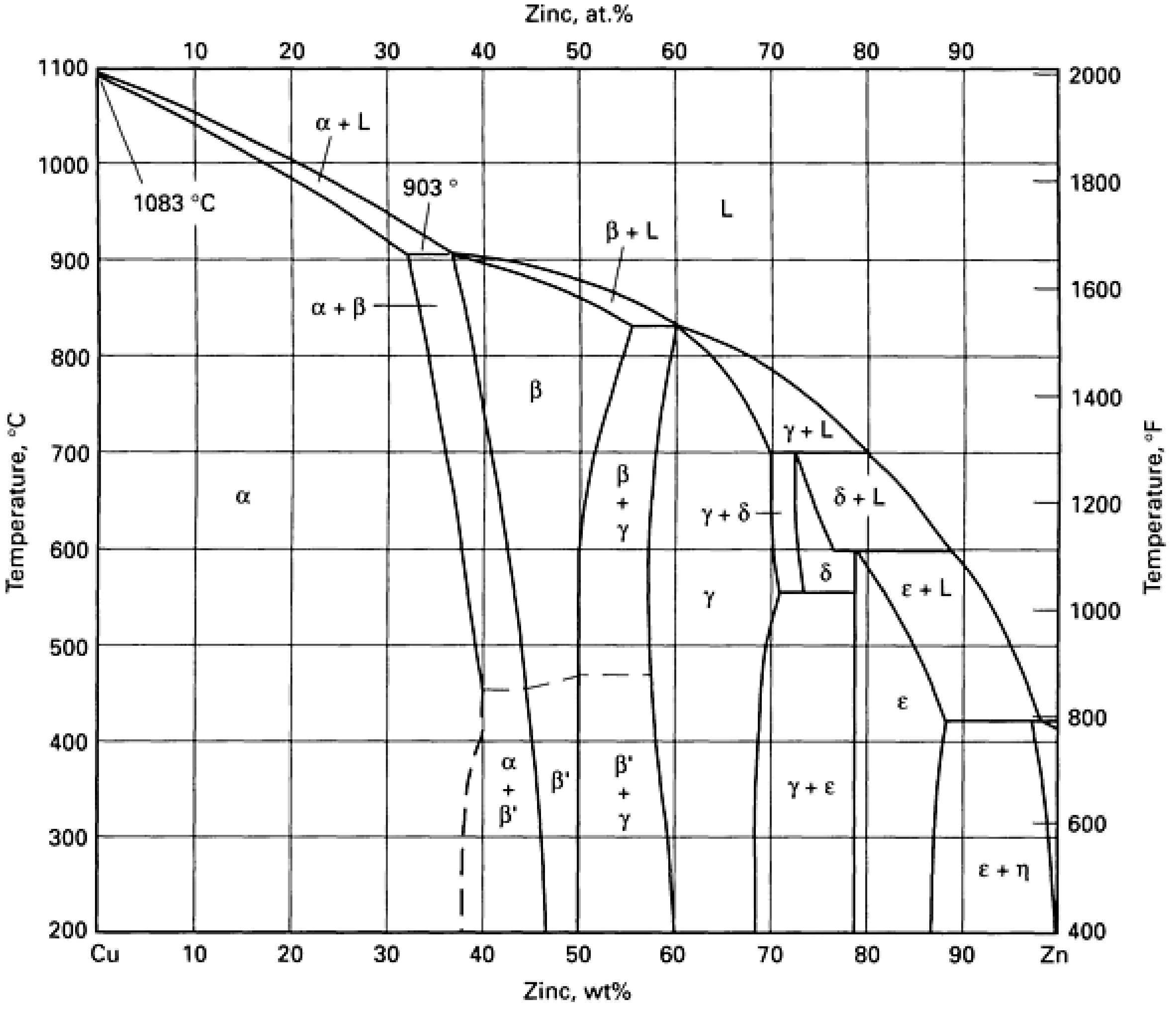

Fig. 33 The Cu-Zn diagram. The β phase is body-centered cubic; the β' phase is an ordered structure based on this arrangement.

On cooling to temperatures below the dashed line (about 450 °C, or 840 °F), the copper and zinc atoms take specific relative positions on the sites, forming an *ordered structure*, or a *superlattice.* This phase is denoted β' in Fig. 33. If the composition is exactly 50 at .% Zn, then the ordered structure is based on a body-centered cubic cell with zinc atoms at the center and copper atoms on the corners (or vice versa).

The formation of an ordered structure from a disordered matrix of the same basic lattice involves the localized exchange of atom positions (via the vacancy mechanism) to the desired structure. This process is depicted schematically in Fig. 34. It can be seen that an ordered region grows by atoms at the β/β' interface, taking on the arrangement of the ordered β' region. When two interfaces from neighboring regions meet, the arrangement of atoms may be out of sequence (out of phase). Such an interface is called an *antiphase boundary*, and the enclosed regions are called *domains.* The properties of the β' ordered structure depend on the degree of perfection (correctness of relative atom location) within the domains and on the domain size, both of which depend on the temperature and time involved in forming β' from β.

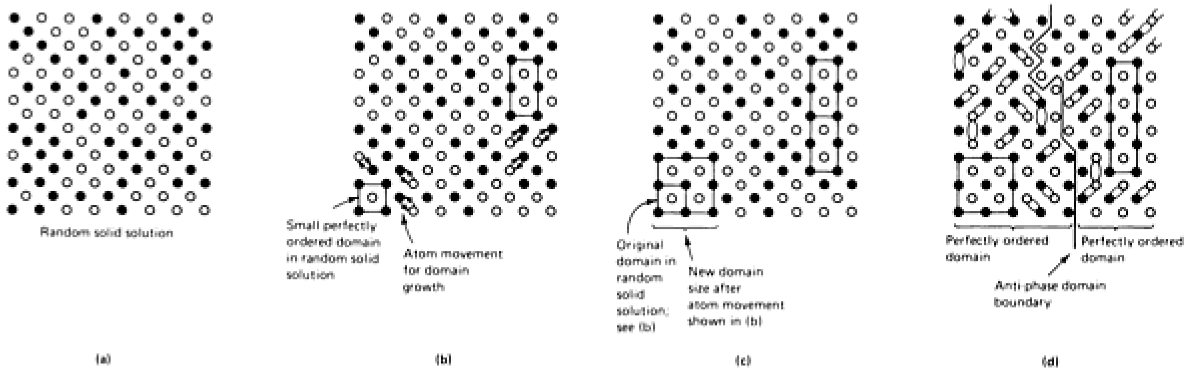

Fig. 34 Schematic illustration of a possible mechanism for the formation of ordered β' from the disordered β in Cu-Zn alloys. Adapted from Ref 5

These alloys in the β' form are not suitable for commercial use, because this structure is brittle. However, alloys in which the β' phase coexists with the ductile α phase are useful. The Cu-40Zn alloy can be heat treated at high temperature so that it is all β. The structure developed at lower temperatures depends on the heat treatment, because this controls precipitation and formation of the α phase. If the alloy is cooled slowly from 800 °C (1470 °F), the phase diagram (Fig. 33) shows that at 25 °C (77 °F) the alloy should consist of approximately equal amounts of α and β'. Figure 35 shows a typical microstructure.

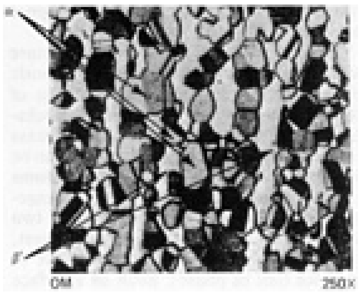

Fig. 35 Typical microstructure of annealed Muntz metal (Cu-40Zn). The clear, white regions are the β', and the dark and gray regions showing annealing twins are α. Optical micrograph. 250×. Adapted from Ref 14

One of the curves in Fig. 36 shows that the amount of β' influences hardness. The alloy was cooled slowly from 700 °C (1290 °F), where it was mostly β, to 25 °C (77 °F), then reheated to temperature for 30 min, followed by rapid cooling. On heating at 800 °C (1470 °F), the structure is all β, and on rapid cooling little α forms. However, the β orders to β', giving a hardness around 90 HB. Reheating for 30 min in the lower temperature range (25 to 500 °C, or 77 to 930 °F) is not sufficient to affect significantly the originally slowly cooled structure, and the hardness remains constant. In this temperature range, the structure consists of approximately equal amounts of α and β'. However, as the temperature increases from 500 °C (930 °F), 30 min is sufficient time to allow the equilibrium amounts and α and β to form. Thus, as the temperature increases, increasing amounts of β and decreasing amounts of α are present at temperature, giving increasing amounts of β' on cooling rapidly to 25 °C (77 °F), and hence a rise in hardness.

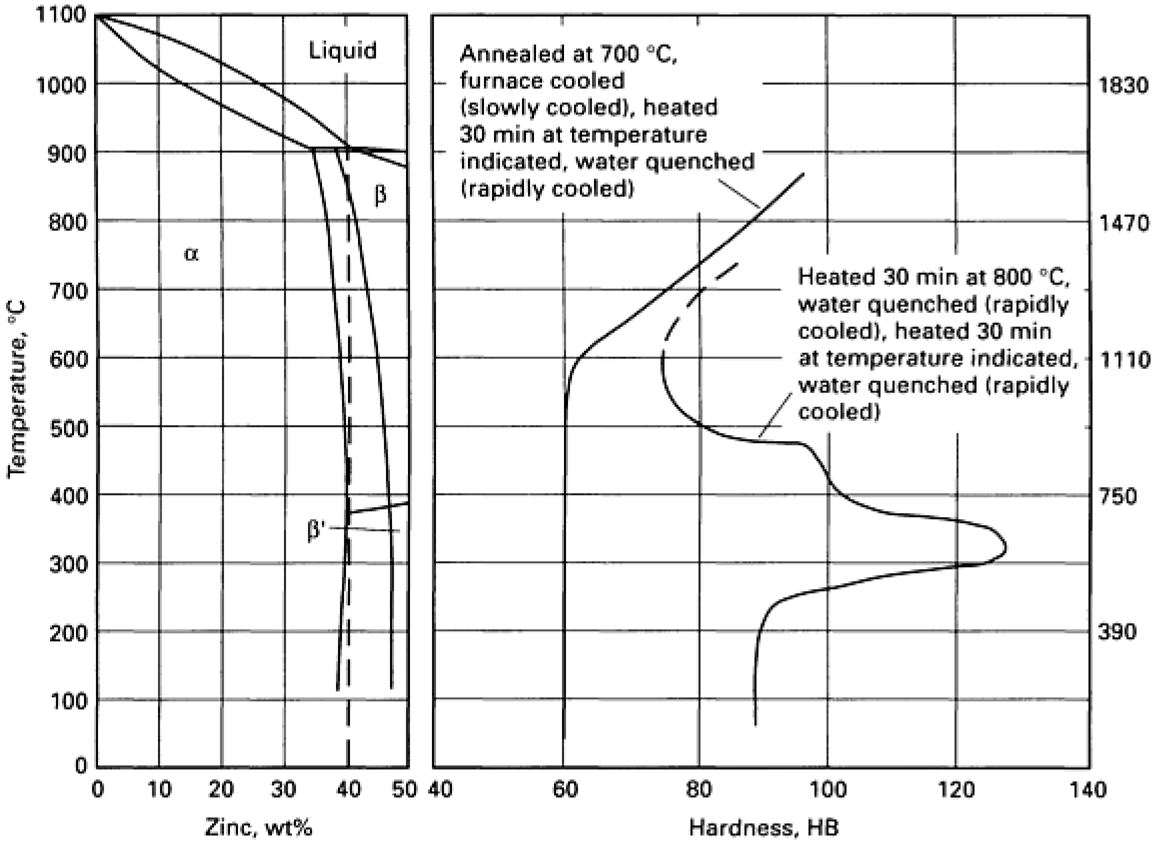

Fig. 36 Influence of heat treatment on the hardness at 25 °C (77 °F) of a Cu-40Zn alloy. Adapted from Ref 15

If the Cu-40Zn alloy is cooled rapidly to 25 °C (77 °F) after sufficient holding (for example, 30 min) above about 750 °C (1380 °F), a structure of essentially all β' is obtained. Often some α is observed to have formed in the β grain boundaries, and the morphology will vary somewhat depending on the exact cooling rate. Usually, the α is present as "needles" emanating from the boundaries, with a clear crystallographic relation between the α and the β' in which it has formed. Figure 37 shows two examples.

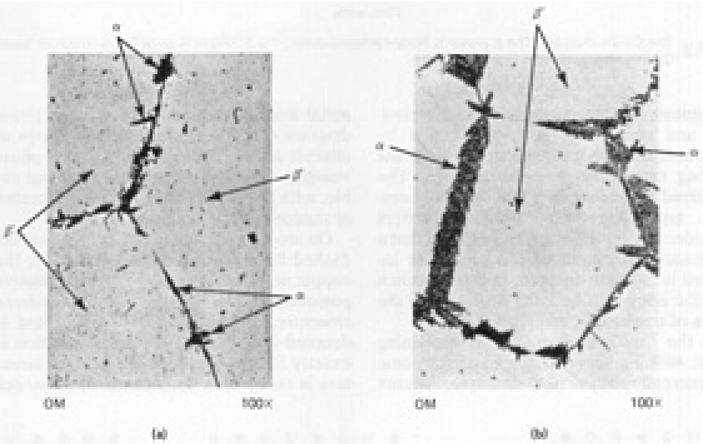

Fig. 37 Microstructures typical of Cu-40Zn alloys cooled rapidly from the β region to 25 °C (77 °F). Even rapid cooling has not prevented some α from forming. (a) Cu-40Zn alloy quenched into ice water from 825 °C (1515 °F). Adapted from Ref 16

On reheating β' in the intermediate temperature range, the morphology of the α formed will vary depending on the exact heat treatment. Also, reheating will influence the change in the ordered structure. Both changes affect properties, and the hardness can be increased considerably by judicious treatment. In Fig. 36 are shown hardness data for a Cu-40Zn alloy after reheating for 30 min following an initial treatment of quenching from 800 °C (1470 °F). Supposedly the maximum hardness obtained by treatment around 300 °C (570 °F) is caused by formation of a fine α precipitate and some changes in the ordered β' phase. The types of microstructures obtained by such heat treatments are illustrated in Fig. 38 for a Cu-42Zn alloy. In this alloy the zinc content is sufficiently high to completely suppress any α formation on rapid cooling from β, giving at 25 °C (77 °F) only β' (Fig. 38a). Reheating for 30 min at 400 °C (750 °F) gives a fine a precipitate on the β' grain boundaries, and a fine inter-crystalline precipitate of α (Fig. 38b). Reheating for 30 min at a higher temperature (600 °C, or 1110 °F) gives a coarser α structure (Fig. 38c).

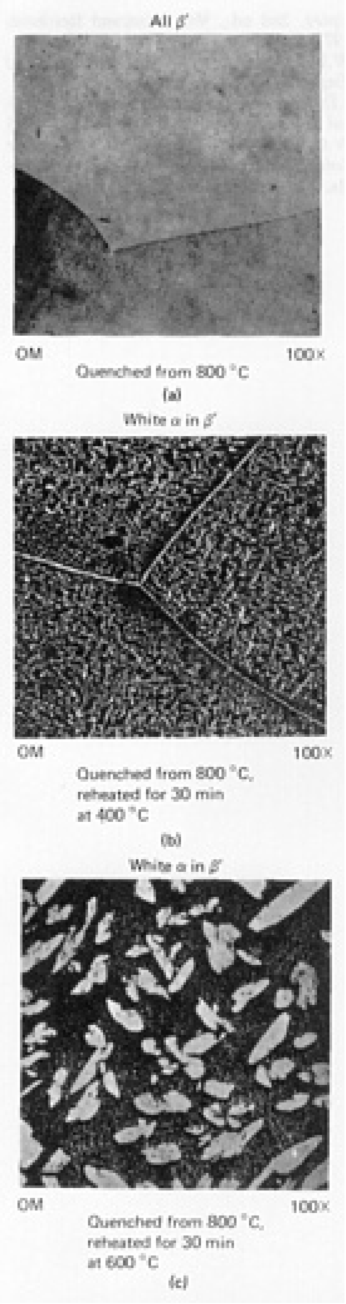

Fig. 38 Microstructures of Cu-42Zn alloy quenched from the β region, then reheated to develop an α precipitate structure. The higher reheating temperature gives a coarser structure and thus a softer material. Adapted from Ref 17

If the rate of cooling from the α region is quite low (several hours to 25 °C, or 77 °F), then α nucleates at a high temperature at which the nucleation rate is low, and the α crystals grow relatively large as few crystals nucleate. This gives a rather coarse structure, typified by Fig. 39(a). As the cooling rate increases, the nucleation rate increases, but the individual α crystals do not have time to grow large before the temperature becomes too low for significant growth to continue. This gives a finer structure (see Fig. 39b) and increases strength. Eventually, the cooling rate becomes sufficient to suppress formation of α altogether, giving a structure entirely of highly unstable β' at 25 °C (77 °F). Figure 40 illustrates the influence of cooling rate from β on hardness.

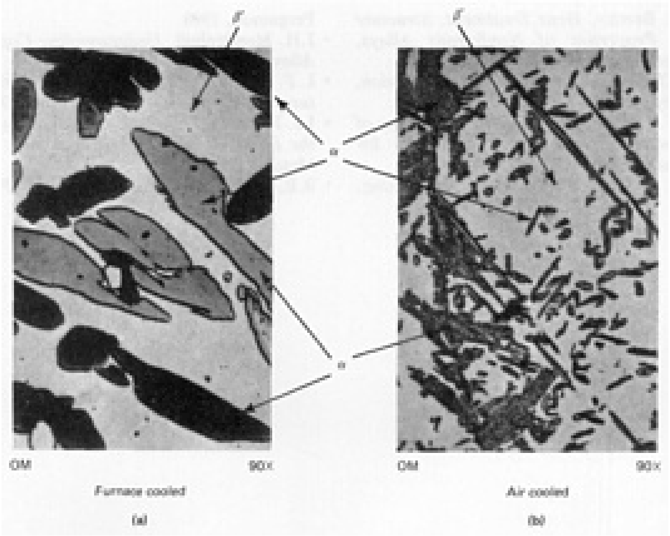

Fig. 39 Microstructures of a Cu-43Zn alloy after cooling from 700 °C (1290 °F), the β region, showing effect of cooling rate on structure of α crystals. Adapted from Ref 18

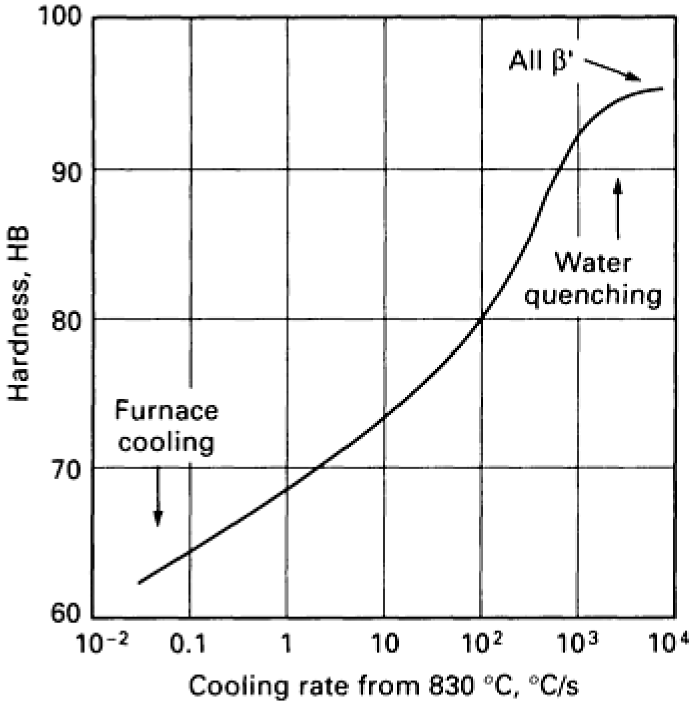

Fig. 40 Effect of cooling rate from the βregion on hardness of a Cu-40Zn alloy. Adapted from Ref 15

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Heat Treating of Aluminum Alloys

Introduction

HEAT TREATING in its broadest sense, refers to any of the heating and cooling operations that are performed for the purpose of changing the mechanical properties, the metallurgical structure, or the residual stress state of a metal product. When the term is applied to aluminum alloys, however, its use frequently is restricted to the specific operations employed to increase strength and hardness of the precipitation-hardenable wrought and cast alloys. These usually are referred to as the "heat-treatable" alloys to distinguish them from those alloys in which no significant strengthening can be achieved by heating and cooling. The latter, generally referred to as "non-heat-treatable" alloys, depend primarily on cold work to increase strength. Heating to decrease strength and increase ductility (annealing) is used with alloys of both types; metallurgical reactions may vary with type of alloy and with degree of softening desired. Except for the low-temperature stabilization treatment sometimes given for 5*xxx* series alloys (which is a mill treatment and not discussed in this article), complete or partial annealing treatments are the only ones used for non-heat-treatable alloys. A general overview of these heat treatments is covered in the article "Principles of Heat Treating of Nonferrous Alloys" in this Volume.

Precipitation from Solid Solution

One essential attribute of a precipitation-hardening alloy system is a temperature-dependent equilibrium solid solubility characterized by increasing solubility with increasing temperature (see, for example, the phase diagrams in Fig. 1 and 2). Although this condition is met by most of the binary aluminum alloy systems, many exhibit very little precipitation hardening, and these alloys ordinarily are not considered heat treatable. Alloys of the binary aluminum-silicon and aluminum-manganese systems, for example, exhibit relatively insignificant changes in mechanical properties as a result of heat treatments that produce considerable precipitation. The major aluminum alloy systems with precipitation hardening include:

- Aluminum-copper systems with strengthening from $CuAl_2$
- Aluminum-copper-magnesium systems (magnesium intensifies precipitation)
- Aluminum-magnesium-silicon systems with strengthening from Mg_2Si
- Aluminum-zinc-magnesium systems with strengthening from $MgZn_2$
- Aluminum-zinc-magnesium-copper systems

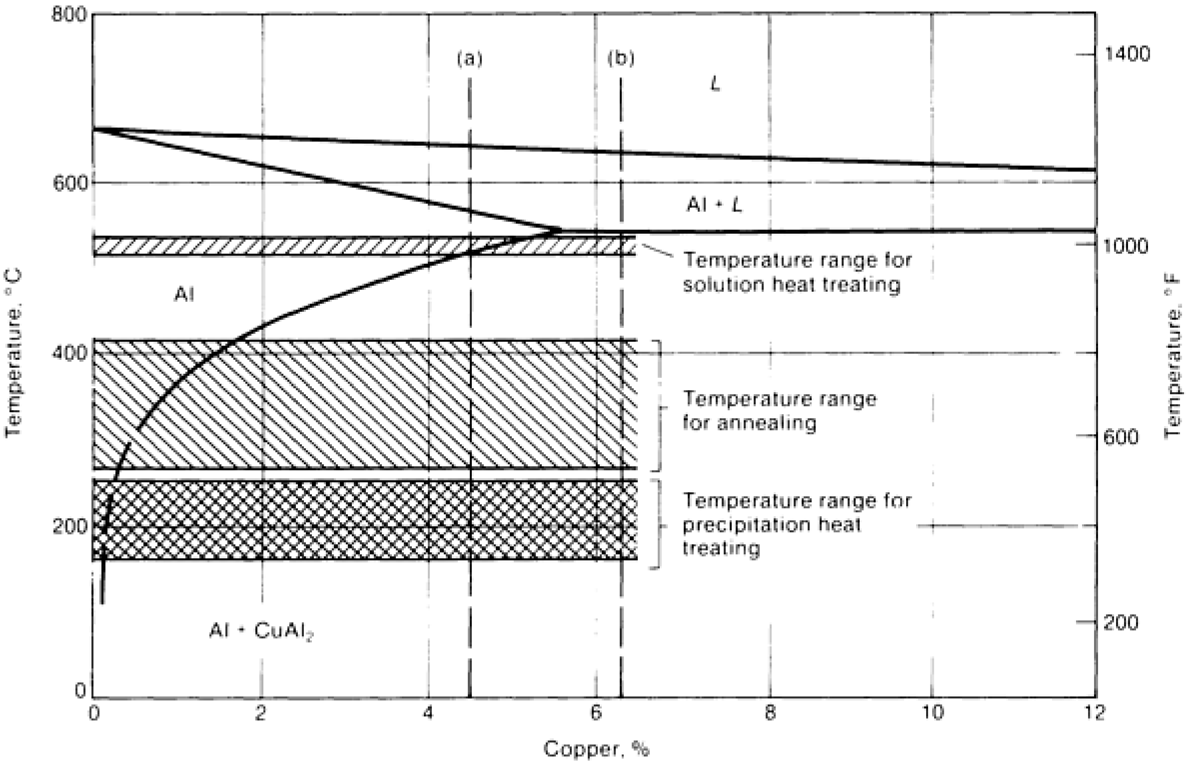


Fig. 1 Portion of aluminum-copper binary phase diagram. Temperature ranges for annealing, precipitation heat treating, and solution heat treating are indicated. The range for solution treating is below the eutectic melting point of 548 °C (1018 °F) at 5.65 wt% Cu.

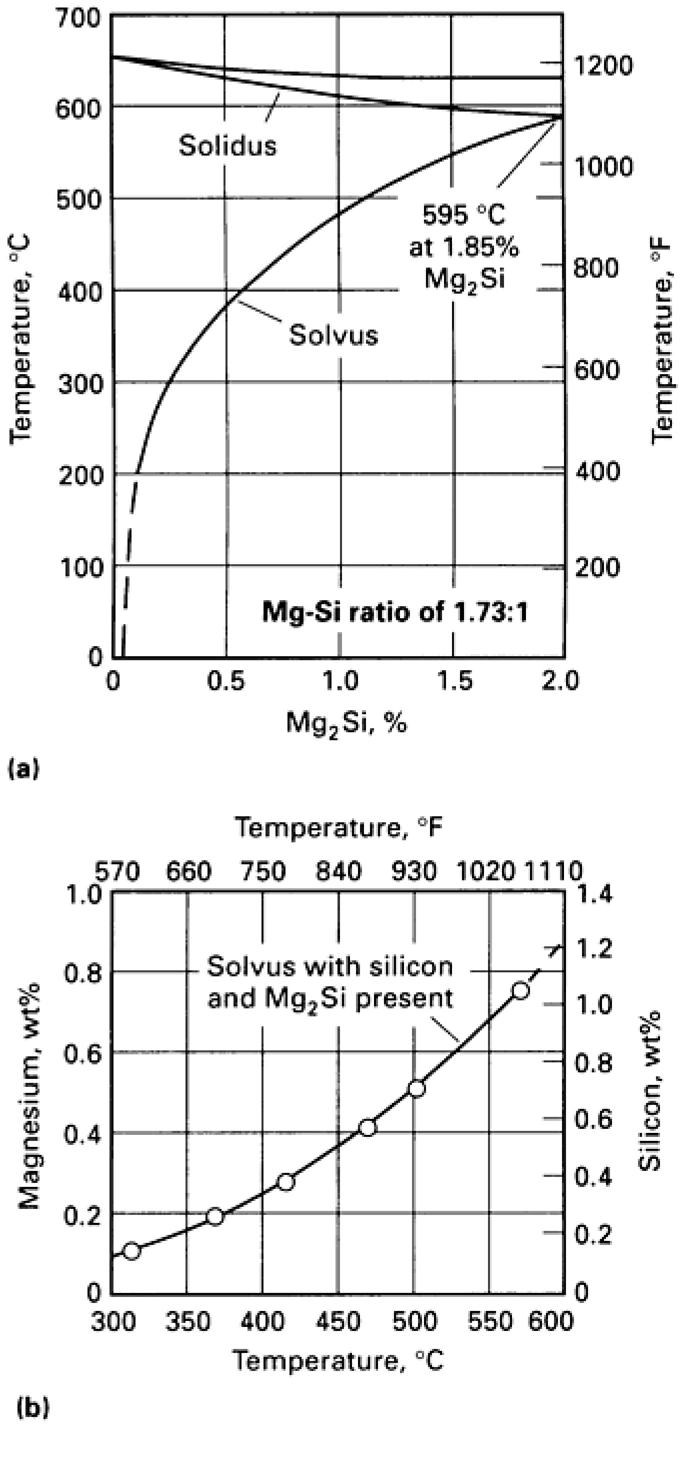


Fig. 2 Equilibrium solubility as function of temperature for (a) Mg_2Si in aluminum with an Mg-Si ratio of 1.73-to-1 and (b) magnesium and silicon in solid aluminum when both Mg_2Si and silicon are present

The general requirement for precipitation strengthening of supersaturated solid solutions involves the formation of finely dispersed precipitates during aging heat treatments (which may include either natural aging or artificial aging). The aging must be accomplished not only below the equilibrium solvus temperature, but below a metastable miscibility gap called the Guinier-Preston (GP) zone solvus line. The supersaturation of vacancies allows diffusion, and thus zone formation, to occur much faster than expected from equilibrium diffusion coefficients. In the precipitation process, the saturated solid solution first develops solute clusters, which then become involved in the formation of transitional (nonequilibrium) precipitates.

The mechanism of strengthening from precipitation involves the formation of coherent clusters of solute atoms (that is, the solute atoms have collected into a cluster but still have the same crystal structure as the solvent phase). This causes a great deal of strain because of mismatch in size between the solvent and solute atoms. Consequently, the presence of the precipitate particles, and even more importantly the strain fields in the matrix surrounding the coherent particles, provide higher strength by obstructing and retarding the movement of dislocations. The characteristic that determines whether a precipitate phase is coherent or noncoherent is the closeness of match or degree of disregistry between atomic spacings on the lattice of the matrix and on that of the precipitate. These changes in properties result from the formation of solute-rich microstructural domains, or GP zones.

The exact size, shape, and distribution of GP zones depend on the alloy in which they form and on the thermal and mechanical history of the specimen. Their shape can sometimes be deduced by refined studies of diffuse x-ray scattering. Under favorable conditions, GP zones can be seen in transmission electron micrographs. Spherical solute-rich zones usually form when the sizes of the solvent and solute atoms are nearly equal, as in the aluminum-silver and aluminum-zinc systems. If there is a large difference in atom sizes, as in the aluminum-copper system, the GP zones usually form as disks whose planes lie parallel with some low-index plane of the matrix lattice. Sometimes, the solute atoms occupy preferred lattice sites within the GP zone, and thus form a small region of lattice order.

The GP zones are of the size range of tens of angstroms in diameter. They are essentially distorted regions of the matrix lattice, rather than discrete particles of a new phase having a different lattice. As such, they are completely coherent with the matrix, imposing local but often large strains on it. These mechanical strains, as well as the presence of a locally solute-rich, sometimes ordered lattice, can account for large changes in mechanical properties of the alloy before any long-range microstructural changes occur.

The GP zones are characteristically metastable and thus dissolve in the presence of a more stable precipitate. This dissolution causes a precipitate-free, visibly denuded region to form around the stable precipitate particles. The final structure consists of equilibrium precipitates, which do not contribute as significantly to hardening. More detailed information about preprecipitation phenomena can be found in the article "Structures Resulting From Precipitation From Solid Solution" in Volume 9 of *ASM Handbook*, formerly 9th Edition *Metals Handbook.*

Precipitation in Aluminum-Copper Alloys. Figure 1, which illustrates the required solubility-temperature relationship needed in precipitation strengthening, shows the temperature ranges required for solution treatment and subsequent precipitate hardening in the aluminum-copper system. The equilibrium solid solubility of copper in aluminum increases as temperature increases--from about 0.20% at 250 °C (480 °F) to a maximum of 5.65% at the eutectic melting temperature of 548 °C (1018 °F). (It is considerably lower than 0.20% at temperatures below 250 °C.) For aluminum-copper alloys containing from 0.2 to 5.6% Cu, two distinct equilibrium solid states are possible. At temperatures above the lower curve in Fig. 1 (solvus), the copper is completely soluble, and when the alloy is held at such temperatures for sufficient time to permit needed diffusion, the copper will be taken completely into solid solution. At temperatures below the solvus, the equilibrium state consists of two solid phases: solid solution, α, plus an intermetallic-compound phase $\theta(Al_2Cu)$. When such an alloy is converted to all solid solution by holding above the solvus temperature and then the temperature is decreased to below the solvus, the solid solution becomes supersaturated and the alloy seeks the equilibrium two-phase condition; the second phase tends to form by solid-state precipitation.

The preceding description is a gross over-simplification of the actual changes that occur under different conditions even in simple binary aluminum-copper alloys. A variety of different nonequilibrium precipitate structures is formed at temperatures below solvus. In alloys of the aluminum-copper system, a succession of precipitates is developed from a rapidly cooled super-saturated solid solution (SSS). These precipitates develop sequentially either with increasing temperature or with increasing time at temperature between room temperature and the solvus. The several stages are identified by the following notation:

$$\text{SSS} \rightarrow \text{GP zones} \rightarrow \theta'' \rightarrow \\ \theta' \rightarrow \theta(Al_2Cu)$$

At temperatures in the natural aging range (about -20 to 60 °C, or 0 to 140 °F), the distribution of copper atoms changes with time from random to the disklike planar aggregates (GP zones), which form on particular crystallographic planes of the aluminum matrix. These aggregates create coherency strain fields that increase resistance to deformation, and their formation is responsible for the changes in mechanical properties that occur during natural aging. At higher temperatures, transition forms of approximate composition Al_2Cu develop and further increase strength. In the highest strength

condition, both the θ" and θ' transition precipitates may be present. When time and temperature are increased sufficiently to form high proportions of the equilibrium θ, the alloy softens and is said to be "overaged."

The commercial heat-treatable aluminum alloys are, with few exceptions, based on ternary or quaternary systems with respect to the solutes involved in developing strength by precipitation. Commercial alloys whose strength and hardness can be significantly increased by heat treatment include 2*xxx*, 6*xxx*, and 7*xxx* series wrought alloys (except 7072) and 2*xx*.0, 3*xx*.0, and 7*xx*.0 series casting alloys. Some of these contain only copper, or copper and silicon, as the primary strengthening alloy addition(s). Most of the heat-treatable alloys, however, contain combinations of magnesium with one or more of the elements copper, silicon, and zinc. Characteristically, even small amounts of magnesium in concert with these elements accelerate and accentuate precipitation hardening, while alloys in the 6*xxx* series contain silicon and magnesium approximately in the proportions required for formulation of magnesium silicide (Mg_2Si). Although not as strong as most 2*xxx* and 7*xxx* alloys, 6*xxx* series alloys have good formability, weldability, machinability, and corrosion resistance, with medium strength.

In the heat-treatable wrought alloys, with some notable exceptions (2024, 2219, and 7178), such solute elements are present in amounts that are within the limits of mutual solid solubility at temperatures below the eutectic temperature (lowest melting temperature). In contrast, some of the casting alloys of the 2*xx*.0 series and all of the 3*xx*.0 series alloys contain amounts of soluble elements that far exceed solid-solubility limits. In these alloys, the phase formed by combination of the excess soluble elements with the aluminum will never be dissolved, although the shapes of the undissolved particles may be changed by partial solution.

Most of the heat-treatable aluminum alloy systems exhibit multistage precipitation and undergo accompanying strength changes analogous to those of the aluminum-copper system. Multiple alloying additions of both major solute elements and supplementary elements employed in commercial alloys are strictly functional and serve with different heat treatments to provide the many different combinations of properties--physical, mechanical, and electrochemical--that are required for different applications. Some alloys, particularly those for foundry production of castings, contain amounts of silicon far in excess of the amount that is soluble or needed for strengthening alone. The function here is chiefly to improve casting soundness and freedom from cracking, but the excess silicon also serves to increase wear resistance, as do other microstructural constituents formed by manganese, nickel, and iron. Parts made of such alloys are commonly used in gasoline and diesel engines (pistons, cylinder blocks, and so forth).

Alloys containing the elements silver, lithium, and germanium are also capable of providing high strength with heat treatment, and in the case of lithium, both increased elastic modulus and lower density, which are highly advantageous--particularly for aerospace applications (see the following section "Aluminum-Lithium Alloys" in this article). Commercial use of alloys containing these elements has been restricted either by cost or by difficulties encountered in producing them. Such alloys are used to some extent, however, and research is being directed toward overcoming their disadvantages.

In the case of alloys having copper as the principal alloying ingredient and no magnesium, strengthening by precipitation can be greatly increased by adding small fractional percentages of tin, cadmium, or indium, or combinations of these elements. Alloys based on these effects have been produced commercially but not in large volumes because of costly special practices and limitations required in processing, and in the case of cadmium, the need for special facilities to avoid health hazards from formation and release of cadmium vapor during alloying. Such alloys, as well as those containing silver, lithium, or other particle-forming elements, may be used on a selective basis in the future.

Aluminum-Lithium Alloys. Like other age-hardened aluminum alloys, aluminum-lithium alloys achieve precipitation strengthening by thermal aging after a solution heat treatment. The precipitate structure is sensitive to a number of processing variables, including, but not limited to, the quenching rate following the solution heat treatment, the degree of cold deformation prior to aging, and the aging time and temperature. Minor alloying elements can also have a significant effect on the aging process by changing the interface energy of the precipitate, by increasing the vacancy concentration, and/or by raising the critical temperature for homogeneous precipitation. Like some other age-hardened 2*xxx* aluminum alloys, aluminum-lithium-base alloys also gain increased strength and toughness from deformation prior to aging. This unusual phenomenon has given rise to a number of thermomechanical processing steps for aluminum-lithium alloys aimed at optimizing mechanical properties after artificial aging.

The age hardening of aluminum-lithium alloys involves the continuous precipitation of δ' (Al_3Li) from a supersaturated solid solution. The aluminum and lithium in the δ' precipitates are positioned at specific locations. The eight shared corner sites are occupied by lithium, and the six shared faces are occupied by aluminum. This gives rise to the aluminum-lithium composition of δ' precipitates. The geometrical similarity between the lattice of the precipitates and the face-centered

cubic lattices of the solid solution facilitates the observed cube/cube orientation. The lattice parameters of the precipitate are also closely matched to those of the matrix. Consequently, the microstructure of an aluminum-lithium alloy solution heat treated and aged for short times below the δ' solvus is characterized by a homogeneous distribution of coherent, spherical δ' precipitates.

Aluminum-lithium-base alloys are microstructurally unique. They differ from most of the aluminum alloys in that once the major strengthening precipitate (δ') is homogeneously precipitated, it remains coherent even after extensive aging. In addition, extensive aging at high temperatures (>190 °C, or 375 °F) can result in the precipitation of icosahedral grain-boundary precipitates with five-fold symmetry. Although the quasi-crystalline structure and the composition of these grain-boundary precipitates are not yet exactly known, it has been suggested that both the precipitates and the precipitate-free zones (PFZs) near the grain boundaries might play a major role in the fracture process.

The low ductility and toughness of binary aluminum-lithium alloys can be traced, at least in part, to the inhomogeneous nature of their slip, resulting from coherent-particle hardening of spherical δ' precipitates. The presence of equilibrium δ(aluminum-lithium) precipitates at grain boundaries can also cause PFZs, which can induce further strain localization and promote intergranular failure. Consequently, for the development of commercial alloys, slip has been homogenized by introducing dispersoids (manganese, zirconium) and semicoherent/incoherent precipitates, such as T_1 (Al_2CuLi), θ' (Al_2Cu), or S (Al_2LiMg), through copper or magnesium additions. Magnesium and copper improve the strength of aluminum-lithium alloys through solid-solution and precipitate strengthening, and they can minimize the formation of PFZs near grain boundaries. Zirconium, which forms the cubic Al_3Zr coherent dispersoid, stabilizes the subgrain structure and suppresses recrystallization.

Development of commercially available aluminum-lithium-base alloys was started by adding lithium to aluminum-copper, aluminum-magnesium, and aluminum-copper-magnesium alloys. These alloys were chosen to superimpose the precipitation-hardening characteristics of aluminum-copper-, aluminum-copper-magnesium-, and aluminum-magnesium-base precipitates to the hardening of lithium-containing precipitates. Proceeding in this manner, alloys 2020 (Al-Cu-Li-Cd), 01429 (Al-Mg-Li), 2090 (Al-Cu-Li), and 2091 and 8090 (Al-Cu-Mg-Li) evolved. Besides these registered alloys, other commercial aluminum-lithium alloys include Weldalite 049 and CP276. Properties and applications of these alloys are discussed in the article "Aluminum-Lithium Alloys" in ***Properties and Selection: Nonferrous Alloys and Special-Purpose Materials,*** Volume 2 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.*

In terms of δ' precipitation, the only effect of magnesium appears to be a reduction in the solubility of lithium. The microstructure of an aluminum-magnesium-lithium alloy in the early stages of aging is similar to that of an aluminum-lithium alloy. Precipitation in the aluminum-copper-lithium system is more complicated than that in either the aluminum-lithium or aluminum-magnesium-lithium systems.

Effects on Physical and Electrochemical Properties. The above description of the precipitation processes in commercial heat-treatable aluminum alloys (as well as the heat-treatable binary alloys, none of which is used commercially in wrought form) affect not only mechanical properties but also physical properties (density and electrical and thermal conductivities) and electrochemical properties (solution potential). On the microstructural and submicroscopic scales, the electrochemical properties develop point-to-point nonuniformities that account for changes in corrosion resistance.

Measurements of changes in physical and electrochemical properties have played an important role in completely describing precipitation reactions and are very useful in analyzing or diagnosing whether heat-treatable products have been properly or improperly heat treated. Although they may be indicative of the strength levels of products, they cannot be relied upon to determine whether or not the product meets specified mechanical-property limits. Since elements in solid solution are always more harmful to electrical conductivity than the same elements combined with others as intermetallic compounds, thermal treatments are applied to ingots used for fabrication of electrical conductor parts. These thermal treatments are intended to precipitate as much as possible of the dissolved impurities. Iron is the principal element involved, and although the amount precipitated is only a few hundredths of a percent, the effect on electrical conductivity of the wire, cable, or other product made from the ingot is of considerable practical importance. These alloys may or may not be heat treatable with respect to mechanical properties. Electrical conductor alloys 6101 and 6201 are heat treatable. These alloys are used in tempers in which their strengthening precipitate, the transition form of Mg_2Si, is largely out of solid solution to optimize both strength and conductivity.

Heat Treating of Aluminum Alloys

Strengthening by Heat Treatment

Heat treatment to increase strength of aluminum alloys is a three-step process:

- Solution heat treatment: dissolution of soluble phases
- Quenching: development of supersaturation
- Age hardening: precipitation of solute atoms either at room temperature (natural aging) or elevated temperature (artificial aging or precipitation heat treatment)

Each of these steps and the use of quench-factor analysis are described in the following four sections. Typical solution and precipitation heat treatments for mill products are given in Tables 1(a), 1(b), 1(c) and Table 2, and treatments for castings are given in Table 3. Temper designations are defined at the end of this article.

Table 1(a) Typical solution and precipitation heat treatments for commercial heat-treatable aluminum alloy mill products with copper alloying

Alloy	Product form	Solution heat treatment[a]			Precipitation heat treatment			
		Metal temperature[b]		Temper designation	Metal temperature[b]		Time[c], h	Temper designation
		°C	°F		°C	°F		
Al-Cu alloys without magnesium alloying								
2011	Rolled or cold finished rod and bar	525	975	T3[d]	160	320	14	T8[d]
				T4	. . .	. . .	. . .	. . .
				T451[e]	. . .	. . .	. . .	. . .
2025	Die forgings	515	960	T4	170	340	10	T6
2219[f]	Flat sheet	535	995	T31[d]	175	350	18	T81[d]
				T37[d]	165	325	24	T87[d]
				T42	190	375	36	T62
	Plate	535	995	T31[d]	175	350	18	T81[d]
				T37[d]	175	350	18	T87[d]
				T351[e]	175	350	18	T851[e]

				T42	190	375	36	T62
	Rolled or cold finished wire, rod, and bar	535	995	T351[e]	190	375	18	T851[e]
2219[f]	Extruded rod, bar, shapes, and tube	535	995	T31[d]	190	375	18	T81[d]
				T3510[e]	190	375	18	T8510[e]
				T3511[e]	190	375	18	T8511[e]
				T42	190	375	36	T62
	Die forgings and rolled rings	535	995	T4	190	375	26	T6
	Hand forgings	535	995	T4	190	375	26	T6
				T352[f]	175	350	18	T852f)
Al-Cu-Mg alloys								
2018	Die forgings	510[g]	950[g]	T4	170	340	10	T61
2024[h]	Flat sheet	495	920	T3[d]	190	375	12	T81[d]
				T361[d]	190	375	8	T861[d]
				T42	190	375	9	T62
					190	375	16	T72
2024[h]	Coiled sheet	495	920	T4	. . .	. . .	. . .	. . .
				T42	190	375	9	T62
					190	375	16	T72
	Plate	495	920	T351[e]	190	375	12	T851[e]
				T361[d]	190	375	8	T861[d]

				T42	190	375	9	T62
	Rolled or cold finished wire, rod, and bar	495	920	T4	190	375	12	T6
				T351[e]	190	375	12	T851[e]
				T36[d]	190	375	8	T86[d]
				T42	190	375	16	T62
	Extruded rod, bar, shapes, and tube	495	920	T3	190	375	12	T81
				T3510[e]	190	375	12	T8510[e]
				T3511[e]	190	375	12	T8511[e]
				T42	190	375	16	T62
	Drawn tube	495	920	T3[d]	. . .	. . .	. . .	. . .
				T42	. . .	. . .	. . .	. . .
2036	Sheet	500	930	T4	. . .	. . .	. . .	. . .
2038	Sheet	540	1000	T4	205	400	2	T6
2218	Die forgings	510[g]	950[g]	T4	170	340	l0	T61
		510[i]	950[i]	T41	240	460	6	T72
Al-Cu-Mg-Si alloys								
2008	Sheet	510	950	T4[d][j]	205	400	1	T62[e]
2014[h]	Flat sheet	500	935	T3[d]	160	320	18	T62
				T42	160	320	18	T6
	Coiled sheet	500	935	T4	160	320	18	T6
				T42	160	320	18	T62

	Plate	500	935	T42	160	320	18	T62
				T451(e)	160	320	18	T651(e)
	Rolled or cold finished wire, rod, and bar	500	935	T4	160(k)	320(k)	18	T6
				T42	160(k)	320(k)	18	T62
				T451(e)	160(k)	320(k)	18	T651(e)
	Extruded rod, bar, shapes, and tube	500	935	T4	160(k)	320(k)	18	T6
				T42	160(k)	320(k)	18	T62
				T4510(e)	160(k)	320(k)	18	T6510(e)
	Drawn tube	500	935	T4	160(k)	320(k)	18	T6
				T42	160(k)	320(k)	18	T62
	Die forgings	500(l)	935(l)	T4	170	340	10	T6
2017	Rolled or cold finished wire, rod, and bar	500	935	T4	. . .	. . .	. . .	. . .
				T42	. . .	. . .	. . .	. . .
2117	Rolled or cold finished wire and rod	500	935	T4	. . .	. . .	. . .	. . .
				T42	. . .	. . .	. . .	. . .
2618	Forgings and rolled rings	530	985	T4	200	390	20	T61
4032	Die forgings	510(h)	950(h)	T4	170	340	10	T6
Al-Cu-Li alloys								
2090	Sheet	540	1000	T3(d)	165	325	24	T83(d)
2091	Sheet	530	990	T3(d)	120	250	24	T84(d)
	Extruded bar	530	990	T3(d)	190	375	12	Peak aged(d)

8090	Extruded bar	530	990	T3[d]	190	375	12	Peak aged[d]
CP276	Extruded bar	540	1000	T3[d]	190	375	12-15	Peak aged[d]

(a) Material should be quenched from the solution-treating temperature as rapidly as possible and with minimum delay after removal from the furnace. When material is quenched by total immersion in water, unless otherwise indicated, the water should be at room temperature, and should be suitably cooled so that it remains below 38 °C (100 °F) during the quenching cycle. Use of high-velocity, high-volume jets of cold water also is effective for some materials.

(b) The nominal temperatures listed should be attained as rapidly as possible and maintained within ±6 °C (± 10 °F) of nominal during the time at temperature.

(c) Approximate time at temperature. The specific time will depend on the time required for the load to reach temperature. The times shown are based on rapid heating, with soak time measured from the time the load reaches a temperature within 6 °C (10 °F) of the applicable temperature.

(d) Cold working subsequent to solution heat treatment and prior to any precipitation heat treatment is necessary to attain the specified properties for this temper.

(e) Stress relieved by stretching to produce a specified amount of permanent set subsequent to solution heat treatment and prior to any precipitation heat treatment.

(f) Stress relieved by 1 to 5% cold reduction after solution treatment and prior to precipitation heat treatment.

(g) Quenched in water at 100 °C (212 °F).

(h) These heat treatments also apply to alclad sheet and plate of these alloys.

(i) Quenched with room-temperature air blast.

(j) See U.S. Patent 4,840,852.

(k) An alternative heat treatment of 8 h at 177 °C (350 °F) may also be used.

(l) Quenched in water at 60 to 80 °C (140 to 180 °F).

Table 1(b) Typical solution and precipitation heat treatments for Mg-Si aluminum alloys (6*xxx* series alloys)

Alloy	**Product form**	**Solution heat treatment[a]**		Precipitation heat treatment		
		Metal temperature[b]	**Temper designation**	**Metal temperature[b]**	**Time[c], h**	Temper designation

		°C	°F		°C	°F		
6005	Extruded rod, bar, shapes, and tube	530[(d)]	985[(d)]	T1	175	350	8	**T5**
6009[(e)]	Sheet	555	1030	T4	205	400	1	**T6[(e)]**
6010	Sheet	565	1050	T4	205	400	1	**T6[(e)]**
6053	Die forgings	520	970	T4	170	340	10	**T6**
6061[(f)]	Sheet	530	985	T4	160	320	18	**T6**
				T42	160	320	18	**T62**
	Plate	530	985	T4[(g)]	160	320	18	**T6[(g)]**
				T42	160	320	18	**T62**
				T451[(h)]	160	320	18	**T651[(h)]**
	Rolled or cold finished wire, rod, and bar	530	985	T4	160[(i)]	320[(i)]	18	**T6**
					160[(i)]	320[(i)]	18	**T89[(j)]**
					160[(i)]	320[(i)]	18	**T93[(k)]**
					160[(i)]	320[(i)]	18	**T913[(k)]**
					160[(i)]	320[(i)]	18	**T94[(k)]**
				T42	160[(i)]	320[(i)]	18	**T62**
				T451[(h)]	160[(i)]	320[(i)]	18	**T651[(h)]**
	Extruded rod, bar, shapes, and tube	530[(d)]	985[(d)]	T4	175	350	8	**T6**
				T4510[(h)]	175	350	8	**T6510[(h)]**
				T4511[(h)]	175	350	8	**T6511[(h)]**
		530	985	T42	175	350	8	**T62**

6061[f]	Drawn tube	530	985	T4	160[i]	320[i]	18	**T6**
				T42	160[i]	320[i]	18	**T62**
	Die and hand forgings	530	985	T4	175	350	8	**T6**
	Rolled rings	530	985	T4	175	350	8	**T6**
				T452[l]	175	350	8	**T652[l]**
6063	Extruded rod, bar, shapes, and tube	[d]	[d]	T1	205[m]	400[m]	1	**T5**
		520[d]	970[d]	T4	175[n]	350[n]	8	**T6**
		520	970	T42	175[n]	350[n]	8	**T62**
	Drawn tube	520	970	T4	175	350	8	**T6**
					175	350	8	**T83[j][d]**
					175	350	8	**T831[j][d]**
					175	350	8	**T832[j][d]**
				T42	175	350	8	**T62**
6013[o]	Sheet	570	1055	W[p]	190	375	4	**T6**
	Plate	570	1055	W[p]	190	375	4	**T651**
6066	Extruded rod, bar, shapes, and tube	530	990	T4	175	350	8	**T6**
				T42	175	350	8	**T62**
				T4510[h]	175	350	8	**T6510[h]**
				T4511[h]	175	350	8	**T6511[h]**
	Drawn tube	530	990	T4	175	350	8	**T6**
				T42	175	350	8	**T62**

	Die forgings	530	990	T4	175	350	8	**T6**
6070	Extruded rod, bar, shapes, and tube	545[d]	1015[d]	T4	160	320	18	**T6**
				T42	160	320	18	**T62**
6111	Sheet	560	1040	T4	175	350	8	**T6[q]**
6151	Die forgings	515	960	T4	170	340	10	**T6**
	Rolled rings	515	960	T4	170	340	10	**T6**
				T452[l]	170	340	10	**T652[l]**
6262	Rolled or cold finished wire, rod, and bar	540	1000	T4	170	340	8	**T6**
					170	340	12	**T9[k]**
				T451	170	340	8	**T651[h]**
				T42	170	340	8	**T62**
6262	Extruded rod, bar, shapes, and tube	540[d]	1000[d]	T4	175	350	12	**T6**
				T4510[h]	175	350	12	**T6510[h]**
		540	1000	T42	175	350	12	**T62**
	Drawn tube	540	1000	T4	170	340	8	**T6**
					170	340	8	**T9[k]**
				T42	170	340	8	**T62**
6463	Extruded rod, bar, shapes, and tube	[d]	[d]	T1	205[m]	400[m]	1	**T5**
		520[d]	970[d]	T4	175[n]	350[n]	8	**T6**
		520	970	T42	175[n]	350[n]	8	**T62**
6951	Sheet	530	985	T4	160	320	18	**T6**

				T42	**160**	**320**	**18**	**T62**

(a) Material should be quenched from the solution-treating temperature as rapidly as possible and with minimum delay after removal from the furnace. When material is quenched by total immersion in water, unless otherwise indicated, the water should be at room temperature, and should be suitably cooled so that it remains below 38 °C (100 °F) during the quenching cycle. Use of high-velocity, high-volume jets of cold water also is effective for some materials.

(b) The nominal temperatures listed should be attained as rapidly as possible and maintained within ±6 °C (±10 °F) of nominal during the time at temperature.

(c) Approximate time at temperature. The specific time will depend on the time required for the load to reach temperature. The times shown are based on rapid heating, with soak time measured from the time the load reaches a temperature within 6 °C (10 °F) of the applicable temperature.

(d) By suitable control of extrusion temperature, product may be quenched directly from extrusion press to provide specified properties for this temper. Some products may be adequately quenched in room-temperature air blast.

(e) Alternate heat treatments of 4 h at 190 °C (375 °F) or 8 h at 175 °C (350 °F) may also be used. See U.S. Patent 4,082,578.

(f) These heat treatments also apply to alclad sheet and plate in these alloys.

(g) Applicable to tread plate only.

(h) Stress relieved by stretching to produce a specified amount of permanent set prior to precipitation heat treatment.

(i) An alternative heat treatment of 8 h at 170 °C (340 °F) also may be used.

(j) Cold working after solution treatment is necessary to attain specified properties during precipitation heat treatments.

(k) Cold working after precipitation heat treatment is necessary to attain specified properties.

(l) Stress relieved by 1 to 5% cold reduction subsequent to solution heat treatment and prior to precipitation heat treatment.

(m) An alternative treatment of 3 h at 182 °C (360 °F) also may be used.

(n) An alternative treatment of 6 h at 182 °C (360 °F) also may be used.

(o) See U.S. Patent 4,589,932.

(p) Two weeks of natural aging to a T4 condition.

(q) Artificially aged in laboratory from T4 to T6.

Table 1(c) Typical solution and precipitation heat treatments for heat-treatable Zn-Mg aluminum alloys from the 7*xxx* series

Alloy	**Product form**	**Solution heat treatment**[(a)]			Precipitation heat treatment			
		Metal temperature[(b)]		**Temper designation**	**Metal temperature**[(b)]		**Time**[(c)], **h**	Temper designation
		°C	**°F**		**°C**	**°F**		
7001	Extruded rod, bar, shapes, and tube	465	870	W	120	250	24	**T6**
					120	250	24	**T62**
				W510[(d)]	120	250	24	**T6510**[(d)]
				W511[(d)]	120	250	24	**T6511**[(d)]
7005	Extruded rod, bar, and shapes	. . .	. . .	. . .	. . .	. . .	. . .	**T53**[(e)]
7050	Plate	475	890	W51[(d)]	[(f)]	[(f)]	[(f)]	**T7651**[(g)]
					[(h)]	[(h)]	[(h)]	**T7451**[(g)]
	Extrusions	475	890	W510[(d)]	[(f)]	[(f)]	[(f)]	**T76510**[(g)]
				W511[(d)]	[(f)]	[(f)]	[(f)]	**T76511**[(g)]
	Die and hand forgings	475	890	W	[(h)]	[(h)]	[(h)]	**T74**[(g)]
				W52[(d)]	[(h)]	[(h)]	[(h)]	**T7452**[(g)]
7075[(i)]	Sheet	480	900	W	120[(j)]	250[(j)]	24	**T6**
					120[(j)]	250[(j)]	24	**T62**
					[(f)]	[(f)]	[(f)]	**T76**[(g)]
					[(h)(k)]	[(h)(k)]	[(h)(k)]	**T73**[(g)]

	Plate	480	900	W	120[j]	250[j]	24	**T62**
				W51[d]	[h][k]	[h][k]	[h][k]	**T7351 [d][g]**
					120[j]	250[j]	24	**T651[d]**
					[f]	[f]	[f]	**T7651[g]**
7075[i]	Rolled or cold finished wire, rod, and bar	490	915	W	120	250	24	**T6**
					120	250	24	**T62**
					[h][k]	[h][k]	[h][k]	**T73[g]**
				W51[d]	120	250	24	**T651[d]**
					[h][k]	[h][k]	[h][k]	**T7351[d][g]**
	Extruded rod, bar, shapes, and tube	465	870	W	120[l]	250[l]	24	**T6**
					120[l]	250[l]	24	**T62**
					[h][k]	[h][k]	[h][k]	**T73[g]**
					[f]	[f]	[f]	**T76[g]**
				W510[d]	120[l]	250[l]	24	**T6510[d]**
					[h][k]	[h][k]	[h][k]	**T73510[d][g]**
					[f]	[f]	[f]	**T76510[g]**
				W511[d]	120[l]	250[l]	24	**T6511[d]**
					[h][k]	[h][k]	[h][k]	**T73511 [d][g]**
					[f]	[f]	[f]	**T76511[g]**
	Drawn tube	465	870	W	120	250	24	**T6**
					120	250	24	**T62**

					(h)(k)	(h)(k)	(h)(k)	**T73**[g]
	Die forgings	470[m]	880[h]	W	120	250	24	**T6**
					(h)	(h)	(h)	**T73**[g]
				W52[n]	(h)	(h)	(h)	**T7352**[n][g]
	Hand forgings	470[m]	880[h]	W	120	250	24	**T6**
					(h)	(h)	(h)	**T73**[g]
				W52[n]	120	250	24	**T652**[n]
					(h)	(h)	(h)	**T7352**[n][g]
	Rolled rings	470	880	W	120	250	24	**T6**
7175	Die forgings	(o)	(o)	W	(o)	(o)	(o)	**T66**[o]
		(o)	(o)	W	(o)	(o)	(o)	**T74**[g][o]
		(o)	(o)	W52[n]	(o)	(o)	(o)	**T7452**[n][g][o]
	Hand forgings	(o)	(o)	W	(o)	(o)	(o)	**T74**[g][o]
		(o)	(o)	W52[n]	(o)	(o)	(o)	**T7452**[n][g][o]
7475	Sheet	515[p]	960[p]	W	120	250	3	
					plus 155	315	3	**T61**[p]
					(f)	(f)	(f)	**T761**[g][p]
	Plate	510[p]	950[p]	W51[d]	120	250	24	**T651**[p]
					(f)	(f)	(f)	**T7651**[g][p]
					(h)	(h)	(h)	**T7351**[g][p]
Alclad 7475	Sheet	495	920	W	120	250	3	

7475					plus 155	315	3	**T61**[p]
					[f]	[f]	[f]	**T761**[g][p]

(a) Material should be quenched from the solution-treating temperature as rapidly as possible and with minimum delay after removal from the furnace. When material is quenched by total immersion in water, unless otherwise indicated, the water should be at room temperature, and should be suitably cooled so that it remains below 38 °C (100 °F) during the quenching cycle. Use of high-velocity, high-volume jets of cold water also is effective for some materials.

(b) The nominal temperatures listed should be attained as rapidly as possible and maintained within ±6 °C (±10 °F) of nominal during the time at temperature.

(c) Approximate time at temperature. The specific time will depend on the time required for the load to reach temperature. The times shown are based on rapid heating, with soak time measured from the time the load reaches a temperature within 6 °C (10 °F) of the applicable temperature.

(d) Stress relieved by stretching to produce a specified amount of permanent set after solution treatment and prior to precipitation heat treatment.

(e) No solution heat treatment; 72 h at room temperature following press quench followed by two-stage precipitation heat treatment comprised of 8 h at 107 °C (225 °F) plus 16 h at 149 °C (300 °F).

(f) Aging practice varies with product, size, nature of equipment, loading procedures, and furnace-control capabilities. The optimum practice for a specific item can be ascertained only by actual trial treatment of the item under specific conditions. Typical procedures involve a two-stage treatment comprised of 3 to 30 h at 121 °C (250 °F) followed by 15 to 18 h at 163 °C (325 °F) for extrusions. An alternative two-stage treatment of 8 h at 99 °C (210 °F) followed by 24 to 28 h at 163 °C (325 °F) also may be used.

(g) Aging of aluminum alloys 7050, 7075, 7175, and 7475 from any temper to the T73 or T76 temper series requires closer-than-normal controls on aging variables such as time, temperature, heatup rate, and so forth, for any given item. In addition, when material in a T6-type temper is reaged to a T73- or T76-type temper, the specific condition of the T6 material (such as property levels and other effects of processing variables) is extremely important and will affect the capability of the reaged material to conform to the requirements specified for the applicable T73- or T76-type temper.

(h) Two-stage treatment comprised of 6 to 8 h at 107 °C (225 °F) followed by: 24 to 30 h at 163 °C (325 °F) for sheet and plate; 8 to 10 h at 177 °C (350 °F) for rolled or cold finished rod and bar; 6 to 8 h at 177 °C (350 °F) for extrusions and tube; 8 to 10 h at 177 °C (350 °F) for forgings in the T73 temper; and 6 to 8 h at 177 °C (350 °F) for forgings in the T7352 temper.

(i) These heat treatments also apply to alclad sheet and plate of these alloys.

(j) An alternative two-stage treatment comprised of 4 h at 96 °C (205 °F) followed by 8 h at 157 °C (315 °F) also may be used.

(k) For sheet, plate, tube, and extrusions, an alternative two-stage treatment comprised for 6 to 8 h at 107 °C (225 °F) followed by 14 to 18 h at 168 °C (335 °F) may be used, provided that a heatup rate of approximately 14 °C/h (25 °F/h) is employed. For rolled or cold finished rod and bar, the alternative treatment is 10 h at 177 °C (350 °F).

(l) An alternative three-stage treatment comprised of 5 h at 99 °C (210 °F), 4 h at 121 °C (250 °F), and then 4 h at 149 °C (300 °F) may also be used.

(m) Quenched in water at 60 to 80 °C (140 to 180 °F).

(n) Stress relieved by 1 to 5% cold reduction after solution treatment and prior to precipitation heat treatments.

(o) 7175-T74 and -T7452 heat treatments are directed to specific results, may vary from supplier to supplier and are either proprietary or patented.

(p) Must be preceded by soak at 466 to 477 °C (870 to 890 °F). See U.S. Patent 3,791,880.

Table 2 Soak times and maximum quench delays for solution treatment of wrought aluminum alloys

See Table 1(a), 1(b), and 1(c) for solution-treating temperatures.

Thickness[a], mm (in.)	**Soak time, minutes**				Maximum quench delay, s
	Air furnace[b]		**Salt bath[c]**		
	min	**max[d]**	**min**	**max[d]**	
≤ 0.41 (0.016)	20	25	10	15	**5**
0.51 (0.020)	20	30	10	20	**7**
0.64 (0.025)	25	35	15	25	**7**
0.81 (0.032)	25	35	15	25	**7**
1.02 (0.040)	30	40	20	30	**10**
1.27 (0.050)	30	40	20	30	**10**
1.35 (0.053)	30	40	20	30	**10**
1.80 (0.071)	35	45	25	35	**10**
2.03 (0.080)	35	45	25	35	**10**
2.29 (0.090)	35	45	25	35	**10**
2.54 (0.100)	40	55	30	45	**15**
3.18 (0.125)	40	55	30	45	**15**

4.06 (0.160)	50	60	35	45	**15**
4.57 (0.180)	50	60	35	45	**15**
6.35 (0.250)	55	65	35	45	**15**
>6.35 (0.250)-12.7 (0.500)	65	75	45	55	**15**
For each additional 12.7 ($\frac{1}{2}$) or fraction	+30	+30	+20	+20	(e)
Rivets (all)	**60**	**. . .**	**30**	**. . .**	**5**

(a) Minimum dimension of thickest section.

(b) Soak time begins when all pyrometer instruments recover to original operating temperature.

(c) Soak time begins at time of immersion except when a heavy charge causes bath temperature to drop below specified minimum, in which case soak time begins when bath regains minimum temperature.

(d) Applicable to alclad materials only.

(e) Increases in thickness above 12.7 mm ($\frac{1}{2}$ in.) do not affect maximum quench delay, which remains constant at 15 s.

Table 3 Typical heat treatments for aluminum alloy sand and permanent mold castings

Alloy	**Temper**	**Type of casting**(a)	**Solution heat treatment**(b)			Aging treatment		
			Temperature(c)		**Time, h**	**Temperature**(c)		Time, h
			°C	**°F**		**°C**	**°F**	
201.0(d)	T4	S or P	490-500(e)	910-930(e)	2	. . .	. . .	**. . .**
			+ 525-530	+ 980-990	14-20	**Minimum of 5 days at room temperature**		
	T6	S	510-515(e)	950-960(e)	2	. . .	. . .	**. . .**
			+ 525-530	+ 980-990	14-20	155	310	**20**

	T7	S	510-515(e)	950-960(e)	2	. . .	. . .	**. . .**
			+ 525-530	+ 980-990	14-20	190	370	**5**
	T43(f)	. . .	525	980	20	**24 h at room temperature + $\frac{1}{2}$ to 1 h at 160 °C**		
	T71	. . .	490-500(e)	910-930(e)	2	. . .	. . .	**. . .**
			+ 525-530	+ 980-990	14-20	200	390	**4**
204.0(d)	T4	S or P	530	985	12	**Minimum of 5 days at room temperature**		
	T4	S or P	520	970	10	. . .	. . .	**. . .**
	T6(g)	S or P	530	985	12	(g)	(g)	**. . .**
206.0(d)	T4	S or P	490-500(e)	910-930(e)	2	. . .	. . .	**. . .**
			+ 525-530	+ 980-990	14-20	**Minimum of 5 days at room temperature**		
	T6	S or P	490-500(e)	910-930(e)	2	. . .	. . .	**. . .**
			+ 525-530	+ 980-990	14-20	155	310	**12-24**
	T7	S or P	490-500(e)	910-930(e)	2	. . .	. . .	**. . .**
			+ 525-530	+ 980-990	14-20	200	390	**4**
	T72	S or P	490-500(e)	910-930(e)	2	. . .	. . .	**. . .**
			+ 525-530	+ 980-990	14-20	243-248	470-480	
208.0	T55	S	. . .	. . .	. . .	155	310	**16**
222.0	O(h)	S	. . .	. . .	. . .	315	600	**3**
	T61	S	510	950	12	155	310	**11**
	T551	P	. . .	. . .	. . .	170	340	**16-22**

	T65	. . .	510	950	4-12	170	340	**7-9**
242.0	O[i]	S	. . .	. . .	. . .	345	650	**3**
	T571	S	. . .	. . .	. . .	205	400	**8**
		P	. . .	. . .	. . .	165-170	330-340	**22-26**
	T77	S	515	960	5[l]	330-355	625-675	**2 (minimum)**
	T61	S or P	515	960	4-12[l]	205-230	400-450	**3-5**
295.0	T4	S	515	960	12	. . .	. . .	**. . .**
	T6	S	515	960	12	155	310	**3-6**
	T62	S	515	960	12	155	310	**12-24**
	T7	S	515	960	12	260	500	**4-6**
296.0	T4	P	510	950	8	. . .	. . .	**. . .**
	T6	P	510	950	8	155	310	**1-8**
	T7	P	510	950	8	260	500	**4-6**
319.0	T5	S	. . .	. . .	. . .	205	400	**8**
	T6	S	505	940	12	155	310	**2-5**
		P	505	940	4-12	155	310	**2-5**
328.0	T6	S	515	960	12	155	310	**2-5**
332.0	T5	P	. . .	. . .	. . .	205	400	**7-9**
333.0	T5	P	. . .	. . .	. . .	205	400	**7-9**
	T6	P	505	950	6-12	155	310	**2-5**
	T7	P	505	940	6-12	260	500	**4-6**

336.0	T551	P	. . .	. . .	. . .	205	400	**7-9**
	T65	P	515	960	8	205	400	**7-9**
354.0	. . .	(k)	525-535	980-995	10-12	(h)	(h)	**(l)**
355.0	T51	S or P	. . .	. . .	. . .	225	440	**7-9**
	T6	S	525	980	12	155	310	**3-5**
		P	525	980	4-12	155	310	**2-5**
	T62	P	525	980	4-12	170	340	**14-18**
	T7	S	525	980	12	225	440	**3-5**
		P	525	980	4-12	225	440	**3-9**
	T71	S	525	980	12	245	475	**4-6**
		P	525	980	4-12	245	475	**3-6**
C355.0	T6	S	525	980	12	155	310	**3-5**
	T61	P	525	980	6-12	Room temperature		**8 (minimum)**
						155	310	**10-12**
356.0	T51	S or P	. . .	. . .	. . .	225	440	**7-9**
	T6	S	540	1000	12	155	310	**3-5**
		P	540	1000	4-12	155	310	**2-5**
	T7	S	540	1000	12	205	400	**3-5**
		P	540	1000	4-12	225	440	**7-9**
	T71	S	540	1000	10-12	245	475	**3**
		P	540	1000	4-12	245	475	**3-6**

A356.0	T6	S	540	1000	12	155	310	**3-5**
	T61	P	540	1000	6-12	Room temperature		**8 (minimum)**
						155	310	**6-12**
357.0	T6	P	540	1000	8	175	350	**6**
	T61	S	540	1000	10-12	155	310	**10-12**
A357.0	. . .	(k)	540	1000	8-12	(h)	(h)	**(h)**
359.0	. . .	(k)	540	1000	10-14	(h)	(h)	**(h)**
A444.0	T4	P	540	1000	8-12	. . .	. . .	**. . .**
520.0	T4	S	430	810	18(m)	. . .	. . .	**. . .**
535.0	T5(h)	S	400	750	5	. . .	. . .	**. . .**
705.0	T5	S	. . .	. . .	. . .	Room temperature		**21 days**
						100	210	**8**
		P	. . .	. . .	. . .	Room temperature		**21 days**
						100	210	**10**
707.0	T5	S	. . .	. . .	. . .	155	310	**3-5**
		P	. . .	. . .	. . .	Room temperature, or		**21 days**
						100	210	**8**
	T7	S	530	990	8-16	175	350	**4-10**
		P	530	990	4-8	175	350	**4-10**
710.0	T5	S	. . .	. . .	. . .	Room temperature		**21 days**
711.0	T1	P	. . .	. . .	. . .	Room temperature		**21 days**

712.0	T5	S	. . .	. . .	. . .	Room temperature, or		**21 days**
						155	315	**6-8**
713.0	T5	S or P	. . .	. . .	. . .	Room temperature, or		**21 days**
						120	250	**16**
771.0	T53[h]	S	415[n]	775[n]	5(n)	180[n]	360[n]	**4[n]**
	T5	S	. . .	. . .	. . .	180[n]	355[n]	**3-5[n]**
	T51	S	. . .	. . .	. . .	205	405	**6**
	T52	S	. . .	. . .	. . .	[h]	[h]	**[h]**
	T6	S	590[n]	1090[n]	6[n]	130	265	**3**
	T71	S	590[i]	1090[i]	6[i]	140	285	**15**
850.0	T5	S or P	. . .	. . .	. . .	220	430	**7-9**
851.0	T5	S or P	. . .	. . .	. . .	220	430	**7-9**
	T6	P	480	900	6	220	430	**4**
852.0	**T5**	**S or P**	**. . .**	**. . .**	**. . .**	**220**	**430**	**7-9**

(a) S, sand; P, permanent mold.

(b) Unless otherwise indicated, solution treating is followed by quenching in water at 65-100 °C (150-212 °F).

(c) Except where ranges are given, listed temperatures are ±6 °C or ±10 °F.

(d) Casting wall thickness, solidification rate, and grain refinement affect the solution heat-treatment cycle in alloys 201.0, 204.0, and 206.0, and care must be taken in approaching the final solution temperature. Too rapid an approach can result in the occurrence of incipient melting.

(e) For castings with thick or other slowly solidified sections, a pre-solution heat treatment ranging from about 490 to 515 °C (910 to 960 °F) may be needed to avoid too rapid a temperature rise to the solution temperature and the melting of $CuAl_2$.

(f) Temper T43 for 201.0 was developed for improved impact resistance with some decrease in other mechanical properties. Typical Charpy value is 20 J (15 ft · lb).

(g) The French precipitation treatment technology for the heat treatment of 204.0 alloy requires 12 h at temperature. The aging temperatures of 140, 160, or 180 °C (285, 320, or 355 °F) are selected to meet the required combination of properties.

(h) Stress relieve for dimensional stability as follows: hold 5 h at 413 ± 14 °C (775 ± 25 °F); furnace cool to 345 °C (650 °F) over a period of 2 h or more; furnace cool to 230 °C (450 °F) over a period of not more than $\frac{1}{2}$ h; furnace cool to 120 °C (250 °F) over a period of approximately 2 h; cool to room temperature in still air outside the furnace.

(i) No quench required; cool in still air outside the furnace.

(j) Air-blast quench from solution-treating temperature.

(k) Casting process varies (sand, permanent mold, or composite) depending on desired mechanical properties.

(l) Solution heat treat as indicated, then artificially age by heating uniformly at the temperature and for the time necessary to develop the desired mechanical properties.

(m) Quench in water at 65-100 °C (150-212 °F) for 10-20 s only.

(n) Cool to room temperature in still air outside the furnace.

Solution Heat Treating

To take advantage of the precipitation-hardening reaction, it is necessary first to produce a solid solution. The process by which this is accomplished is called solution heat treating, and its objective is to take into solid solution the maximum practical amounts of the soluble hardening elements in the alloy. The process consists of soaking the alloy at a temperature sufficiently high and for a time long enough to achieve a nearly homogeneous solid solution.

Nominal commercial solution heat-treating temperature is determined by the composition limits of the alloy and an allowance for unintentional temperature variations. Although ranges normally listed allow variations of ±6 °C (±10 °F) from the nominal, some highly alloyed, controlled-toughness, high-strength alloys require that temperature be controlled within more restrictive limits. Broader ranges may be allowable for alloys with greater intervals of temperature between their solvus and eutectic melting temperatures.

Overheating. Care must be exercised to avoid exceeding the initial eutectic melting temperature. If appreciable eutectic melting occurs as a result of overheating, properties such as tensile strength, ductility, and fracture toughness may be degraded. Materials that exhibit microstructural evidence of overheating are generally categorized as unacceptable by specification. Evidence of grain-boundary melting that occurs above the eutectic melting temperature of the alloy usually is not detectable by either visual examination or nondestructive testing.

Although maximum temperature must be restricted to avoid melting, the lower limit should, when possible, be above the temperature at which complete solution occurs (solvus). In the alloy represented by line (a) in Fig. 1, these temperatures would be about 575 and 515 °C (1065 and 960 °F), respectively. However, under production conditions, the temperature interval for solution treatment (shown in Fig. 1 for typical 2*xxx* or 2*xx.x*) alloys provides a margin to safeguard against eutectic melting and a cushion on the low side for increased solution and diffusion rates.

For alloys containing more than 5.65% Cu, complete solution can never occur. For these alloys, such as alloy 2219 (which has 5.8 to 6.8% Cu), the minimum solution heat-treating temperature is established so that it is as close as practical to the eutectic temperature while providing a margin of safety commensurate with the capability of the equipment. Line (b) in Fig. 1 is another example of a composition above 5.65% Cu that does not allow complete dissolution of aluminum-copper precipitates.

For more complex ternary and quaternary systems, solution treatments are modified according to the effect of new elements on the solid solubility and/or the eutectic melting points of the basic binary system. In aluminum-lithium alloys, for example, magnesium reduces the solubility of lithium in aluminum. In the aluminum-copper system, magnesium also lowers the eutectic melting point. The proximity of typical solution-treating temperature ranges to eutectic melting temperatures for three common aluminum-copper-magnesium alloys is shown in the following table:

Alloy	**Solution-treating temperature**		Eutectic melting temperature	
	°C	**°F**	**°C**	°F
2014	496-507	925-945	510	**950**
2017	496-507	925-945	513	**955**

Similar considerations apply to other age-hardenable alloy systems such as aluminum-magnesium-silicon alloys. For example, according to Fig. 2(a), a 1.08% Mg_2Si alloy would be soaked at a temperature in excess of 500 °C (930 °F) but below the solidus of 595 °C (1100 °F) to avoid incipient melting. However, because some alloy constituents may form complex eutectics that melt at temperatures below the equilibrium eutectic temperature, the upper limit for solution treatment of aluminum-magnesium-silicon alloys is in the range of 515 to 540 °C (960 to 1000 °F). At 540 °C (1000 °F), about 0.6% Mg can be placed in solution (Fig. 2b).

Nonequilibrium Melting. When high heating rates are employed, the phenomenon of nonequilibrium melting must be considered. This phenomenon can also be explained with the help of the aluminum-copper phase diagram (Fig. 1). The room-temperature microstructure of an F-temper product containing 4% Cu consists of a solid solution of copper in aluminum and particles of Al_2Cu. When this product is heated slowly, the Al_2Cu begins to dissolve, and if heating is slow enough, all of the Al_2Cu is dissolved when temperatures above the solvus (500 °C, or 932 °F) are reached. When the heating rate is high, however, much of the Al_2Cu remains undissolved. If a material with this microstructure is heated at or above the eutectic temperature of 548 °C (1018 °F), melting will begin at the interface between the Al_2Cu and the matrix. With sufficient time above the eutectic temperature, this metastable liquid will dissolve to form a solid solution and will leave no trace provided that hydrogen gas has not condensed at the interface to form a void. If the product is quenched before the liquid has time to equilibrate, however, it will solidify and form fine eutectic rosettes. This nonequilibrium melting should not be confused with true equilibrium melting, which would occur in any alloy containing more than 5.65% Cu. In such an alloy, eutectic melting is equilibrium melting. No matter how long such an alloy is held above the eutectic temperature, the liquid will never solidify. In commercial alloys, which usually are ternaries or quaternaries of the major alloying elements, the situation is more complex. Different phases have different solvus temperatures, and non-equilibrium melting may occur at different temperatures depending on composition, size of precipitates, and rate of heating. When new solution heat-treating equipment (which provides higher heating rates) is employed, careful examination of alloy microstructures should be included as part of the certification process.

Underheating. When the temperatures attained by the parts or pieces being heat treated are appreciably below the normal range, solution is incomplete, and strength somewhat lower than normal is expected. In the aluminum-copper

system (Fig. 1), the shallow slope of the solvus at its intersection with the composition line indicates that a slight decrease in temperature will result in a large reduction in the concentration of the solid solution and a correspondingly significant decrease in final strength. The effect of solution-treating temperature on the strength of two aluminum alloys is illustrated by the following data:

Solution-treating temperature		**Tensile strength**		Yield strength	
°C	**°F**	**MPa**	**ksi**	**MPa**	ksi
6061-T6 sheet 1.6 mm (0.064 in.) thick					
493	920	301	43.7	272	**39.4**
504	940	316	45.8	288	**41.7**
516	960	333	48.3	305	**44.3**
527	980	348	50.5	315	**45.7**
2024-T4 sheet 0.8 mm (0.032 in.) thick					
488	910	419	60.8	255	**37.0**
491	915	422	61.2	259	**37.5**
493	920	433	62.8	269	**39.0**
496	**925**	**441**	**63.9**	**271**	39.3

In the tabulation above, note especially the effects of small increments of temperature, within the normal range, on the properties of 0.8 mm (0.032 in.) 2024-T4 sheet.

Solution-Treating Time. The time at the nominal solution heat-treating temperature (soak time) required to effect a satisfactory degree of solution of the undissolved or precipitated soluble phase constituents and to achieve good homogeneity of the solid solution is a function of microstructure before heat treatment. This time requirement can vary from less than a minute for thin sheet to as much as 20 h for large sand or plaster-mold castings. Guideline information for soak times required for wrought products of various section thicknesses is given in Table 2. Similar guidelines for castings are presented in Table 3. The time required to heat a load to the treatment temperature in furnace heat treatment also increases with section thickness and furnace loading, and thus total cycle time increases with these factors.

Soak time for alclad sheet and for parts made from alclad sheet must be held to a minimum, because excessive diffusion of alloying elements from the core into the cladding reduces corrosion protection. For the same reason, reheat treatment

of alclad sheet less than 0.75 mm (0.030 in.) thick generally is prohibited, and the number of reheat treatments permitted for thicker alclad sheet is limited.

The soak times for wrought alloys take into account the normal thermal lag between furnace and part and the difference between surface and center temperatures for commercial equipment qualified to the standards of MIL-H-6088. The rapid heating rates of salt baths permit all immersion time to be counted as soak time unless the bath temperature drops below the minimum of the range. Even then, soak time begins as soon as the bath temperature returns to the minimum. In air furnaces, soak time does not begin until all furnace instruments return to their original set temperature--that is, the temperature reading before insertion of the load.

In air furnaces, thermocouples may also be attracted to, or buried in, parts located in the load in such a manner as to represent the hottest and coldest temperatures in each zone. In this way, it is possible to ensure that adequate soaking is obtained.

Special consideration is given also to establishing soak times for hand and die forgings; soak time in some specifications is extended to complete solution and homogenization in areas that received marginal reduction during forging. Considerable variation exists in the amount of soak time added; some specifications call for an arbitrary addition, such as one hour, and others require one hour per inch of thickness of the original forging.

In air furnaces, careful attention should be given to arrangement of the load. Air how and natural temperature distribution within the furnace should be arranged to:

- Offer minimum resistance to air flow
- Produce the least disturbance in the natural temperature distribution
- Afford constant replenishment of the envelope of air around each part

It is common practice to specify a minimum spacing of 50 mm (2 in.) between parts, but large complex shapes may require considerably greater spacing. Many operators have found conservative loading practices to be more economical in the long run than heavier loading, because with lighter loads heating rates are higher and fewer rejections and service failures are encountered.

High-Temperature Oxidation. There is a condition, commonly but erroneously known as HTO or high-temperature oxidation, which can lead to deterioration of properties in aluminum alloys. High-temperature oxidation is a misnamed condition of hydrogen diffusion that affects surface layers during elevated-temperature treatment. This condition can result from moisture contamination in the furnace atmosphere and is sometimes aggravated by sulfur (as in heat-treatment furnaces also used for magnesium alloy castings) or other furnace refractory contamination.

Moisture in contact with aluminum at high temperatures serves as a source of nascent hydrogen, which diffuses into the metal. Foreign materials, such as sulfur compounds, function as decomposers of the natural oxide surface film, eliminating it as a barrier either between the moisture and the aluminum or between the nascent hydrogen and the aluminum. The most common manifestation of high-temperature oxidation is surface blistering, but occasionally the only manifestations are internal discontinuities or voids, which can be detected only by careful ultrasonic inspection or by metallographic techniques.

It is important to recognize that the symptoms of high-temperature oxidation are identical to those of unsoundness or high gas content in the original ingot or of other improper mill practice. Blisters resulting from ingot defects, improper extrusion or improper rolling may be lined up in the direction of working. However, it usually is impossible to distinguish among defect sources, and therefore the possibility that a contaminated atmosphere is the cause of the defects must be checked.

Not all alloys and product forms are equally vulnerable to this type of attack. The 7*xxx* series alloys are most susceptible, followed by the 2*xxx* alloys. Extrusions undoubtedly are the most susceptible form; forgings are probably second. Low-strength alloys and alclad sheet and plate are relatively immune to high-temperature oxidation. (Blistering of alclad material as a result of inadequate bonding is not the same as the blistering caused by high-temperature oxidation.)

If the protective oxide film formed during mill operations is removed from the mill product by a subsequent mechanical conditioning operation such as sanding, the conditioned surface will be more susceptible to high-temperature oxidation than those from which the film was not removed.

Moisture can be minimized by thoroughly drying parts and racks before they are charged. Drain holes often are needed in racks of tubular construction to avoid entrapment of water. Another common requirement is adjustment of the position of the quench tank with respect to furnace doors and air intake. Because it is unlikely that all moisture can be eliminated from the atmosphere in a production heat-treating furnace, it is extremely important to eliminate all traces of other contaminants from both the parts and the furnace atmosphere.

The most virulent contaminants in attacking aluminum are sulfur compounds. Residues from forming or machining lubricants, or from a sulfur dioxide protective atmosphere used in prior heat treatment of magnesium, are potential sources of sulfur contamination. In one plant, surface contamination resulted from sulfur-containing materials in tote boxes used to transport parts. In another, an epidemic of blistering was cured by rectifying a "sour" degreaser. In a third instance, it was found that a vapor-degreasing operation was not completely removing a thin, hard waxy residue, and an alkaline cleaning operation was added.

Very often, the source of contamination is obscure and difficult to detect, and the problem must be combated in another way. The most common of the alternative methods is use of a protective fluoborate compound in the furnace. Such a compound usually is effective in minimizing the harmful effects of moisture and other undesirable contaminants because it forms a barrier layer or film on the aluminum surface. The additive is not a universal solution; in some applications, high-temperature oxidation has occurred even though a fluoborate compound was employed. Also, the use of such compounds, particularly ammonium fluoborate, may present a hazard to personnel if used in poorly sealed furnaces or in furnaces that discharge their atmospheres into enclosed areas.

Protective fluoborate compounds accentuate staining or darkening of the parts being treated. (At times, this attack, particularly on parts located near the protective-compound container during heat treatment, has been severe enough to be termed "corrosion.") Although this minor nuisance might be considered a small price to pay for solution of a problem of high-temperature oxidation, the residual compound in the furnace dissipates slowly. Therefore, subsequent loads of alloys and product forms whose end uses require bright surfaces, and that are not susceptible to high-temperature oxidation, may be detrimentally affected.

Successful use of fluoborate protective compounds appears to depend on specifying the right amount for each furnace; this must be established on a trial-and-error basis. One aircraft manufacturer adds 4 g/m^3 (0.004 oz/ft^3) of furnace chamber to each load. Another adds 0.45 kg (1 lb) per shift to a metal container hung on the furnace chamber wall, thus avoiding loss of the compound during quenching.

A second method of combating high-temperature oxidation is to anodize the work before it is heat treated. The resultant aluminum oxide film prevents attack by contaminants in the furnace atmosphere. The only deterrents to the use of anodizing are its cost (in money and time) and the slight surface frostiness which results from the subsequent stripping operation.

The usual objection to the blistered surface produced by high-temperature oxidation is its unsightly appearance. This often can be improved (for salvage purposes) by applying local pressure to flatten each blister and then finishing by a mechanical process such as polishing, buffing, sanding, or abrasive blasting. In general, the effect of HTO on static properties and fatigue strength is slight. However, if a void resulting from HTO is located close to another stress concentration, such as a hole, much greater degradation of fatigue strength is likely. In critical aluminum alloy forgings, any blistering must be evaluated carefully for its effect on the integrity of the part. Any "cosmetic" salvage should be performed only after it has been established that the blisters are superficial and will not remain in the finished product.

Precipitation Heat Treating without Prior Solution Heat Treatment. Certain alloys that are relatively insensitive to cooling rate during quenching can be either air cooled or water quenched directly from a final hot-working operation. In either condition, these alloys respond strongly to precipitation heat treatment. This practice is widely used in producing thin extruded shapes of alloys 6061, 6063, 6463, and 7005. Upon precipitation heat treating after quenching at the extrusion press, these alloys develop strengths nearly equal to those obtained by adding a separate solution heat treating operation. Changes in properties occurring during the precipitation treatment follow the principles outlined in the discussion of solution heat-treated alloys.

Quenching

Quenching is in many ways the most critical step in the sequence of heat-treating operations. The objective of quenching is to preserve the solid solution formed at the solution heat-treating temperature, by rapidly cooling to some lower temperature, usually near room temperature. From the preceding general discussion, this statement applies not only to retaining solute atoms in solution, but also to maintaining a certain minimum number of vacant lattice sites to assist in promoting the low-temperature diffusion required for zone formation. The solute atoms that precipitate either on grain boundaries, dispersoids, or other particles, as well as the vacancies that migrate (with extreme rapidity) to disordered regions, are irretrievably lost for practical purposes and fail to contribute to the subsequent strengthening.

In most instances, to avoid those types of precipitation that are detrimental to mechanical properties or to corrosion resistance, the solid solution formed during solution heat treatment must be quenched rapidly enough (and without interruption) to produce a supersaturated solution at room temperature--the optimum condition for precipitation hardening. The resistance to stress-corrosion cracking of certain copper-free aluminum-zinc-magnesium alloys, however, is improved by slow quenching. Most frequently, parts are quenched by immersion in cold water or, in continuous heat treating of sheet, plate, or extrusions in primary fabricating mills, by progressive flooding or high-velocity spraying with cold water. However, parts of complex shape, often with both thin and thick sections (such as die forgings, most castings, impact extrusions, and components formed from sheet) are commonly quenched in a medium that provides somewhat slower cooling. This medium may be water at 65 to 80 °C (150 to 180 °F), boiling water, an aqueous solution of polyalkylene glycol, or some other fluid medium such as forced air or mist.

If appreciable precipitation during cooling is to be avoided, two requirements must be satisfied. First, the time required for transfer of the load from the furnace to the quenching medium must be short enough to preclude slow precooling into the temperature range where very rapid precipitation takes place. For alloy 7075, this range was determined to be 400 to 290 °C (750 to 550 °F), and some sources quote this range (or a slightly different range) as the most critical range for quenching of any aluminum alloy. Later work has shown that the most critical range is alloy-dependent, and as will be discussed in detail under "Quench-Factor Analysis ," significant errors can result from the assumption that precipitation is negligible outside of a so-called "critical range."

The second requirement for avoidance of appreciable precipitation during quenching is that the volume, heat-absorption capacity, and rate of flow of the quenching medium be such that little or no precipitation occurs during cooling. Any interruption of the quench that might allow reheating into a temperature range where rapid precipitation can occur must be prohibited.

For maximum dimensional stability, some forgings and castings are fan cooled or still-air cooled. In such instances, precipitation-hardening response is limited, but satisfactory values of strength and hardness are obtained. Extrusions produced without separate solution heat treatment can be air or mist quenched, but thicker sections may require water quenching by immersion or spraying. Alloys that are relatively dilute, such as 6063 and 7005, are particularly well suited to air quenching, and their mechanical properties are not greatly affected by its low cooling rate. Lower quenching rates are also employed for forgings, castings, and complex shapes to minimize warpage or other distortion and the magnitude of residual stresses developed as a consequence of temperature nonuniformity from surface to interior.

Effect of Quench Rate on Properties. As a broad generalization, the highest strengths attainable and the best combinations of strength and toughness are those associated with the most rapid quenching rates. Resistance to corrosion and stress-corrosion cracking are other characteristics that are generally improved by maximum rapidity of quenching. Some of the alloys used in artificially aged tempers, and in particular the copper-free 7*xxx* alloys, are exceptions to this rule. The effect of quench rate on mechanical properties may also depend on the desired temper. In the underaged condition, for example, a slow quench rate is more detrimental on ductility and fracture toughness. Strength would be more affected after near-to-peak aging.

Because of these effects, much work has been done over the years to understand and predict how quenching conditions and product form influence properties. The relative effects of quench methods can be compared in terms of average quench rates. In Fig. 3, for example, the effects of quenching on the yield strength of four alloys are compared in terms of average quenching rates through the range from 400 to 290 °C (750 to 550 °F). For alloys relatively high in sensitivity to quenching rate, such as 7075, rates of about 300 °C/s (540 °F/s) or higher are required in order to obtain near-maximum strength after precipitation heat treatment. The other alloys in Fig. 3 maintain their strengths at cooling rates as low as about 100 °C/s (180 °F/s). Similar comparisons in terms of average quench rates are shown in Tables 4 and 5.

Table 4 Effect of average quench rate on tensile properties of aluminum-lithium alloy 2090

Average quench rate at center of plate	Condition	Yield strength[a]		Tensile strength[a]		Elongation[a], %
		MPa	ksi	MPa	ksi	
0.5 °C/s (13 mm plate, air cooled)	As-quenched 6% stretch + aged 8 h at 190 °C	162		334		**2**
		448		513		**5**
36 °C/s (38 mm plate, quenched in room-temperature water)	As-quenched 6% strecth + aged 8 h at 190 °C	128		312		**12**
		338		476		**6**
46 °C/s (13 mm plate, quenched in boiling water)	As-quenched 6% stretch + aged 8 h at 190 °C	138		331		**16**
		530		570		**9**
48 °C/s (13 mm plate, quenched in room-temperature water)	As-quenched 6% stretch + aged 8 h at 190 °C	139		331		**17**
		526		570		**7**
85 °C/s (13 mm plate, quenched in ice brine)	As-quenched 6% stretch + aged 8 h at 190 °C	135		349		**19**
		535		**575**		**7**

(a) Data are averages from 4 specimens.

Table 5 The effect of quench rate on the mechanical properties of age-hardened aluminum-lithium alloy 8090

Alloy composition	Cooling from solution treatment[a]	Stretch, %	Aging treatment	Yield strength[b]		Ultimate tensile strength[b]		Elongation in 50 mm (2 in.)[b], %
				MPa	ksi	MPa	ksi	
Al-2.28Li-0.86Cu-0.90Mg-0.13Zr-0.13Fe-0.06Si	Air cool (~0.25 °C/s)	2	190 °C for 16 h	380	55	446	64.5	**7.7**
		4	170 °C for 24 h	401	58	465	67.5	**6.0**

	Polymer quench (~18 °C/s)	2	190 °C for 16 h	415	60	481	70	**8.0**
		4	170 °C for 24 h	415	60	481	70	**7.2**
	Water quench (~120 °C)	2	190 °C for 16 h	428	62	492	71.4	**8.1**
		4	170 °C for 24 h	417	60	483	70	**7.5**
Al-2.58Li-1.36Cu-0.89Mg-0.13Zr-0.17Fe-0.04Si	Air cool (~0.25 °C/s)	2	190 °C for 16 h	417	60	485	70.3	**6.5**
		4	170 °C for 24 h	442	64	503	73	**4.5**
	Polymer quench (~18 °C/s)	2	190 °C for 16 h	448	65	524	76	**6.8**
		4	170 °C for 24 h	448	65	519	75	**5.0**
	Water quench (~120 °C/s)	2	190 °C for 16 h	464	67	535	77.5	**8.2**
		4	**170 °C for 24 h**	**448**	**65**	**517**	**75**	**6.3**

(a) Solution treatment of 550 °C (1020 °F) for 1 h.

(b) Data are averages from two specimens.

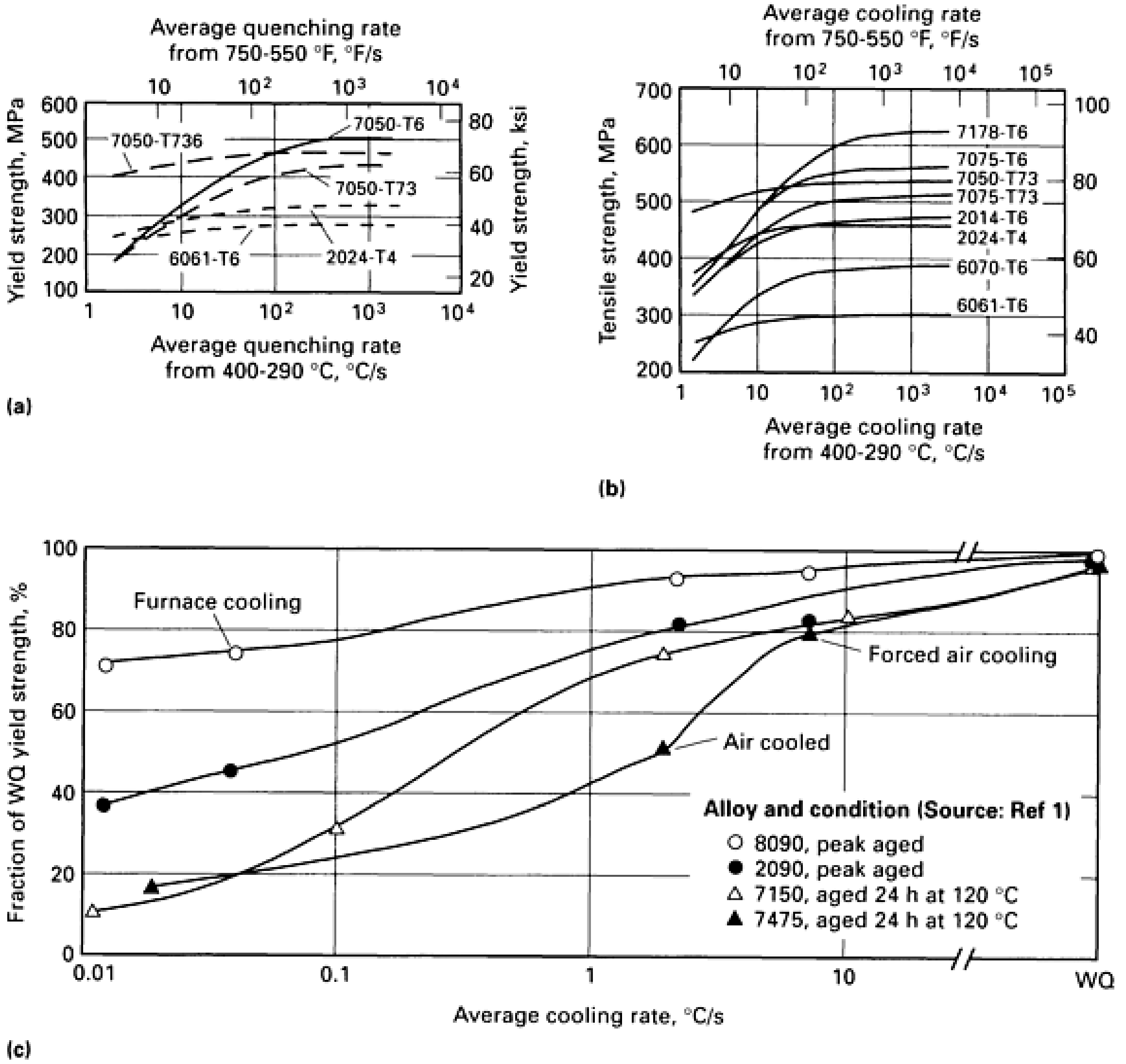


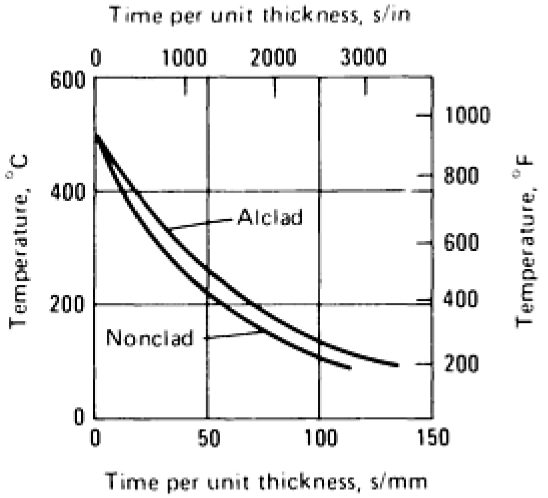
Fig. 3 Quench sensitivity of various aluminum alloys as a function of average quench rates. (a) Yield strength after aging of four wrought alloys. (b) Tensile strength after aging of eight wrought alloys. (c) Relative quench sensitivity of two aluminum-lithium alloys (2090 and 8090, both solution treated for 1 h at 520 °C, or 970 °F) and two Zn-Mg-Cu aluminum alloys (7150 and 7475, both solution treated for 40 min at 480 °C, or 895 °F)

Average quench rates are useful in comparing experimental results from various quench methods. In Table 4, for example, a severe reduction in strength occurred at the average quench rate of 36 °C/s (65 °F/s). However, average quench rates only compare results in a "critical" temperature range, where precipitation is most likely to occur. This method is not entirely accurate, because significant precipitation can also occur outside the specified critical temperature range of average quench rates. Moreover, for high-strength alloys, toughness and corrosion resistance may be impaired without significant loss of tensile strength.

Therefore, a more sophisticated comparison, known as quench-factor analysis, is needed for quantitative property prediction or property optimization. Quench-factor analysis, as discussed in a later section, is useful when cooling rates are nonuniform.

Delay in Quenching. Whether the transfer of parts from the furnace to the quench is performed manually or mechanically, it must be completed in less than the specified maximum time. The maximum allowable transfer time or "quench delay" varies with the temperature and velocity of the ambient air and the mass and emissivity of the parts. From cooling curves such as those illustrated in Fig. 4, maximum quench delays (see table accompanying Fig. 4) can be determined that will ensure complete immersion before the parts cool below 400 °C (750 °F). MIL-H-6088 specifies maximum quench delays for high-strength alloys of 5, 7, 10, and 15 s for thickness ranges of up to 0.016 in. (0.41 ram),

0.017 to 0.031 in. (0.43 to 0.79 mm), 0.032 to 0.090 in. (0.81 to 2.29 mm), and over 0.090 in., respectively. Quench delay is conservatively defined as commencing "when the furnace door begins to open or the first corner of a load emerges from a salt bath" and ending "when the last corner of the load is immersed in the water quench tank." Recommended maximum quench-delay times are listed in Table 2. However, exceeding the maximum delay time is permitted if temperature measurements of the load prove that all parts are above 415 °C (775 °F) when quenched. The C-curves used in quench-factor analysis can also assist in determining a maximum allowable delay.



Thickness		Maximum quench delay, s	
mm	**in.**	**Alclad**	Nonclad
0.41	0.016	6.4	**4.4**
0.51	0.020	8.0	**5.5**
0.64	0.025	10.0	**6.8**
0.81	0.032	12.8	**8.8**
1.02	**0.040**	**20.0**	**11.0**

Fig. 4 Cooling curves for alclad and nonclad aluminum products cooled from 495 °C (920 °F) in forced air. Air temperature, 25 °C (80 °F); air velocity, 2.3 m/s (450 ft/min). Tabulated values of quench delay (maximum delay before the material being quenched has cooled below 400 °C, or 750 °F) were determined from cooling curves shown.

It is relatively easy to control quench delay in day-to-day operations by using a stopwatch or, if necessary, by attaching thermocouples to parts. However, although the cooling rate between 400 and 260 °C (750 and 500 °F) is most critical and must be extremely high for many high-strength alloys, it cannot be directly measured in production operations. It is usual

to rely on standardized practices, augmented by results of tension tests and tests of susceptibility to intergranular corrosion.

Water-immersion quenching normally is controlled in practice by stipulating maximum quench-delay time and maximum water temperature. The first requirement controls the cooling rate during transfer and, for high-strength alloys, often is based on the criterion of complete immersion before the metal cools below 415 °C (775 °F). This specification of 415 °C (775 °F) is based on a critical temperature for alloy 7075, which has one of the more severe C-curves (Fig. 5). Therefore, the criterion for complete immersion of other alloys might be based on a temperature lower than the 415 °C (775 °F) specification, depending on the characteristics of the particular C-curve.

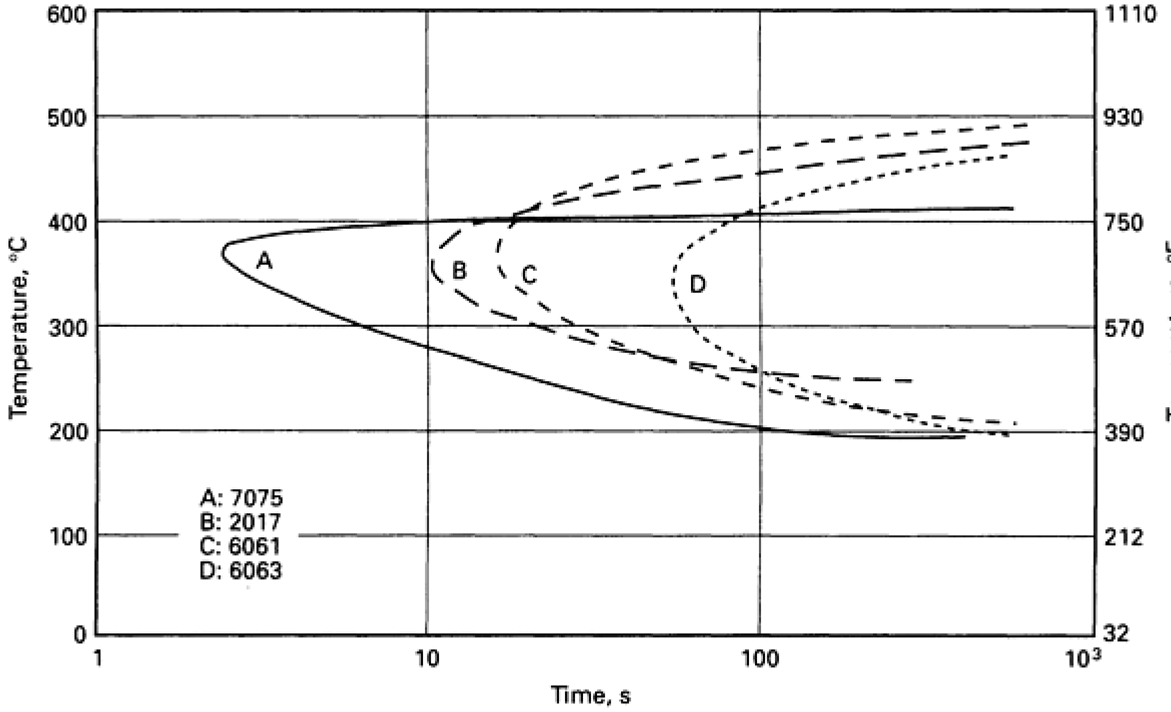


Fig. 5 Time-temperature-property curves at 95% of maximum tensile stress for various alloys. See the section "Quench-Factor Analysis" for discussion. Source: Ref 2

The second requirement controls the cooling rate during immersion. MIL-H-6088 specifies that for water-immersion quenching, except quenching of forgings and castings, the temperature of the water shall not exceed 38 °C (100 °F) upon completion of quenching. This requirement controls both the temperature of the quench water prior to immersion and the ratio of the combined mass of load and rack to the volume of water. However, to ensure adequate quenching effectiveness, it is necessary also that the cooling fluid flow past all surfaces of each part during the first few seconds after immersion. Before parts enter the furnace, their placement in racks or baskets should be compatible with this requirement. During the first few seconds of quenching, agitation of the parts or the water should be sufficient to prevent local increases in temperature due to the formation of steam pockets.

In one application, it was found that 2024-T4 plates 13 by 760 by 760 mm ($\frac{1}{2}$ by 30 by 30 in.), quenched singly into a large volume of still water, were quite susceptible to intergranular corrosion. This susceptibility disappeared completely when the quenching practice was modified by adding sufficient agitation to break up the insulating blanket of steam that formed on the surface of the hot metal. Quenching practices for small parts such as fasteners and hydraulic fittings have been modified for the same reason. Dumping in bulk from baskets has been replaced by methods, such as the use of shaker hearth furnaces or special racking, which permit parts to be quenched singly.

Spray Quenching. For spray quenching, the quench rate is controlled by the velocity of the water and by volume of water per unit area per unit time of impingement of the water on the workpiece. Rate of travel of the workpiece through the sprays is an important variable.

Local increases in temperature that occur within the first few seconds of quenching, caused by a phenomenon such as plugged spray nozzles, are particularly deleterious. The remaining "internal heat" may be sufficient to reheat the surface region. When this happens, a large loss in strength occurs at the previously quenched surface. The loss of strength in the affected area of a heavy part is much more severe than that caused by an inadequate quenching rate alone. This is illustrated for 75 mm (3 in.) thick 7075-T62 plate in Fig. 6, which compares, at various depths, the properties of a plate for which quenching was interrupted on one side after 3 s with those of a plate that was quenched from one side only.

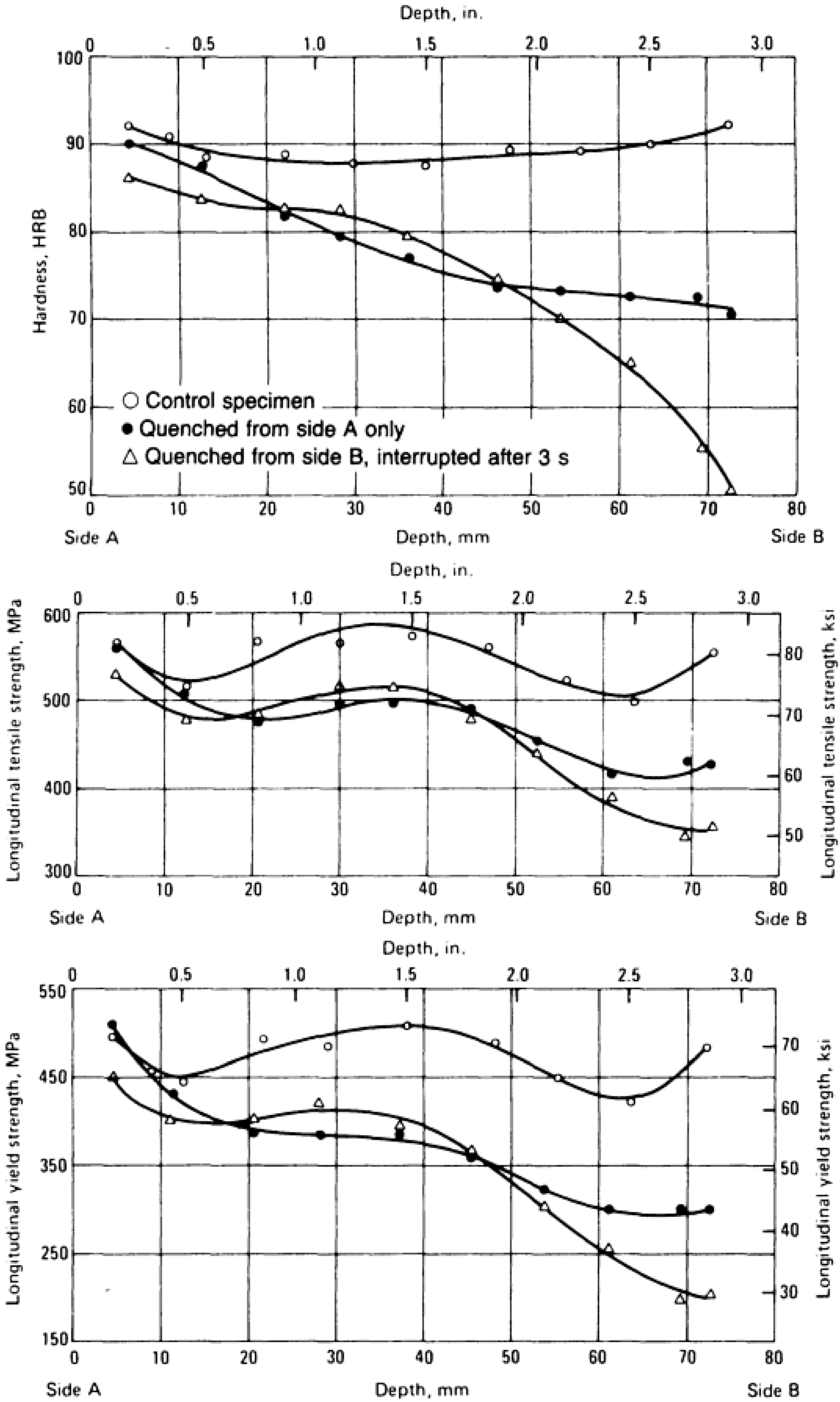


Fig. 6 Through-thickness property variations due to quench rate and temperature-rise effects in 7075-T62

plate 75 mm (3 in.) thick

Quench Severity and Quenchant Selection. Quench severity is commonly expressed in terms of an *H*-value (or Grossmann number), where the *H*-value is related to the thermal conductivity (k) of the part(s) and the coefficient of heat transfer (C) between the quenchant and the part. These quantities are related by the equation $H = C/2k$, where the coefficient of heat transfer (C) is affected by the quenchant velocity at the surface of the part and several inherent characteristics of the quenchant (such as quenchant boiling point, viscosity, density, thermal conductivity, and specific heat).

Water, which is the most widely used and effective quenching medium, can obtain cooling rates up to about 200 °C/s (400 °F/s) at the midplane of 25 mm (1 in.) thick aluminum alloy plate (see the dashed line in Fig. 7). No rates higher than those defined by this line have been observed, although rates approaching them were measured with impinging spray quenches. Lower cooling rates are achieved by immersion in heated water (Fig. 7) or by reducing the velocity of the quenchant around the part (Table 6). Cooling rates can also be reduced by lowering surface tension or by increasing the stability of the vapor film around the part.

Table 6 Grossmann numbers and heat transfer coefficients (*C*) of quenchant-to-part films

Quenchant					**Grossmann Number ($H = C/2k$)**	Effective film heat transfer coefficient (C)	
Type	**Temperature**		**Velocity**				
	°C	**°F**	**m/s**	**ft/min**		**$W/cm^2 \cdot K$**	$Btu/ft^2 \cdot h \cdot °F$
Water	27	80	0.00	0	1.07	3.55	**2460**
			0.25	50	1.35	4.78	**3105**
			0.50	100	1.55	5.14	**3565**
Water	38	100	0.00	0	0.99	3.28	**2275**
			0.25	50	1.21	4.01	**2785**
			0.50	100	1.48	4.91	**3400**
Water	49	120	0.00	0	1.10	3.65	**2530**
			0.25	50	1.29	4.29	**2970**
			0.50	100	1.60	5.31	**3680**
Water	60	140	0.00	0	0.86	2.85	**1980**
			0.25	50	1.09	3.62	**2510**

			0.50	100	1.33	4.41	**3060**
Water	71	160	0.00	0	0.21	0.70	**485**
			0.25	50	0.57	1.89	**1310**
			0.50	100	0.79	2.62	**1815**
Water	82	180	0.00	0	0.11	0.36	**255**
			0.25	50	0.21	0.69	**485**
			0.50	100	0.27	0.89	**620**
Water	93	200	0.00	0	0.06	0.20	**138**
			0.25	50	0.08	0.27	**184**
			0.50	100	0.09	0.30	**207**
Water	100	212	0.00	0	0.04	0.13	**92**
			0.25	50	0.04	0.13	**92**
			0.50	100	0.04	0.13	**92**
Polyalkylene glycol (UCON A)[a]	30	85	0.00	0	0.19	0.63	**429**
			0.25	50	0.21	0.70	**475**
			0.50	100	0.23	0.77	**529**
Polyvinyl pyrrolidone (PVP90)[a]	30	85	0.00	0	0.44	1.49	**1012**
			0.25	50	0.40	1.34	**912**
			0.50	**100**	**0.42**	**1.41**	**966**

Source: Ref 4

(a) Polymer quenchants with concentrations of 25%. *K* is equal to the thermal conductivity of the aluminum alloy (7075).

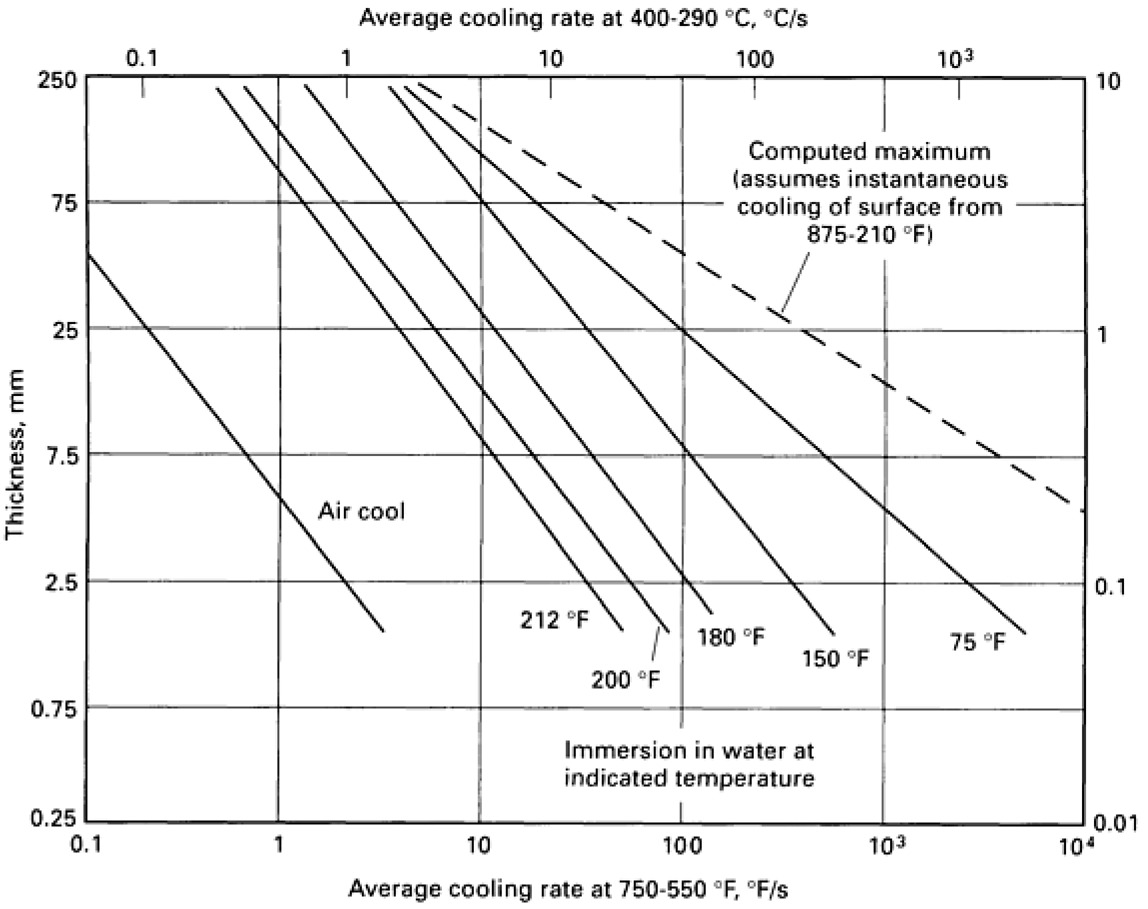


Fig. 7 Effects of thickness and quenching medium on average cooling rates at midplane of aluminum alloy sheet and plate quenched from solution temperatures. The dashed line delineates the maximum cooling rates theoretically obtainable at the midplane of plate, assuming an infinite heat transfer coefficient (*C*) and a diffusivity factor of 1400 cm^2/s. Source: Ref 3

Polymer quenchants, which retard cooling rates by the formation of films around the part, are compared with water in Table 6. The effective film coefficient is essentially the heat transfer coefficient (*C*), which is related to the Grossmann number (*H*). The application of polymer quenchants is covered in AMS specifications 3025 and 2770, although many aluminum and aerospace companies have developed internal specifications that differ from AMS-2770. Typical parameters for quenching wrought products (other than forgings) in glycol-water solutions are presented in Table 7.

Table 7 Limits for quenching in glycol-water solutions

Data are for wrought aluminum alloy products other than forgings.

Glycol concentration, vol%	**Alloys**	Maximum thickness	
		mm	in.
12-16	2014, 2117, 2024, 2219	2.03	**0.080**
	7075, 7175	25.4	**1.000**
17-22	2014, 2017, 2117, 2024, 2219	1.80	**0.071**

	7075, 7079, 7175, 7178, 6061	12.7	**0.500**
23-28	2014, 2017, 2117, 2024, 2219	1.60	**0.063**
	7075, 7079, 7175, 7178, 6061	9.53	**0.375**
29-34	2014, 2017, 2117, 2024, 2219	1.02	**0.040**
	7075, 7079, 7175, 7178, 6061	6.35	**0.250**
35-40	**7075, 7079, 7175, 7178, 6061**	**2.03**	**0.080**

Other Factors Affecting Quench Rate. Quenching rates are very sensitive to the surface condition of the parts. Lowest rates are observed with products having freshly machined or bright-etched, clean surfaces, or products that have been coated with materials that decrease heat transfer. The presence of oxide films or stains increases cooling rates. Further marked changes can be effected through the application of nonreflective coatings, which also accelerate heating (Fig. 8). Surface roughness exerts a similar effect; this appears related to vapor film stability. The manner in which complex products, such as engineered castings and die forgings, enter the quenching medium can significantly alter the relative cooling rates at various points, thereby affecting mechanical properties and residual stresses established during quenching. Similarly, quenching complex extruded shapes whose wall thicknesses differ widely poses special problems if distortion and stresses are to be minimized. In batch heat-treating operations, placement and spacing of parts on the racks can be a major factor in determining the quenching rates. In immersion quenching, adequate volumes of the quenching medium must be provided to prevent an excessive temperature rise in the medium. When jet agitation is used to induce water flow between parts, jets should not impinge directly and cause rapid localized cooling.

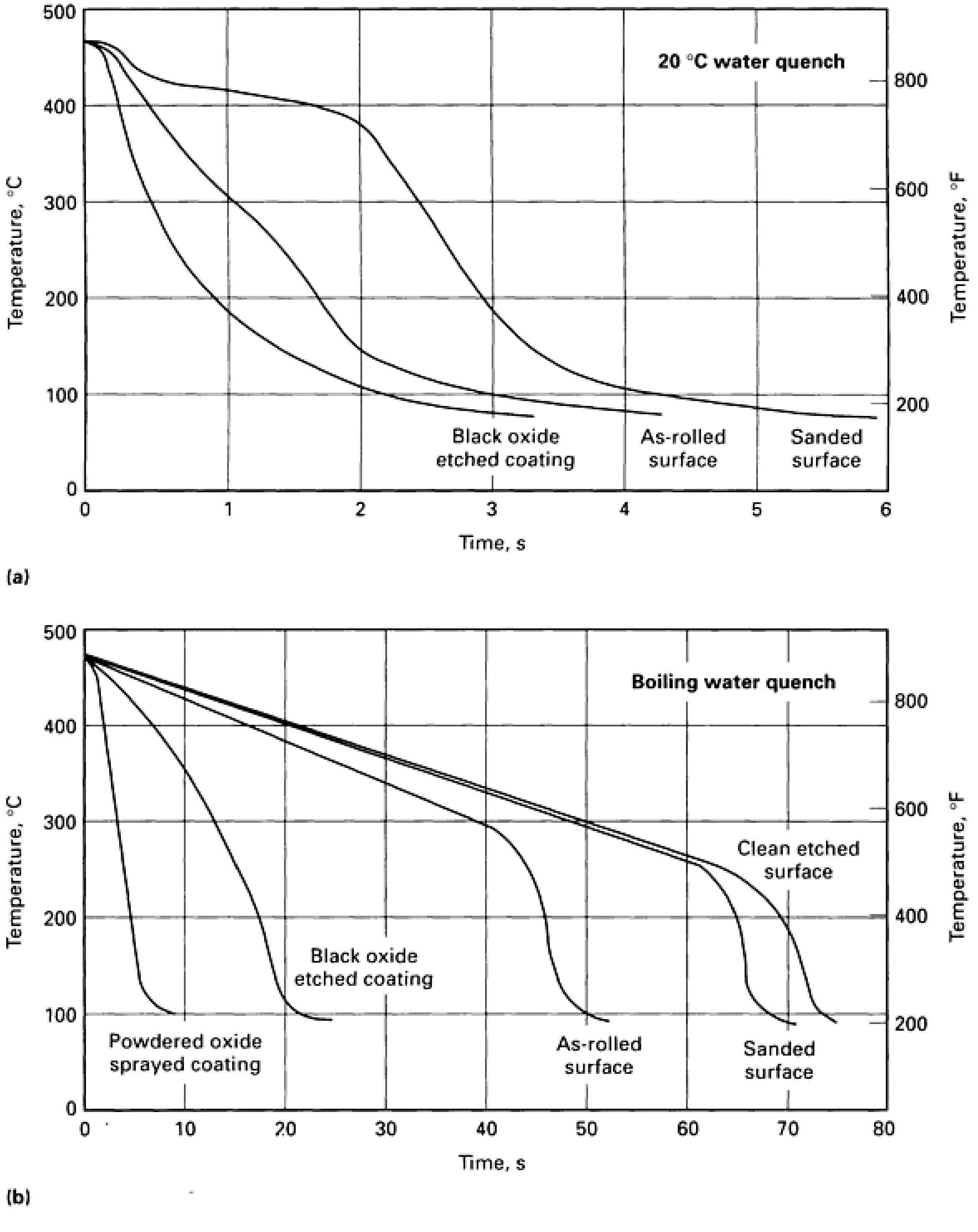


Fig. 8 Effect of surface conditions on the midplane cooling of a 13 mm (0.5 in.) thick plate of 7075 from quenching in (a) 20 °C (70 °F) water and (b) boiling water. Source: Ref 5

Quenching to Minimize Residual Stress and Warpage. Although cold-water immersion or flushing is most common, because it produces the most effective quench (and has been required by MIL-H-6088 for 2014, 2017, 2024, 2117, 7075, and 7178 alloys except forgings), it presents problems involving residual stress and warpage.

Residual stresses in heavy sections of aluminum alloys originate from differential thermal expansion during quenching -- that is, the still-warm central material contracts, pulling in the already cooled outer shell. The magnitude of stresses increases with section size, as shown in Fig. 9.

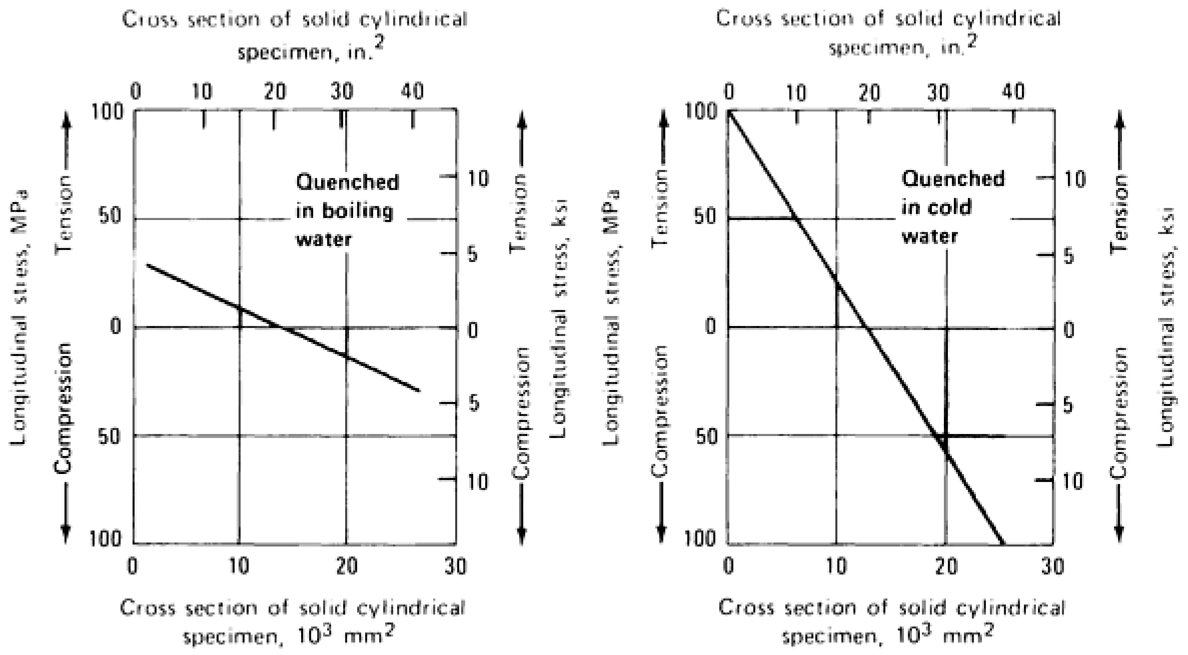


Fig. 9 Effect of quenching from 540 °C (1000 °F) on residual stresses in solid cylinders of alloy 6151

The distribution pattern of residual stresses in as-quenched parts (compression in the outer layers and tension in the central portion) is usually desirable in service. Compressive stresses inhibit failure by fatigue and stress corrosion--two mechanisms that initiate in the outer fibers. Unfortunately, metal-removal operations required after heat treating often expose material that is stressed in tension. Also, metal-removal operations that are asymmetrical (with respect to residual stresses) cause distortion by redistributing residual stresses. When close-tolerance parts are being fabricated, the resulting warpage can be costly and difficult to correct.

Although service performance is sometimes a factor, the major incentive for reducing residual stress differentials has been a reduction in warpage during machining or an improvement in shape before machining.

One approach to reducing the cooling-rate differential between surface and center is the use of a milder quenching medium--water that is hotter than that normally used or water-glycol solutions. Boiling water, which is the slowest quenching medium used for thick sections, is sometimes employed for quenching wrought products even though it lowers mechanical properties and corrosion resistance. Quenching of castings in boiling water, however, is standard practice, and is reflected in design allowables.

Another approach to the minimization of residual stresses that is generally successful consists of rough machining to within 3.2 mm (0.125 in.) or less of finish dimensions, heat treating, and then finish machining. This procedure is intended to reduce the cooling-rate differential between surface and center by reducing thickness; other benefits that accrue if this technique is used to reduce or reverse surface tension stresses in finished parts are improvements in strength, fatigue life, corrosion resistance, and reduced probability of stress-corrosion cracking.

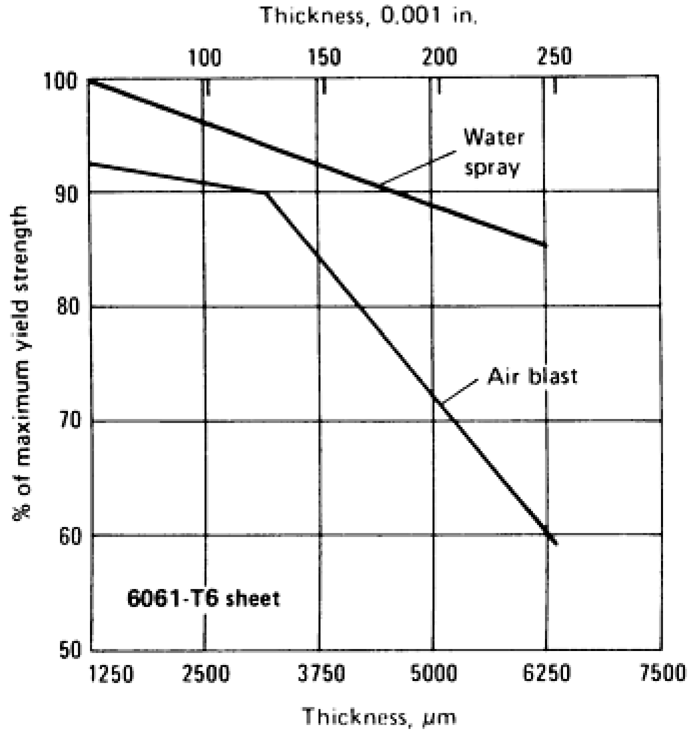
Several factors (especially quenching warpage) sometimes preclude general use of this procedure. The thinner and less symmetrical a section, the more it will warp during quenching, and the residual stresses resulting from straightening of warped parts (plus straightening costs) often are less desirable than the quenching stresses. Holding fixtures and die quenching may be helpful, but precautions must be taken to ensure that they do not retard quenching rates excessively. Other factors that must be considered are the availability of heat-treating facilities and whether or not the advantages of such a manufacturing sequence offset the delay and cost entailed in a double-machining setup.

Warpage of thin sections during quenching is also a problem. Even in the same load, symmetry of cooling usually varies significantly among identical parts and the resultant inconsistent warpage usually requires costly hand straightening. Consequently, a significant amount of effort has been devoted to reducing or eliminating warpage by changing racking positions to achieve symmetry of cooling.

For sheet-metal parts, one manufacturer uses a double screen floor in the quenching rack to reduce the force of initial contact between water and parts. Others allow parts to "free fall" from rack to quench tank. Spacing and positioning on the rack are carefully controlled so that parts will enter the water with minimum impact. With this technique, water turbulences must be avoided, because it will often cause parts to float for a few seconds, greatly reducing their cooling rate.

Because of the difficulties encountered with quenching in cold water, milder quenchants have been employed. Indiscriminate use of milder quenchants can have catastrophic effects; however, when their use is based on sound engineering judgment and a metallurgical knowledge of the effects on the specific alloy, significant cost savings or performance improvements can be realized.

The most frequent advantage is the reduction in costly straightening operations and in resultant uncontrolled residual stresses. For example, one aircraft manufacturer utilizes water-spray and air-blast quenching for weldments and complex formed parts made from 6061, an alloy whose corrosion resistance is insensitive to quenching rate. Straightening requirements are negligible and, through careful control of racking and coolant flow, the decrease in mechanical properties is minimized, as shown by the data in Fig. 10.



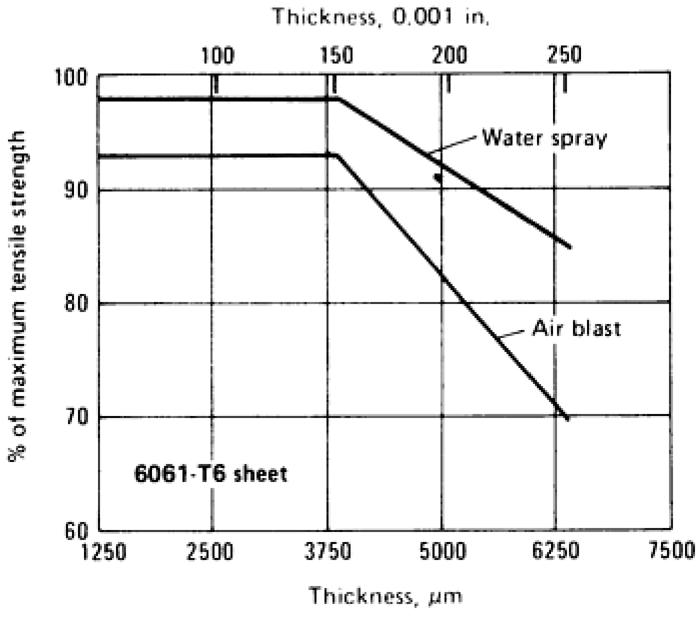


Fig. 10 Effect of quenching medium on strength of 6061-T6 sheet. Water-immersion quench equals 100%. Control of coolant flow will minimize decrease in mechanical properties.

Another development for reducing straightening costs is quenching in water-polymer solutions. Quenching of formed sheet-metal parts in aqueous solutions of polyalkylene glycol or in similar inversely soluble media has significantly reduced the cost of straightening these parts after quenching. The SAE heat-treatment specification AMS-2770 recommends, for several alloys, maximum thicknesses that can be quenched in solutions of specific concentrations while maintaining acceptable property levels. Typical parameters for quenching wrought products (other than forgings) in glycol-water solutions are presented in Table 7. Additional information on polymer quenchants for aluminum alloys can be found in Ref 5.

Forming and Straightening after Quenching. Immediately after being quenched, most aluminum alloys are nearly as ductile as they are in the annealed condition. Consequently, it is often advantageous to form or straighten parts in this temper. Moreover, at the mill level, controlled mechanical deformation is the most common method of reducing

residual quenching stresses. Because precipitation hardening will occur at room temperature, forming or straightening usually follows as soon after quenching as possible. In addition, maximum effectiveness in stress relief is obtained by working the metal immediately after quenching.

Forming and straightening operations vary in degree from minor corrections of warpage to complete forming of complex parts from solution-treated flat blanks. Particular value is gained when enough forming can be done at this stage of processing to eliminate the distortion caused by quenching. However, production operations must be adjusted so that most of the plastic deformation is accomplished before an appreciable amount of precipitation hardening takes place.

Although the most severe forming operations may have to be arranged to avoid natural aging, it often is desirable to allow some natural aging to occur and thus avoid formation of Lüders lines. This condition of nonuniform deformation is most likely to occur shortly after quenching and diminishes significantly after a few hours of natural aging. Complete freedom from Lüders lines, however, may require one or two days of natural aging prior to forming. Thus, the forming operation may have to be timed so as to obtain the most appropriate trade-off of these characteristics for the specific parts involved. Lüders lines also can be reduced by employing low strain rates or by forming at temperatures of 150 to 175 °C (300 to 350 °F).

Residual stresses in sheet-metal parts formed in the quenched condition are higher than those in parts formed in the annealed condition. Consequently, forming in the quenched condition should be selected judiciously for parts that are critical in fatigue (Fig. 11) or stress corrosion.

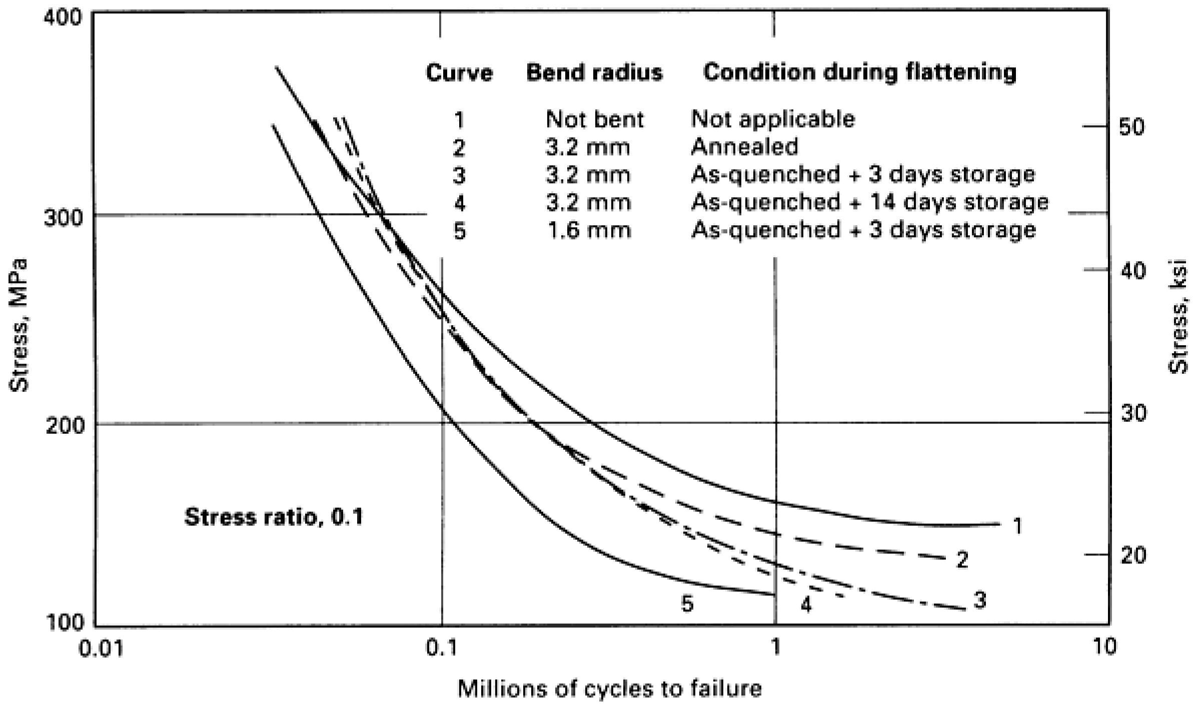


Fig. 11 Fatigue characteristics of 1 mm (0.04 in.) alclad 2024-T4 sheet after 90 ° bending in the annealed condition and subsequent flattening as indicated. Flattening (unbending) was done either in the annealed condition (curve 2), or in the solution-treated and quenched condition (curves 3, 4, 5) with indicated storage times at -18 to -12 °C (0 to 10 °F).

Re-solution heat treatment of parts formed after quenching often causes excessive grain growth in critically strained regions and thus is not recommended.

Quench-Factor Analysis

During the quenching of alloys from a solid-solution temperature condition, the rate of precipitation during quenching is maximized in a so-called "critical" temperature range, because the diffusion of dissolved species and the subsequent

nucleation of precipitates exhibit opposite behavior as a function of temperature. At high temperatures, nucleation rates are small because of the low degree of super-saturation, and so precipitation rates are low despite the high diffusion rates. At low temperatures, diffusion rate is low, and thus precipitation rate is low despite the high degree of supersaturation. At intermediate temperatures, precipitation rate is highest. Consequently, times to produce equal amounts of precipitation follow a C-shape pattern.

Using isothermal quenching techniques, Fink and Willey pioneered the attempts to describe the effects of quench rates with the use of C-curves (Ref 6). The C-curves plot the time required at different temperatures to precipitate a sufficient amount of solute to: reduce strength by a certain amount (Fig. 5); cause a change in the corrosion behavior from pitting to intergranular (Fig. 12); produce a given electrical conductivity (Fig. 13); or relate other properties, such as fracture toughness, to isothermal quench conditions. The nose of the C-curves identifies the critical temperature range (the region of highest precipitation rates). Investigators use critical temperature ranges in conjunction with properties of samples quenched continuously from the solution temperature to compare relative sensitivities of alloys to quenching condition.

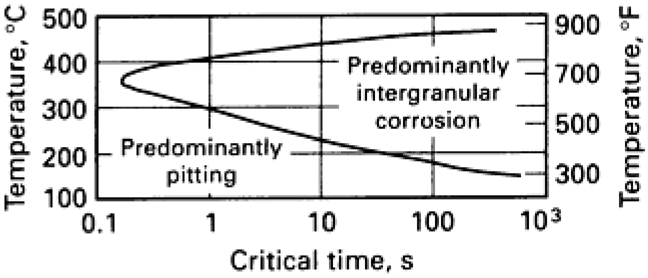


Fig. 12 C-curve indicating type of corrosion attack on 2024-T4 sheet

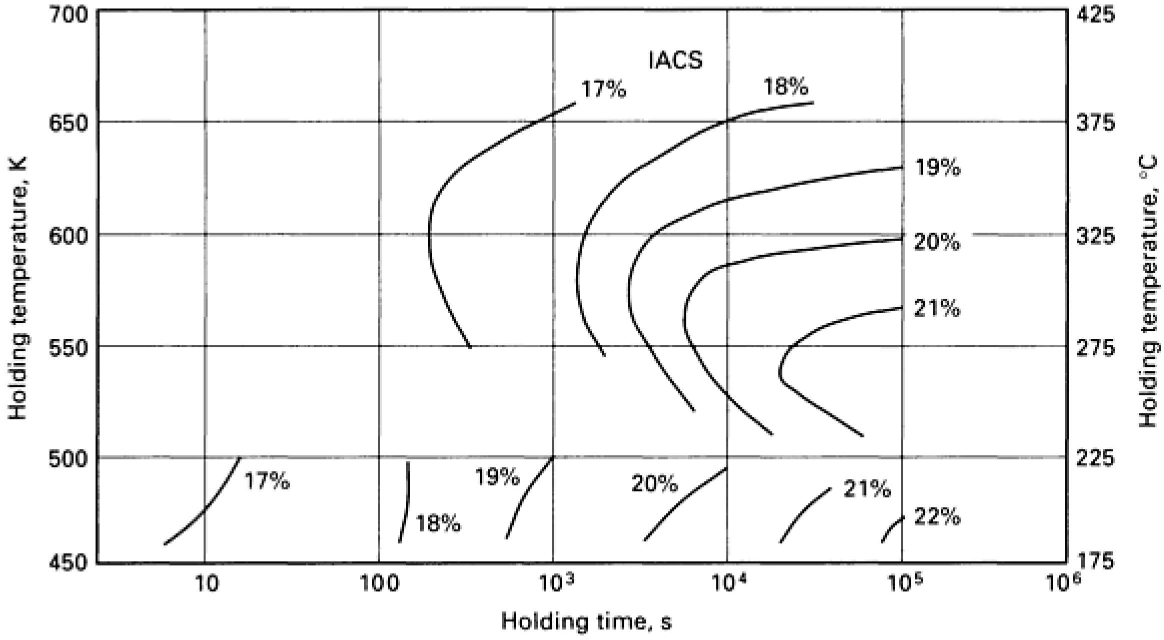


Fig. 13 Change in electrical conductivity of an Al-2.5% Li binary alloy after the following: solution treated at 540 °C (1000 °F) for $\frac{1}{2}$ h, immersed into an adjacent salt or oil bath for the appropriate isothermal holding temperature and time, then quenched into water. Source: Ref 1

Although average quench rates through a critical temperature range can provide reasonable property predictions if cooling rates are fairly uniform, average quench rates cannot provide quantitative predictions when cooling rates vary considerably during the quench. For such instances, a procedure known as "quench-factor analysis" uses information from

the entire C-curve to predict how any quench curve affects properties. Quench-factor analysis is useful in designing suitable limits for quench delays, or when it is not sufficient just to ensure that the cooling curve misses the nose of the C-curve.

The method of quench-factor analysis, as outlined by Evancho and Staley (Ref 7), is based on the determination of a quench factor (τ), which is the major variable in the following equation for precipitation kinetics during continuous cooling:

$$z = 1 - \exp(k\tau) \quad \textbf{(Eq 1)}$$

where z is the fraction transformed and k is a constant related to the transformation fraction of a given C-curve. The quench factor (τ) is defined as:

$$t = \int \frac{dt}{C_t} \quad \textbf{(Eq 2)}$$

where t is time and C_t is critical time as a function of temperature to transform a specified fraction (x). The locus of critical times for a given transformation fraction x (or a percentage of mechanical properties from precipitation) is the C-curve, and the value of k is related to x as follows: $k = \ln(1 - x)$, or $e^k = 1 - x$. Therefore, when $\tau = 1$, the fraction transformed, z , equals the fraction value designated by the C-curve. Equation 2 is based on the assumption that the reaction rate is a function only of the amount transformed and temperature.

The numerical evaluation of the quench factor involves the integration of Eq 2. This integral can be graphically integrated using the method illustrated in Fig. 14. Examples of the way to use the quench factor (τ) in the analysis of quench methods are described below. Neither the average quenching rate through a critical temperature range nor quench-factor analysis can predict strength when the temperature increases during quenching after it is cooled below some critical temperature. Under this condition, strength in the affected areas can be significantly lower than in other areas of the material. The most likely way for this phenomenon to occur is during spray quenching, when the surface cools rapidly by the impinging spray, but reheats by heat flow from the hotter interior when the spray is interrupted.

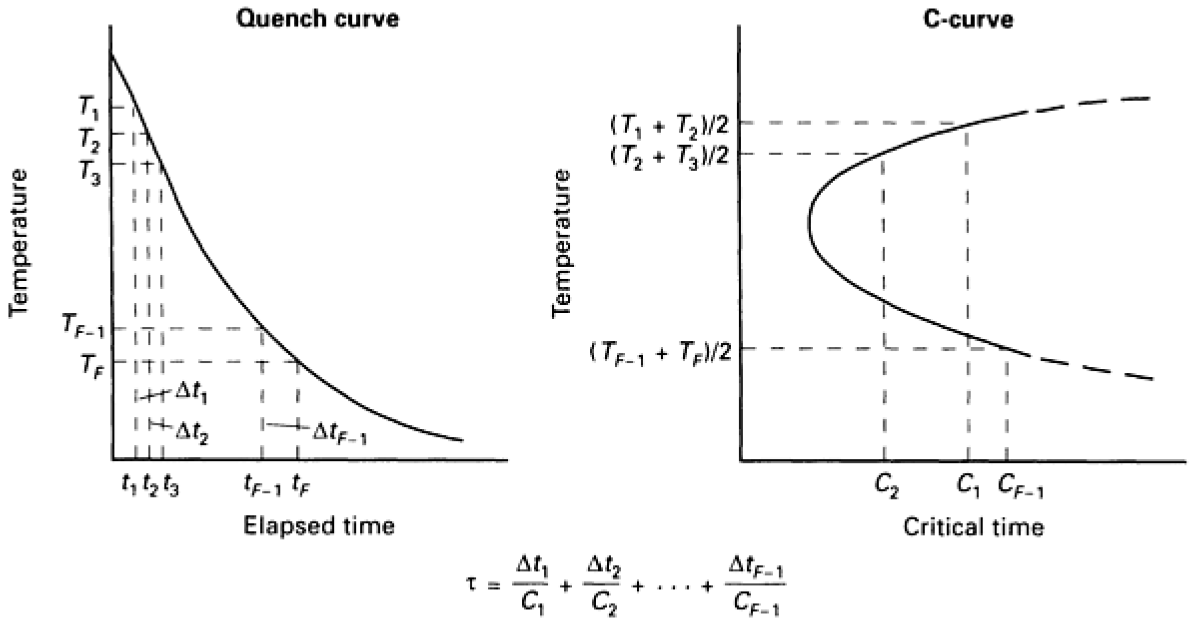


Fig. 14 Method of determining quench factor, τ, using a cooling curve and a C-curve

Predicting Strengths of Thick Products. Effects of the quenching rate on alloy strengths can be represented on a generalized graph of the type shown in Fig. 3, and the expected quenching rates of products having various dimensions can be determined from Fig. 7. Nevertheless, combining these two kinds of information to predict mechanical properties must be done with caution. Inconsistencies were encountered, for example, in correlating properties of thick sections quenched in high-cooling-rate media with properties of thinner sections quenched in media affording milder quenching action. One of the reasons for the inconsistencies is believed to be the different shapes of the cooling curves. This difficulty can be overcome by using quench-factor analysis. The other reason is that the degree of recrystallization and texture of the thick and thin sections may be different.

Predicting Corrosion Behavior. Alloy 2024-T4, for example, is susceptible to intergranular corrosion when a critical amount of solute is precipitated during quenching, but will corrode in the less severe pitting mode when lesser amounts are precipitated. For predicting the effects of proposed quenching conditions on the corrosion characteristics of 2024-T4, the postulated quench curve is drawn and the quench factor is calculated using the C-curve in Fig. 12. Corrosion characteristics are predicted from the plot in Fig. 15. When the quench factor (τ) is less than 1.0, continuously quenched 2024-T4 will corrode by pitting.

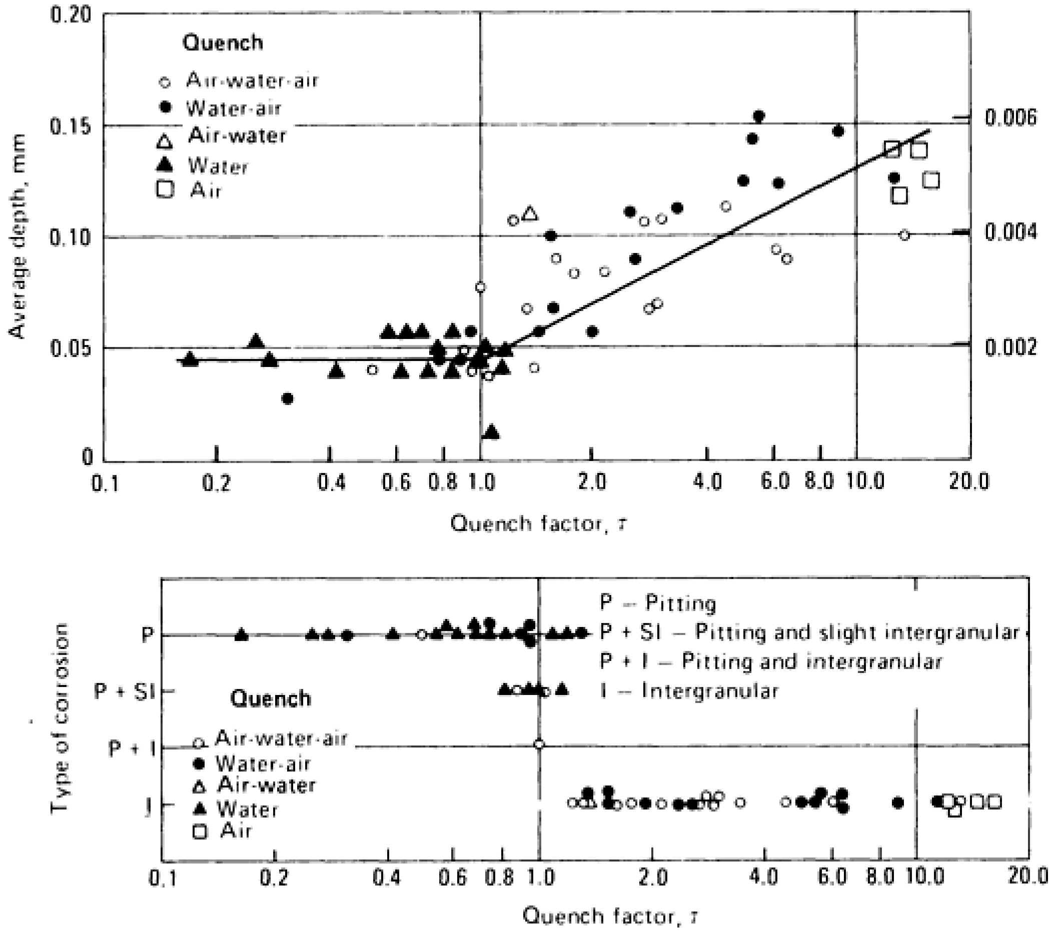


Fig. 15 Type and depth of attack on 2024-T4 sheet versus quench factor

These relationships are applied to studies of effects of proposed changes in quench practice on design of new quenching systems. For example, consider that the goal of a proposed quenching system for 2024-T4 sheet products is to minimize warpage while preventing susceptibility to intergranular corrosion. Warpage occurs when the stresses imposed by temperature differences across the parts exceed the flow stress. As quenching rate decreases, the tendency for large differences in temperature to occur decreases but the tendency for intergranular corrosion to occur increases.

The C-curve in Fig. 12 indicates that quenching rate can be decreased near the solution heat-treating temperature and near room temperature without greatly sacrificing corrosion characteristics, but this information does not provide a quantitative answer. Simple calculations, however, can reveal a multitude of hypothetical cooling curves that provide slow quenching

during a large portion of the quench cycle but sufficiently rapid quenching where critical times are short so that desirable corrosion characteristics are obtained.

As an example, one-, two-, and three-step quench curves that would ensure acceptable corrosion behavior in 2024-T4 sheet (quench factor, 0.99) were calculated. Some of these curves are plotted in Fig. 16. This illustration shows that 2024 can be quenched at a rate of 470 °C/s (850 °F/s) or higher and still develop acceptable corrosion characteristics if the quenching rate is linear from the solution temperature to 150 °C (300 °F). If sheet 3.2 mm (0.125 in.) thick is air-blast quenched (rate of heat removal, 5.68 W/m^2 · °C) to 395 °C (740 °F), however, the quenching rate from 395 to 150 °C must be at least 945 °C/s (1700 °F/s) to maintain the acceptable corrosion behavior. It may also be air-blast quenched to 395 °C (740 °F), spray quenched at 3300 °C/s (6000 °F/s) to 250 °C (480 °F), then air-blast quenched to 150 °C (300 °F).

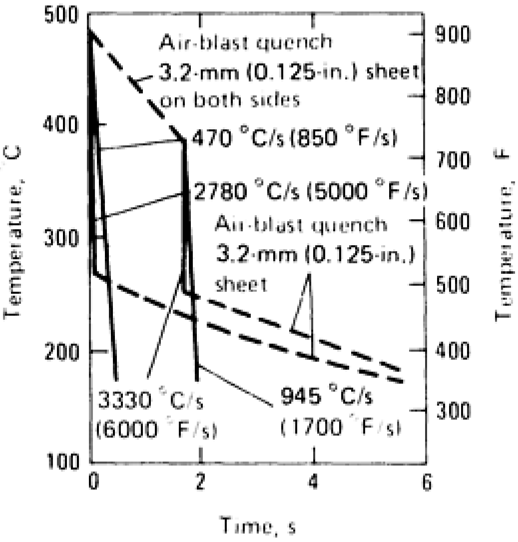


Fig. 16 Quench curves for 2024-T4 sheet, to eliminate susceptibility to intergranular corrosion

Other curves could be drawn, of course, but the important points are that air-blast quenching cannot be continued to more than a few degrees below 395 °C (740 °F) and cannot be initiated at more than a few degrees above 270 °C (520 °F) even if infinite quenching rates are attained from 395 to 270 °C (740 to 520 °F).

Predicting yield strength is more complex than predicting corrosion behavior and requires some knowledge of the relationship between extent of precipitation and loss in ability to develop property. Because attainable strength of precipitation-hardening aluminum alloys is a function of the amount of solute remaining in solid solution after quenching, relationships between strength (σ_x) attainable after continuous cooling and quench factor (τ) can be expressed as follows:

$$\sigma_x = \sigma_{max} \exp (k_1 \tau) \quad \textbf{(Eq 3)}$$

where σ_{max} is the strength attainable with an infinite quenching rate and:

$$t = \int \frac{dt}{C_x} \quad \textbf{(Eq 4)}$$

where t is time and C_x is the C-curve for σ_x--that is, critical time as a function of temperature to reduce attainable strength to x of σ_{max}. The constant k_1 is related to the natural logarithm of x. For example, if τ is based on the C-curve for 99.5% of maximum yield strength, then k_1 = -0.005013 = ln (0.995).

The advantage of predicting yield strength from quench factor instead of from average quenching rate is illustrated by the following comparison. Four specimens of alloy 7075-T6 quenched by various means (see Fig. 17) were selected. Yield strengths were predicted both from average quenching rate between 400 and 290 °C (750 and 550 °F) and from quench

factor. Quench factor was calculated using the C-curve for 99.5% maximum yield strength for 7075-T6 (Fig. 18), and yield strength was estimated from the above equation defining the quench factor (τ) (see Fig. 19).

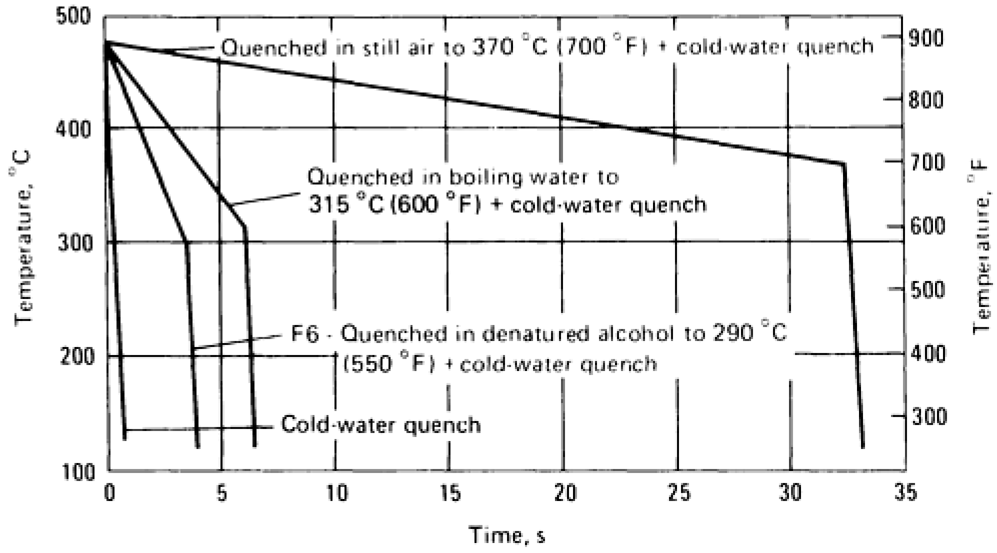


Fig. 17 Cooling curves for 7075-T6 sheet

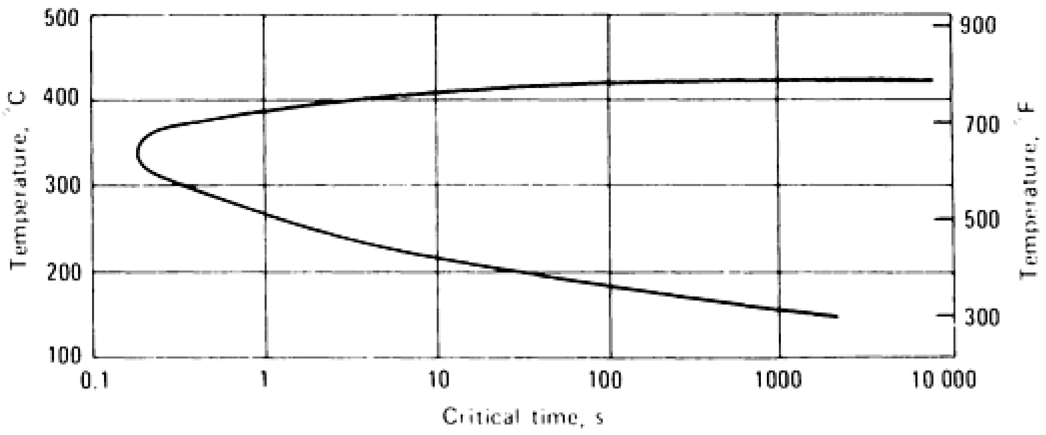


Fig. 18 C-curve for 99.5% maximum yield strength of 7075-T6 sheet

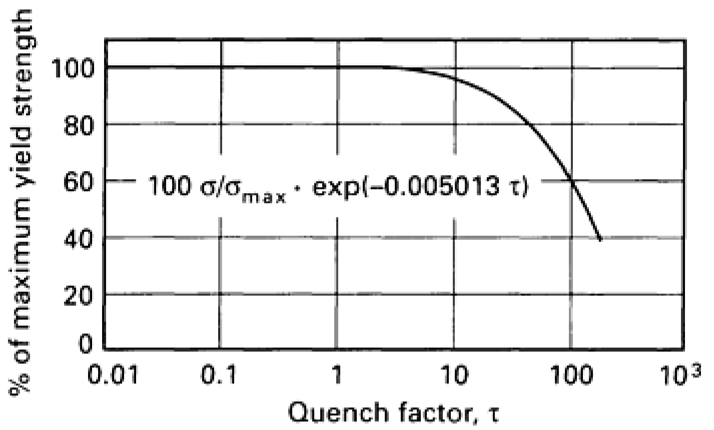


Fig. 19 Yield strength versus quench factor

A comparison of predicted yield strength with actual yield strength is given in Table 8. Yield strengths predicted from quench factor agree very well with measured yield strengths for all specimens, the maximum error being 19.3 MPa (2.8 ksi). Yield strengths predicted from average quenching rates, however, differ from measured values by as much as 226 MPa (32.8 ksi).

Table 8 Yield-strength values for 7075-T6 sheet predicted from cooling curves using average quench rate and quench factor

Quench	**Average quench rate from 400 to 290 °C (750 to 550 °F)**		**Quench factor, τ**	**Measured yield strength**		**Yield strength predicted from average quench rate**		Yield strength predicted from quench factor	
	°C/s	**°F/s**		**MPa**	**ksi**	**MPa**	**ksi**	**MPa**	ksi
Cold water	935	1680	0.464	506	73.4	499	72.4	498	**72.3**
Denatured alcohol to 290 °C (550 °F), then cold water	50	90	8.539	476	69.1	463	67.2	478	**69.4**
Boiling water to 315 °C (600 °F), then cold water	30	55	15.327	458	66.4	443	64.2	463	**67.1**

The advantage of using the quench factor for predicting yield strength from cooling curves is apparent. Cooling curves that have long holding times either above or below the critical temperature range from 400 to 290 °C (750 to 550 °F) cannot be used to predict yield strength from average quenching rate. In such instances, prediction of yield strength on the basis of quench factor is particularly advantageous.

With the use of finite-element analysis, quench factors can also be plotted as a function of Grossmann quench severity values (*H*) or the heat transfer coefficients (*C*) between the quenchant and a particular part (Fig. 20). However, an underlying assumption of both quench-factor analysis and average-cooling-rate estimation is that the only effect of temperature is on the kinetics of precipitation. This assumption is not valid, however, when portions of the metal are quenched locally but reheated significantly before quenching is complete.

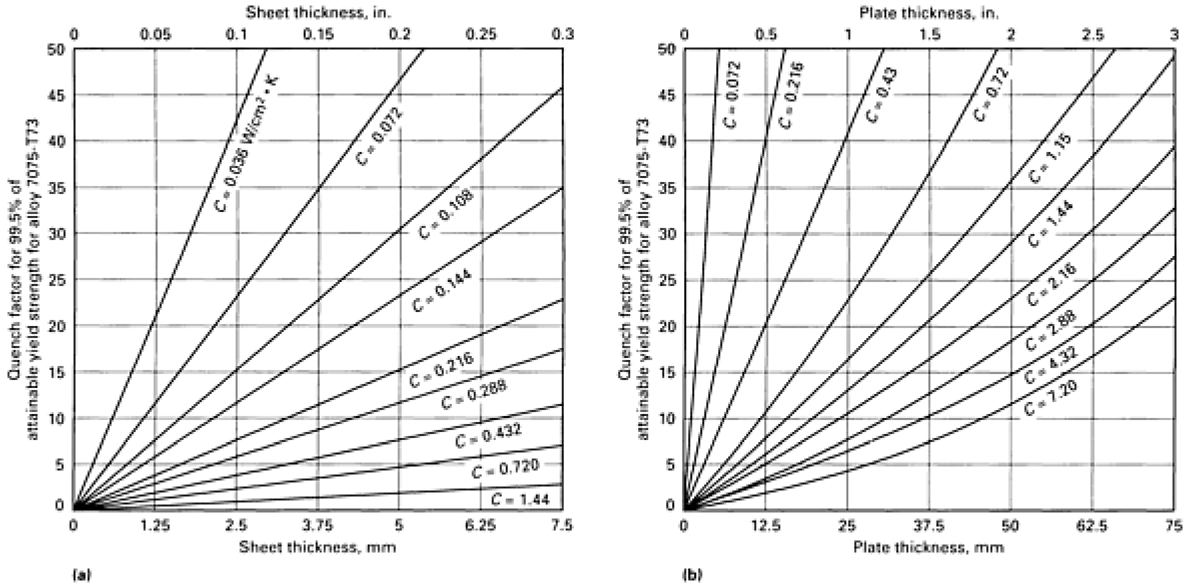


Fig. 20 Plot of quench factors derived from finite element analysis with given product sizes and film (heat transfer) coefficients (*C*). Heat transfer coefficients between the quenchant and part are expressed in $W/cm^2 \cdot K$. Source: Ref 4

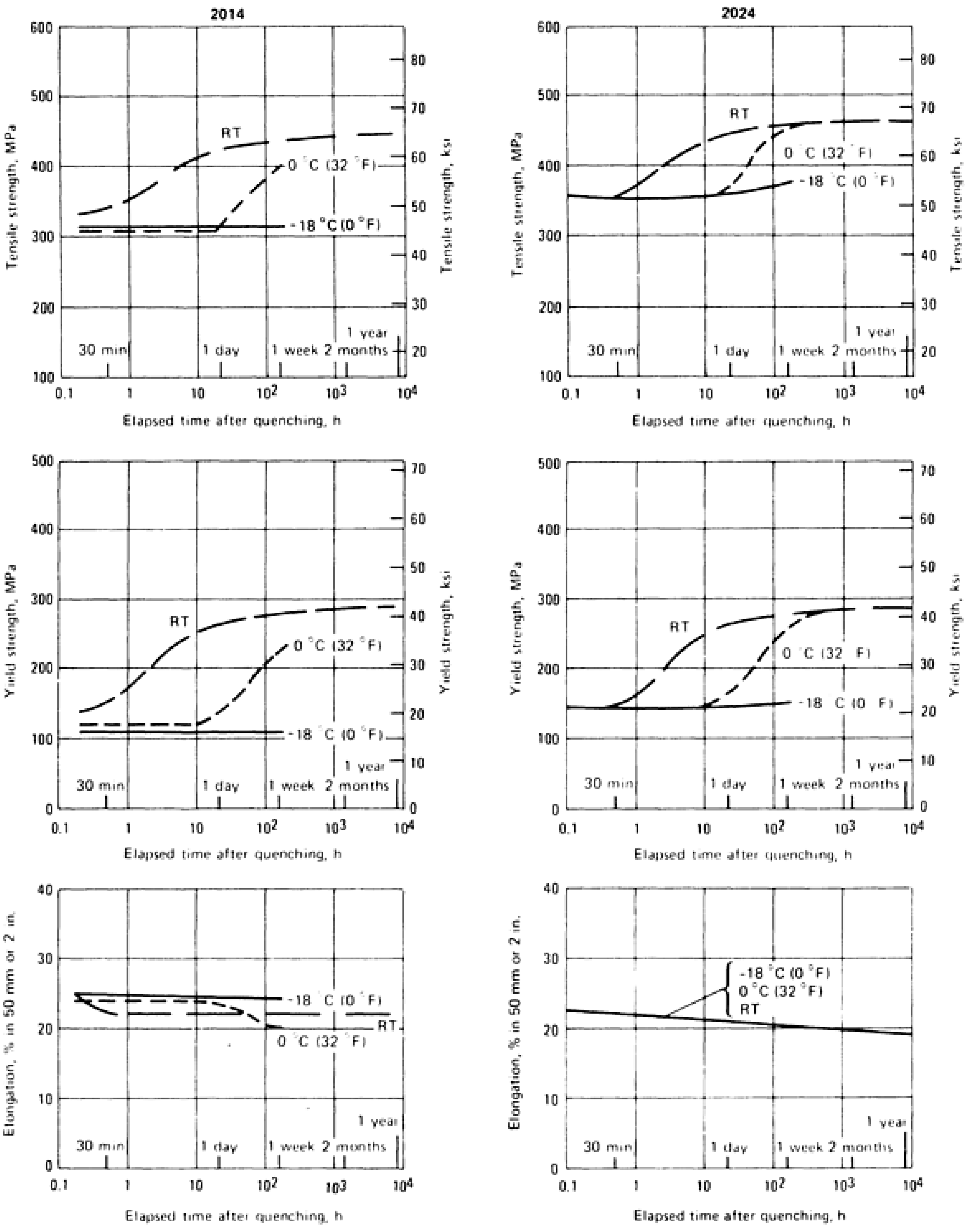
Age Hardening

After solution treatment and quenching, hardening is achieved either at room temperature (natural aging) or with a precipitation heat treatment (artificial aging). In some alloys, sufficient precipitation occurs in a few days at room temperature to yield stable products with properties that are adequate for many applications. These alloys sometimes are precipitation heat treated to provide increased strength and hardness in wrought or cast products. Other alloys with slow precipitation reactions at room temperature are always precipitation heat treated before being used.

In some alloys, notably those of the 2*xxx* series, cold working of freshly quenched material greatly increases its response to later precipitation heat treatment. Mills take advantage of this phenomenon by applying a controlled amount of rolling (sheet and plate) or stretching (extrusion, bar, and plate) to produce higher mechanical properties. However, if the higher properties are used in design, reheat treatment must be avoided.

Natural Aging. The more highly alloyed members of the 6*xxx* wrought series, the copper-containing alloys of the 7*xxx* group, and all of the 2*xxx* alloys are almost always solution heat treated and quenched. For some of these alloys--particularly the 2*xxx* alloys--the precipitation hardening that results from natural aging alone produces useful tempers (T3 and T4 types) that are characterized by high ratios of tensile to yield strength and high fracture toughness and resistance to fatigue. For the alloys that are used in these tempers, the relatively high supersaturation of atoms and vacancies retained by rapid quenching causes rapid formation of GP zones, and strength increases rapidly, attaining nearly maximum stable values in four or five days. Tensile-property specifications for products in T3- and T4-type tempers are based on a nominal natural aging time of four days. In alloys for which T3- or T4-type tempers are standard, the changes that occur on further natural aging are of relatively minor magnitude, and products of these combinations of alloy and temper are regarded as essentially stable after about one week.

In contrast to the relatively stable condition reached in a few days by 2*xxx* alloys that are used in T3- or T4-type tempers, the 6*xxx* alloys and to an even greater degree the 7*xxx* alloys are considerably less stable at room temperature and continue to exhibit significant changes in mechanical properties for many years. The differences in rate and duration of changes in tensile yield strength of representative alloys of the three types are illustrated in Fig. 21. Because of the relative instability of the 7*xxx* alloys, the naturally aged temper (after solution heat treatment and quenching) is designated by the suffix letter W. For a specific description of this condition, the time of natural aging should be included (example: 7075-W, 1 month).


2014
2024
Tensile strength, MPa
Tensile strength, ksi
Yield strength, MPa
Yield strength, ksi
Elongation, % in 50 mm or 2 in.
Elapsed time after quenching, h
RT
0 °C (32 °F)
-18 °C (0 °F)
30 min
1 day
1 week
2 months
1 year
0.1
1
10
10^2
10^3
10^4

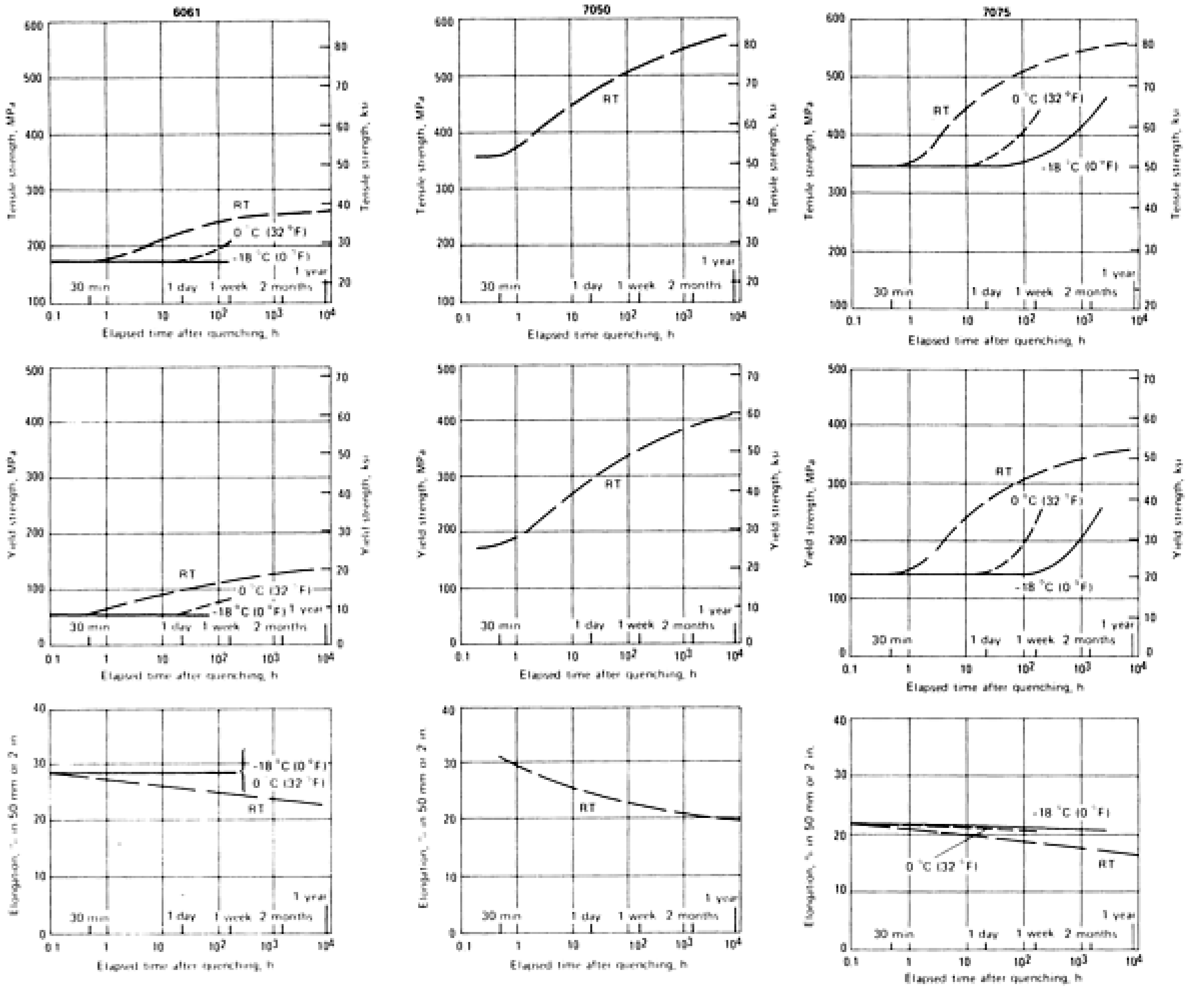


Fig. 21 Aging characteristics of aluminum sheet alloys at room temperature, at 0 °C (32 °F), and at -18 °C (0 °F)

Aging characteristics vary from alloy to alloy with respect to both time to initial change in mechanical properties and rate of change, but aging effects always are lessened by reductions in aging temperature (see Fig. 21). With some alloys, aging can be suppressed or delayed for several days by holding at a temperature of -18 °C (0 °F) or lower. It is usual practice to complete forming and straightening before aging changes mechanical properties appreciably. When scheduling makes this impractical, aging may be avoided in some alloys by refrigerating prior to forming. It is conventional practice to refrigerate alloy 2024-T4 rivets to maintain good driving characteristics. Full-size wing plates for current-generation jet aircraft have been solution heat treated and quenched at the primary fabricating mill, packed in dry ice in specially designed insulated shipping containers and transported by rail about 2000 miles to the aircraft manufacturer's plant for forming.

Unanticipated difficulties may arise as a result of failure to control refrigerator or part temperature closely enough. If opening of the cold box to insert or remove parts is done too frequently, the cooling capacity of the refrigerator may be exceeded. At times, the rate at which heavy-gage parts can be cooled in a still-air cold box has been found to be insufficient. This problem has been solved in one plant by immersing parts in a solvent at -40 °C (-40 °F) before placing them in the refrigerator.

The T3-type tempers are distinguished from T4-type tempers by significant mechanical-property differences resulting from cold work strain hardening associated with certain mechanical operations performed after quenching. Roller or stretcher leveling to achieve flatness or straightness introduces modest strains (on the order of 1 to 4%) that cause changes in mechanical properties (primarily, increases in strength). Further increases in strength can be obtained by cold rolling, additional stretching, combinations of these operations, or for products such as hand forgings, compressive deformation. The tempers produced by these operations followed by natural aging alone (no precipitation heat treatment) are classified as T3-type tempers, and an additional digit is used to indicate a variation in strain hardening that results in significant

changes in properties. In the most recently introduced 2*xxx* aircraft alloy, 2324, high strength is achieved by cold rolling plate to a T39 temper.

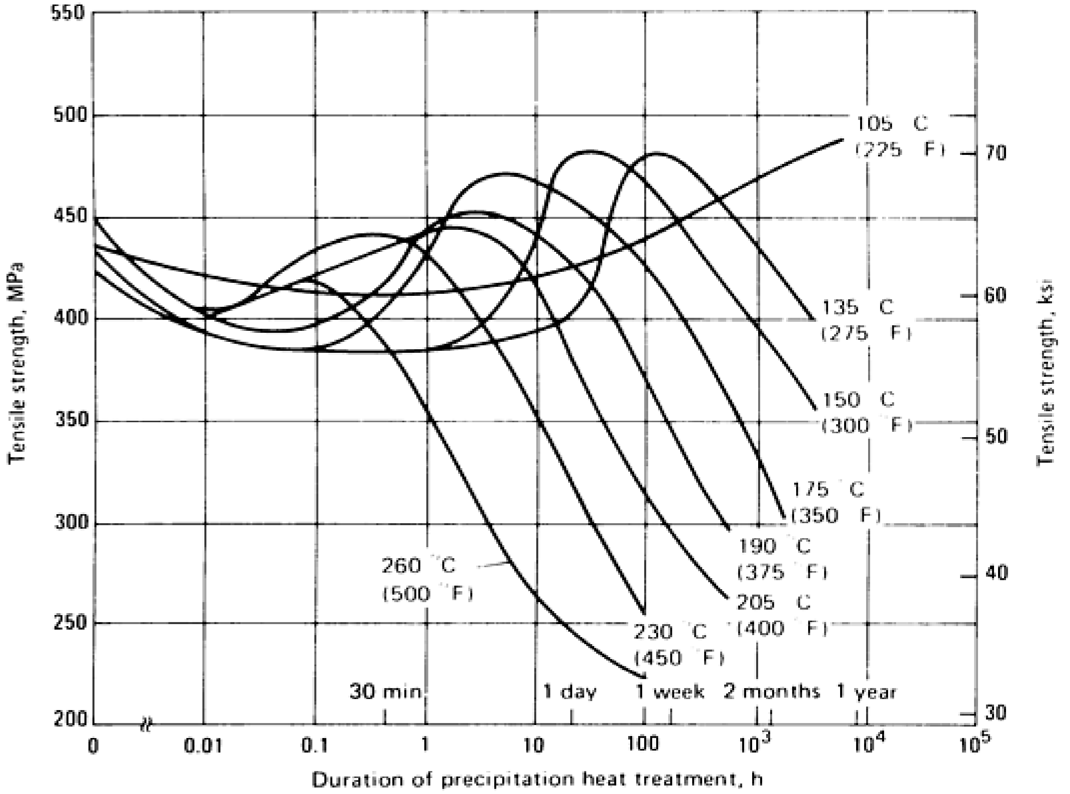
Precipitation heat treatments generally are low-temperature, long-term processes. Temperatures range from 115 to 190 °C (240 to 375 °F); times vary from 5 to 48 h.

Choice of time-temperature cycles for precipitation heat treatment should receive careful consideration. Larger particles of precipitate result from longer times and higher temperatures; however, the larger particles must, of necessity, be fewer in number with greater distances between them. The objective is to select the cycle that produces optimum precipitate size and distribution pattern. Unfortunately, the cycle required to maximize one property, such as tensile strength, is usually different from that required to maximize others, such as yield strength and corrosion resistance. Consequently, the cycles used represent compromises that provide the best combinations of properties.

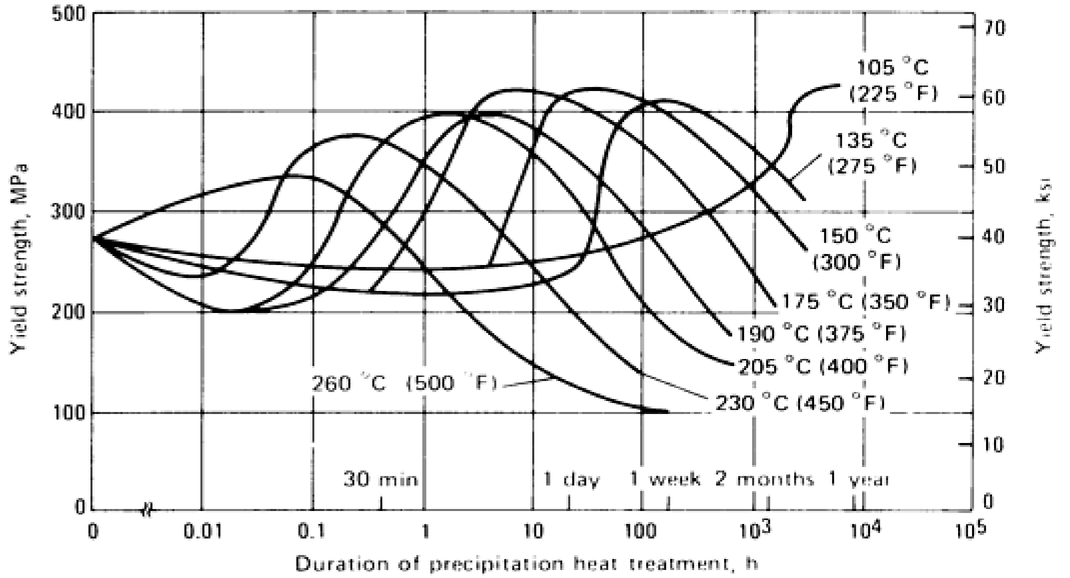
Production of material in T5- through T10-type tempers (see the section on temper designations near the end of this article) necessitates precipitation heat treating at elevated temperatures (artificial aging). Although the hardening precipitate developed by this operation is submicroscopic, structures before and after precipitation heat treatment often can be distinguished by etching metallographic specimens. In aluminum alloys in the solution heat treated and quenched condition, coloration contrast between grains of differing orientation is relatively high, particularly in 2*xxx* series wrought alloys and 2*xx*.0 series casting alloys. This contrast is noticeably decreased by precipitation heat treatment.

Differences in type, volume fraction, size, and distribution of the precipitated particles govern properties as well as the changes observed with time and temperature, and these are all affected by the initial state of the structure. The initial structure may vary in wrought products from unrecrystallized to recrystallized and may exhibit only modest strain from quenching or additional strain from cold working after solution heat treatment. These conditions, as well as the time and temperature of precipitation heat treatment, affect the final structure and the resulting mechanical properties.

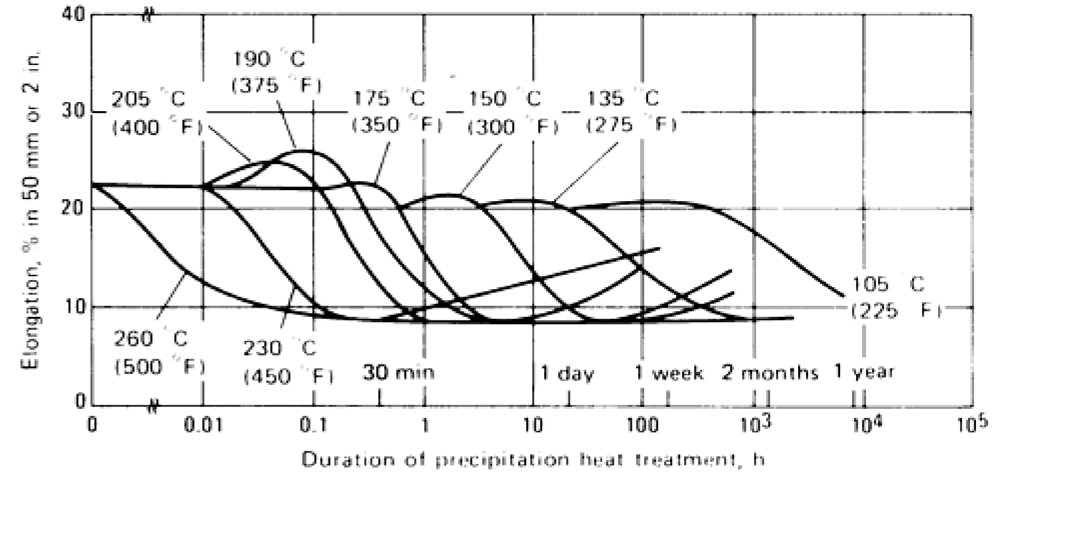
Because mechanical properties and other characteristics change continuously with time and with temperature, as shown in Fig. 22(a), 22(b), 22(c), and 22(d) by typical curves for three wrought alloys, treatment to produce a combination of properties corresponding to a specific alloy-temper combination requires one or more rather specific and coordinated combinations of time and temperature, with both parameters being subject to practical limitations. Recommended commercial treatments often are compromises between time and cost factors and the probability of obtaining the intended properties, with consideration of allowances for variables such as composition within specified range and temperature variations within the furnace and load. Use of higher temperatures may reduce treatment time; but if the temperature is too high, characteristic features of the precipitation-hardening process reduce the probability of obtaining the required properties.



Tensile strength, MPa
Tensile strength, ksi
105 °C (225 °F)
135 °C (275 °F)
150 °C (300 °F)
175 °C (350 °F)
190 °C (375 °F)
205 °C (400 °F)
230 °C (450 °F)
260 °C (500 °F)
30 min
1 day
1 week
2 months
1 year
Duration of precipitation heat treatment, h



Yield strength, MPa
Yield strength, ksi
105 °C (225 °F)
135 °C (275 °F)
150 °C (300 °F)
175 °C (350 °F)
190 °C (375 °F)
205 °C (400 °F)
230 °C (450 °F)
260 °C (500 °F)
30 min
1 day
1 week
2 months
1 year
Duration of precipitation heat treatment, h



Elongation, % in 50 mm or 2 in.
190 °C (375 °F)
205 °C (400 °F)
175 °C (350 °F)
150 °C (300 °F)
135 °C (275 °F)
105 °C (225 °F)
260 °C (500 °F)
230 °C (450 °F)
30 min
1 day
1 week
2 months
1 year
Duration of precipitation heat treatment, h

Fig. 22(a) Aging characteristics of alloy 2014 sheet

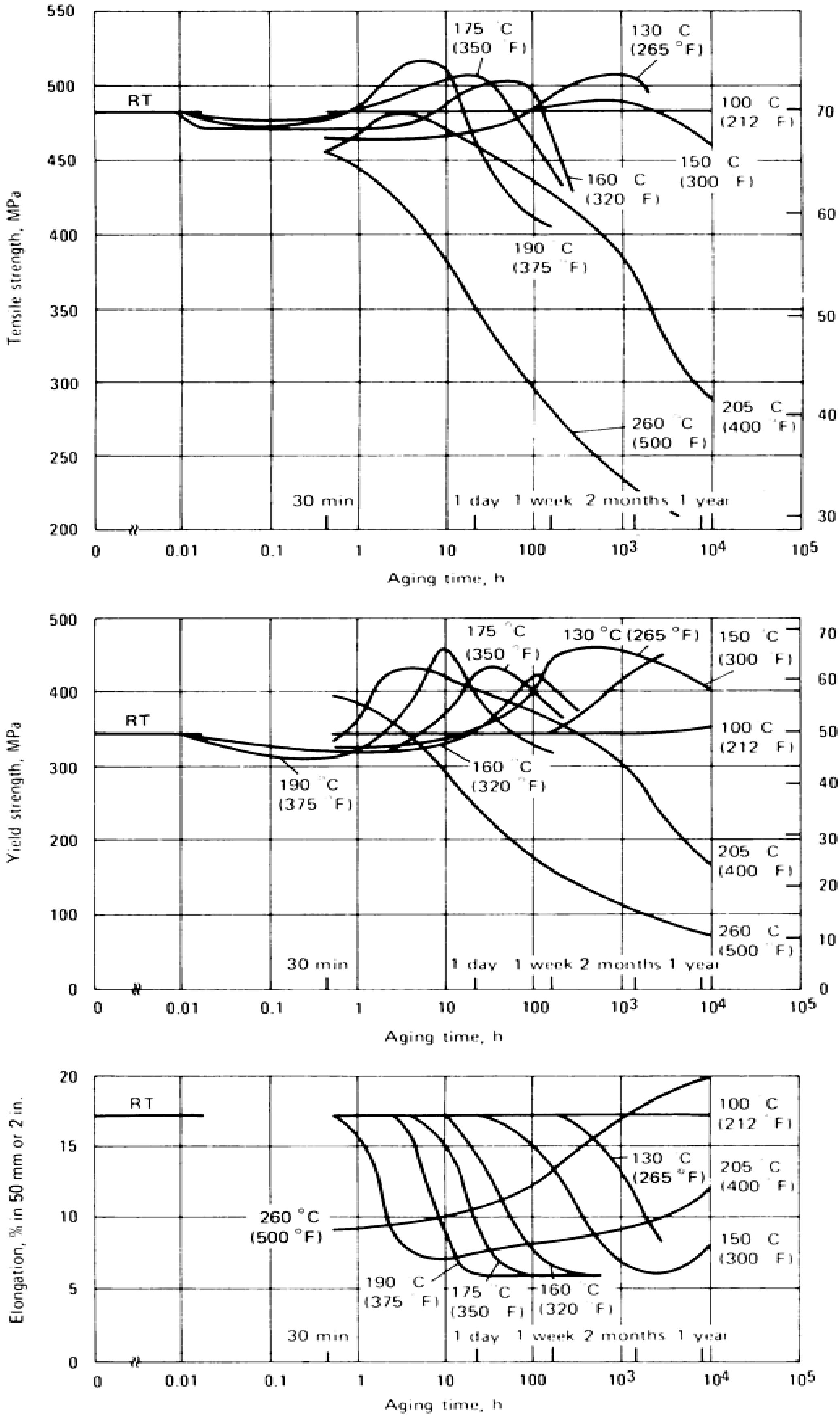


Fig. 22(b) Aging characteristics of alloy 2024 sheet (see also Fig. 22(d))

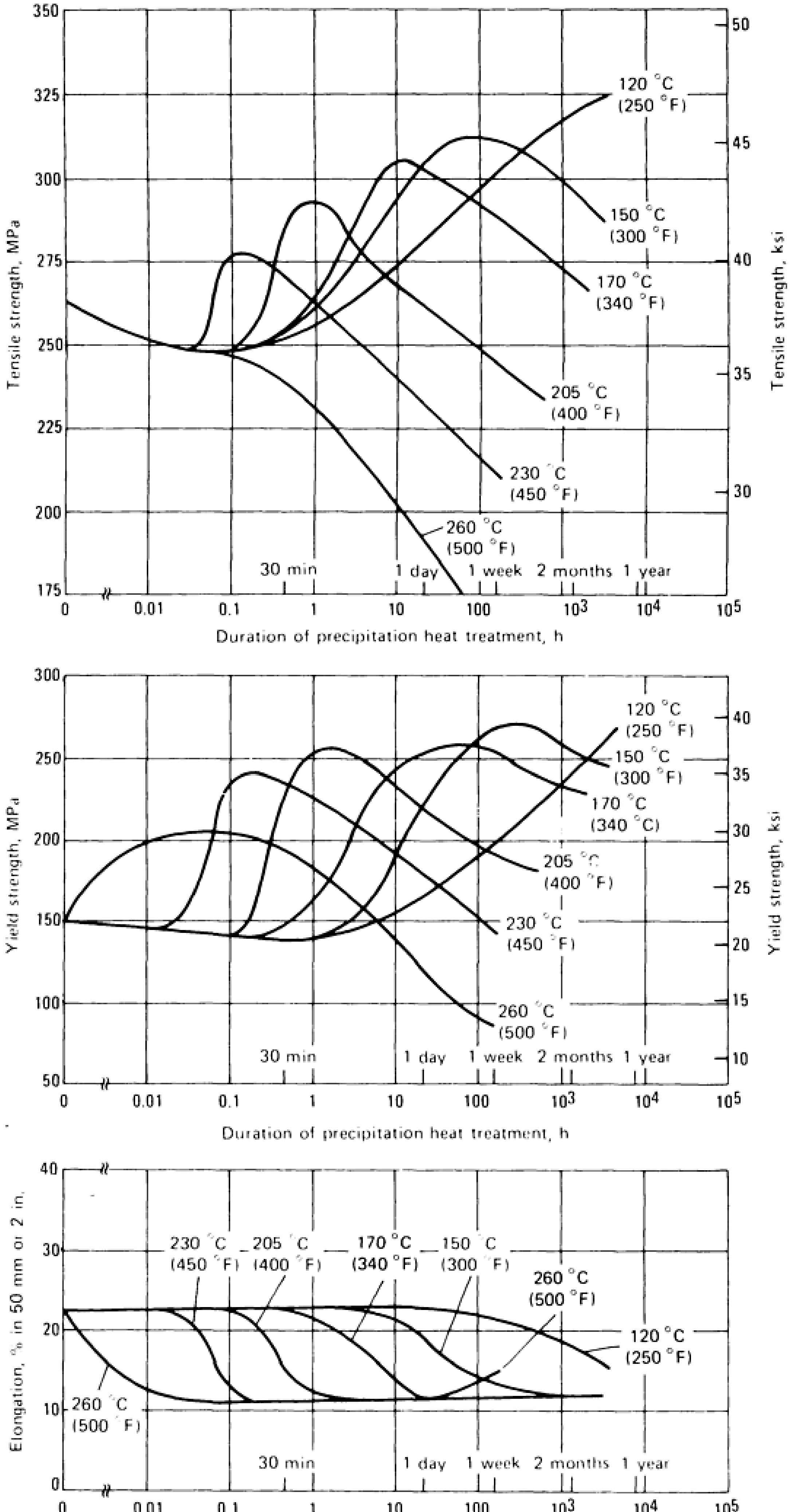

Tensile strength, MPa
Tensile strength, ksi
120 °C (250 °F)
150 °C (300 °F)
170 °C (340 °F)
205 °C (400 °F)
230 °C (450 °F)
260 °C (500 °F)
30 min
1 day
1 week
2 months
1 year
Duration of precipitation heat treatment, h
Yield strength, MPa
Yield strength, ksi
120 °C (250 °F)
150 °C (300 °F)
170 °C (340 °C)
205 °C (400 °F)
230 °C (450 °F)
260 °C (500 °F)
30 min
1 day
1 week
2 months
1 year
Duration of precipitation heat treatment, h
Elongation, % in 50 mm or 2 in.
230 °C (450 °F)
205 °C (400 °F)
170 °C (340 °F)
150 °C (300 °F)
260 °C (500 °F)
120 °C (250 °F)
260 °C (500 °F)
30 min
1 day
1 week
2 months
1 year

Fig. 22(c) Aging characteristics of alloy 6061 sheet

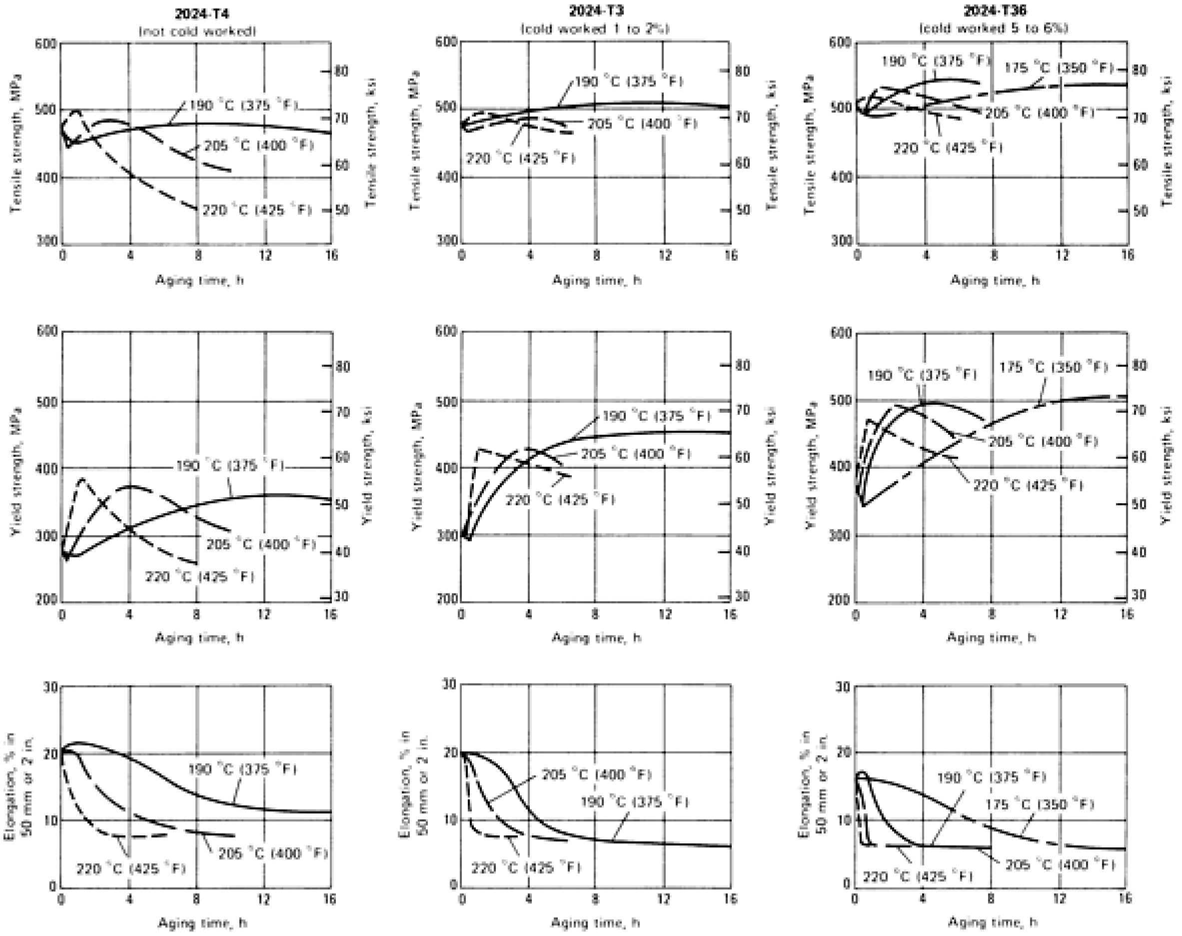


Fig. 22(d) Effects of cold work after quenching and before aging on tensile properties of alloy 2024 sheet

T6 and T7 Tempers. Precipitation heat treatment following solution heat treatment and quenching produces T6- and T7-type tempers. Alloys in T6-type tempers generally have the highest strengths practical without sacrifice of the minimum levels of other properties and characteristics found by experience to be satisfactory and useful for engineering applications. Alloys in T7 tempers are overaged, which means that some degree of strength has been sacrificed or "traded off" to improve one or more other characteristics. Strength may be sacrificed to improve dimensional stability, particularly in products intended for service at elevated temperatures, or to lower residual stresses in order to reduce warpage or distortion in machining. T7-type tempers frequently are specified for cast or forged engine parts. Precipitation heat-treating temperatures used to produce these tempers generally are higher than those used to produce T6-type tempers in the same alloys.

Two important groups of T7-type tempers--the T73 and T76 types--have been developed for the wrought alloys of the 7*xxx* series, which contain more than about 1.25% copper. These tempers are intended to improve resistance to exfoliation corrosion and stress-corrosion cracking, but as a result of overaging, they also increase fracture toughness and, under some conditions, reduce rates of fatigue-crack propagation. The T73-type temper has greatly minimized stress-corrosion cracking of large and complex machined parts made of these alloys, which occasionally occurred with T6-type tempers. The precipitation heat treatment used to produce the T73- and T76-type tempers consist either of a two-stage isothermal precipitation heat treatment or of heating at a controlled rate to a single treatment temperature. The microstructural/electrochemical relationships that are required in order to achieve the desired corrosion-resisting characteristics can be developed by using only a single-stage precipitation heat treatment above about 150 °C (300 °F), but higher strength is obtained by preceding this with a lower-temperature stage or with a slow-controlled heatup. Extended natural aging can provide the same results, but the times required at room temperature are impractical. Either

during the preliminary stage or during slow heatup, a fine, high-density dispersion of GP zones is nucleated. Either the time and temperature of the first step or the rate of heating must be controlled to produce GP zones that will not dissolve but will transform to the η' precipitate when heated to the aging temperature above 150 °C (300 °F). The aging practice that produces the results in the shortest time depends on the GP-zone solvus temperature. This temperature, in turn, depends on vacancy concentration, a factor influenced by solution heat-treating temperature and quench rate, and on composition. If first-step aging time is too short, if first-step aging temperature is too far below the GP-zone solvus, or if heating rates are too high, the GP zones will dissolve above 150 °C (300 °F), and the resultant coarse and widely distributed precipitate will provide lower strength. The T76-type treatments have the same operational sequence but employ second-stage heating only long enough to develop a resistance to exfoliation corrosion higher than that provided by the T6-type tempers. Materials in the T73-type temper also have high resistance to exfoliation corrosion.

Recommended treatments to produce T5- and T6-type tempers, and those of the T7-type employed for dimensional and property stabilization, provide adequate tolerance for normal variations encountered with good operating practices. On the other hand, the T73, T74 (formerly T736), and T76 tempers for alloys 7049, 7050, 7075, 7175, and 7475 involve changes in strength that occur significantly more rapidly at the temperatures employed in the second stage of the T7*x* precipitation heat-treatment cycle compared to the changes occurring at the temperatures employed to produce the T6 temper.

As illustrated in Fig. 23, variations in soak time of several hours, and variations in soak temperature of up to 11 °C (20 °F) from the nominal aging practice of 24 h at 120 °C (250 °F) affect the strength of 7075-T6 by as much as 28 MPa (4 ksi). In contrast, similar variations in second-step soak time and temperature for 7075-T73--that is, variations for 24 h at 165 °C (325 °F)--affect strength by up to 150 MPa (22 ksi).

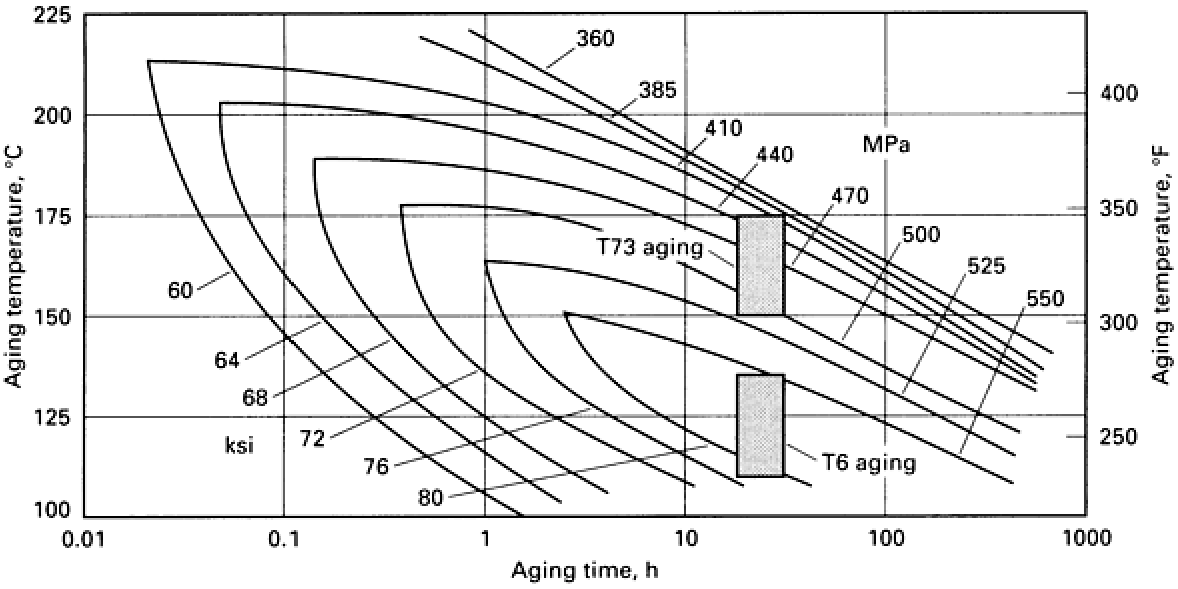


Fig. 23 Iso-yield-strength curves for alloy 7075

Consequently, control of both temperature and time to achieve the mechanical properties and corrosion resistance specified for these tempers is more critical than the control required in producing the T6 temper. Moreover, rate of heating from the first to the second aging step must be considered, because precipitation occurs during this period.

Heat treaters attempt to adjust these new problems by empirically modifying soak times to compensate for precipitation during heating and for effects of soaking at temperatures above or below the nominal. A method has been developed (Ref 8) that permits quantitative compensation for the effects of precipitation during heating and of soaking either above or below the recommended temperature. For overaging, these effects can be described by the following equation:

$$YS = Y \exp - \left(\frac{t_c}{F_{YS}} + q \right) \quad \textbf{(Eq 5)}$$

where *YS* is yield strength; *Y* is a term having units of strength that is dependent on alloy, fabrication, and test direction; t_c is time at soak temperature; F_{YS} is a temperature-dependent term; and

$$q = \int \frac{dt}{F_{YS}} \qquad \textbf{(Eq 6)}$$

where *t* is time during heating.

Equation 5 provides the basis for selection of a nominal aging time that will result in the desired yield strength and gives the furnace operator a method of compensating for heating rate and for differences between desired and attained soak temperatures.

Specifics will be illustrated using data for alloy 7050. The value of F_{YS} (in units of hours) for 7050 can be calculated by the following equation:

$$F_{YS} = 1.45x10^{-16} \exp\left(\frac{32562}{T_F + 460}\right) \qquad \textbf{(Eq 7a)}$$

where T_F is temperature in °F, or

$$F_{YS} = 1.45x10^{-6} \exp\left(\frac{18090}{T_k}\right) \qquad \textbf{(Eq 7b)}$$

where T_K is temperature in K.

In one experiment, lengths of 7050-W (4 days) extrusions were aged at 24 h at 120 °C (250 °F) plus the equivalent of 3 to 42 h at 165 °C (325 °F). For the second step, a logarithmic heatup was used in which 10 h were required for the load to reach 155 °C (315 °F), and nominal soak temperature was 165 °C (325 °F). Figure 24 indicates that yield strength generally agreed with values predicted using Eq 5. The deviation of the curve for short-transverse strength at the short aging times indicates that the method is inadequate for predicting strength on the underaging side of the aging curve.

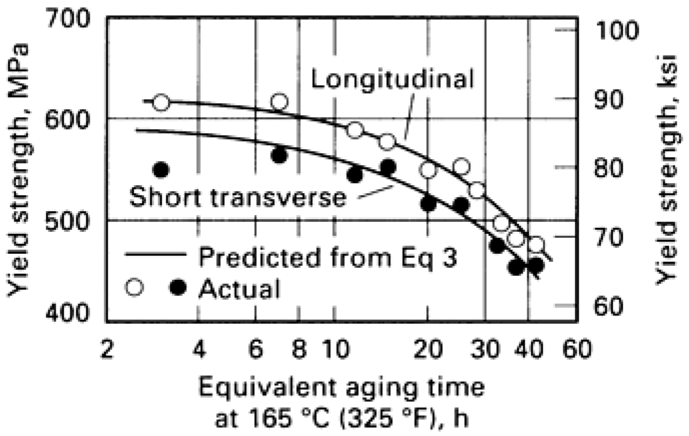


Fig. 24 Actual versus predicted yield strengths for alloy 7050 extrusions

The effects of neglecting to compensate for soaking at temperatures other than the nominal can be large (Fig. 25). For example, the calculated difference in strength between alloy 7050 extrusions soaked 29 h at 160 °C (320 °F) and at 165 °C (325 °F) is about 50 MPa (7 ksi), and the calculated difference in strength between 7050 extrusions soaked 29 h at 155 °C (315 °F) and at 170 °C (335 °F) is about 100 MPa (14 ksi).

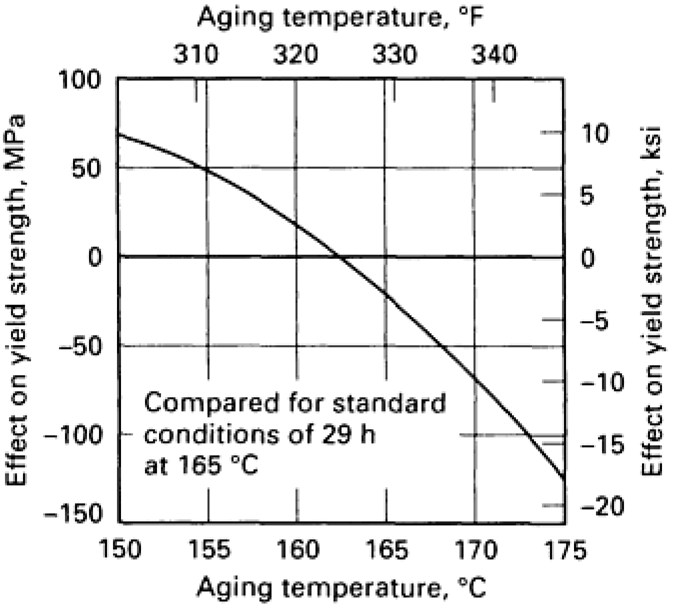


Fig. 25 Effect of aging temperature on yield strength of alloy 7050-T736

Neglecting to compensate for time spent heating the work to the soak temperature will increase the variability. Strength loss attributed to heatup was 14 MPa (2 ksi).

These kinetic relationships also can assist in selection of equivalent aging times for alternate second-step aging temperatures. Equations 5, 7a, and 7b can be rearranged to yield the following equation:

$$t_2 = t_1 \exp \frac{32562}{T_1 + 460} - \frac{32562}{T_2 + 460} \quad \textbf{(Eq 8)}$$

where t_1 is aging time at temperature T_1, t_2 is aging time at temperature T_2 that will provide equivalent yield strength, and T_1 and T_2 are in °F. For example, the time at 175 °C (350 °F) equivalent to aging alloy 7050 for 29 h at 165 °C (325 °F) is calculated as follows:

$$t_{350} = 29/\exp\ (1.28) = 29/3.6 = 8\ \text{h}$$

Thermomechanical effects on aging occur from deformation after solution heat treatment. The deformation step may be warm or cold and before, after, or during aging. The simplest thermomechanical practices are those of the conventional T3, T8, or T9 tempers. The rate and extent of precipitation strengthening are distinctly increased in some alloys by cold working after quenching, whereas other alloys show little or no added strengthening when treated by this sequence of operations.

Alloys of the 2*xxx* series such as 2014, 2124, and 2219 are particularly responsive to cold work between quenching and aging, and this characteristic is the basis for the higher-strength T8 tempers. The strength improvement accruing from the combination of cold working and precipitation heat treating is a result of nucleation of additional precipitate particles by the increased strain. In some alloys of the 2*xxx* series, strain introduced by cold working after solution heat treatment and quenching also induces nucleation of a finer precipitate dispersion that increases strength. Depending on the aging temper, however, toughness may be adversely affected, as illustrated in Fig. 26 for 2024 sheet.

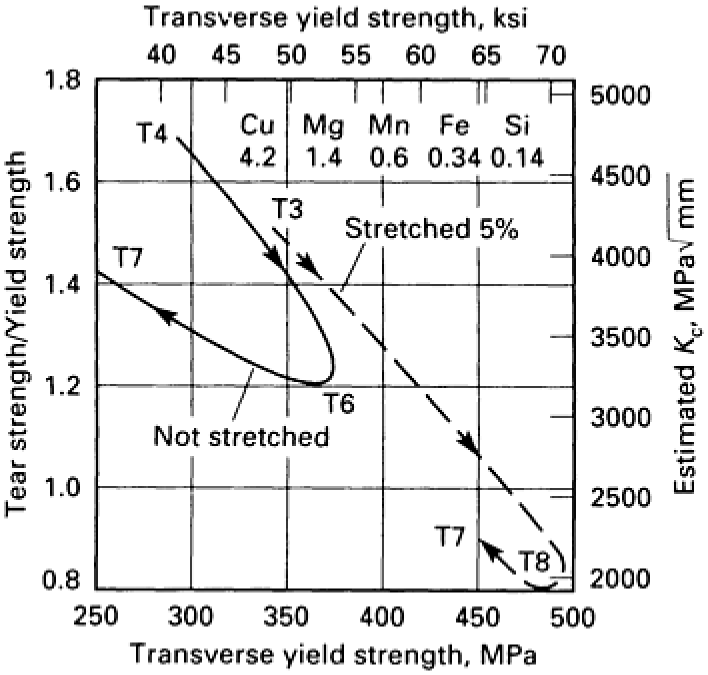


Fig. 26 Effect of stretching and aging on the toughness and yield strength of 2024 sheet

Strengthening from thermomechanical processing is the basis for the higher-strength T8-type tempers of alloys 2011, 2024, 2124, 2219, and 2419, which are produced by applying controlled amounts of cold rolling, stretching, or combinations of these operations. Normally, cold work is introduced by stretching; however, other methods such as cold rolling can be used. Recently, 2324-T39 was developed. The T39 temper is obtained by cold rolling approximately 10% after quenching followed by stretching to stress relieve. This type of approach results in strengths similar to those obtained with T8 processing but with the better toughness and fatigue characteristics of T3 products. Alloys 2024, 2124, and 2219 in T8-type tempers are particularly well suited for supersonic and military aircraft; alloy 2219 in such tempers, and alloy 2014-T65, were the principal materials for the fuel and oxidizer tanks (which also served as the primary structure) of the Saturn V space vehicles. Re-solution heat treatment of mill products supplied in these tempers can result in grain growth and in substantially lower strength than is normal for the original temper. Such reheat treatment is not recommended.

Alloys of the 7*xxx* series do not respond favorably to the sequence of operations used to produce T8-type tempers, and no such tempers are standard for these alloys. The strains associated with stretching or compressing of 7*xxx* alloys have relatively little effect on the mechanical properties of material precipitation heat treated to T6-type tempers. On the other hand, these operations have measurable detrimental effects on final strength when T73-, T736, or T76-type tempers are produced, particularly in the direction opposite the direction of cold work. Accordingly, specification properties are somewhat lower for the stress-relieved versions of these tempers. Decreasing the overaging time to compensate for the loss in strength is not advisable, because this would impair development of the desired corrosion characteristics.

Temperature control and uniformity present essentially the same problems in precipitation heat treating as they do in solution heat treating.

Good temperature control and uniformity throughout the furnace and load are required for all precipitation heat treating. Recommended temperatures are generally those that are least critical and that can be used with practical time cycles. Except for 7*xxx* alloys in T7*x* tempers, these temperatures generally allow some latitude and should have a high probability of meeting property specification requirements. Furnace radiation effects seldom are troublesome except in those few furnaces that are used for both solution and precipitation heat treating. Generally, such situations should be avoided, because the high heat capacity needed for the higher temperatures may be difficult to control at normal aging temperatures.

Soak time in precipitation heat treating is not difficult to control; the specified times carry rather broad tolerances. Heavier loads with parts racked closer together, and even nested, are not abnormal. The principal hazard is undersoaking due to gross excesses in loading practices. Some regions of the load may reach soak temperature long after soak time has been called. Placement of load thermocouples is critical, and limiting the size and spacing of a load may be necessary for aging to the T73 and T76 tempers. As discussed above, soak time is not as critical for peakaged (T6 and T8) tempers.

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Hardening of Cast Alloys

In general, the principles and procedures for heat treating wrought and cast alloys are similar. The major differences between solution-treating conditions for castings and those for wrought products are found in soak times and quenching media. Solution of the relatively large microconstituents present in castings requires longer soaking periods than those used for wrought products (Table 3). When heat treatment of castings must be repeated, solution times become similar to those for wrought products, because the gross solution and homogenization has been accomplished and is irreversible under normal conditions. Reduction of stresses and distortion from quenching are also important, because castings generally are complex shapes with variations in section thickness.

Different casting processes and foundry practices also result in microstructural differences with relevance to heat-treatment practice, because the coarser microstructures associated with slow solidification rates require a longer solution heat treatment exposure. Therefore, the time required at temperature to achieve solution is progressively shorter for investment, sand, and permanent mold castings. Foundry practice (chills, gating, type of mold) also plays an important role in the response of a casting, or a portion of a casting, to heat treatment. For example, thin-wall sand castings produced with extensive use of chills can often display finer microstructures than heavy-section permanent mold parts produced in such a way that process advantages are not exploited.

For these reasons, solution heat-treatment practices can be optimized for any specific part to achieve solution with the shortest reasonable cycle once production practice is finalized, even though most foundries and heat treaters will standardize a practice with a large margin of safety. There also exists a fundamental difference between unmodified and modified alloys in which the size and shape of silicon crystals are modified with additions of elements such as calcium, sodium, strontium, or antimony. Modified alloys undergo rapid spheroidization while complete spheroidization is not achieved in unmodified alloys even after very long times. The practical implication is that shorter solution heat treatment could be employed in fully modified castings. The microsegregation of silicon and magnesium is not severe in the aluminum-silicon-magnesium casting alloys, and hence it takes only a short time to homogenize the alloy and to place the Mg_2Si into solution.

Quenchants. Quenching of aluminum castings is often done in boiling water or a milder medium to reduce quenching stresses in complex shapes. A commercially important variety is a mixture of polyalkylene glycol and water, which has no detrimental effect on properties for thicknesses under approximately 3.2 mm (0.125 in.). Quenchant additions can be made for the following purposes:

- To promote stable vapor film boiling by the deposition of compounds on the surface of parts as they are submerged in the quench solution
- To suppress variations in heat flux by increasing vapor film boiling stability through chemically decreased quench solution surface tension
- To moderate quench rate for a given water temperature

The key to the compromise between goals involving property development and the physical consequences of quenching is uniformity of heat extraction, which is in turn a complex function of the operable heat extraction mechanism. Nucleate, vapor film, and convective boiling occur with dramatically different heat extraction rates at different intervals. Differences in section thickness, load density, positioning, racking methods, surface condition, and casting geometry also influence the results.

Property Development. Yield strength is largely controlled by the limiting hardening-element level, and tensile strength (in a general sense) is related to the ductility at a given yield strength. Ductility, however, is controlled for a given yield strength by soundness and microstructural fineness, and is thus determined in the foundry and not by the heat treater. This effect of casting methods on property development is shown in Fig. 27. Because of the finer cast structure and higher supersaturation of the more rapidly solidified permanent mold castings, their tensile properties are superior to those of sand castings of the same composition similarly heat treated.

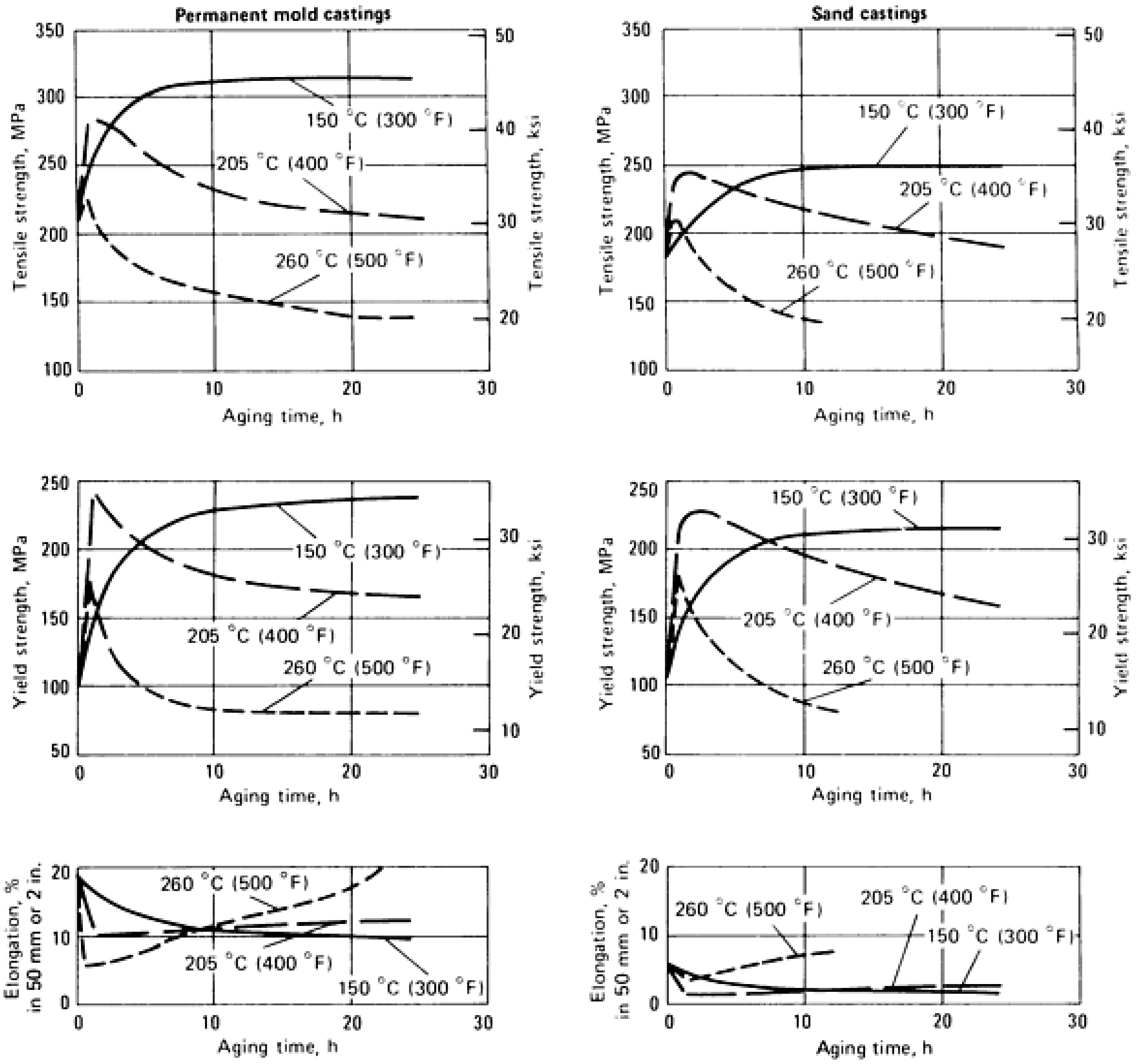


Fig. 27 Comparison of the precipitation-hardening characteristics of 356.0-T4 sand and permanent mold

castings

Tempers. Cast products of heat-treatable aluminum alloys have the highest combinations of strength, ductility, and toughness when produced in T6-type tempers. Developing T6-type tempers in cast products requires the same sequence of operations employed in developing tempers of the same type in wrought products--solution heat treating, quenching, and precipitation heat treating. Premium-quality casting specifications such as MIL-A-21180 can require different strengths and ductility levels in the same casting.

Among precipitation treatments unique to castings are those resulting in the T5 and T7 tempers. The T5 temper is produced merely by applying a precipitation treatment to the as-cast casting, without previous solution treatment. A moderate increase in strength is achieved without warpage and subsequent straightening. High hardness and dimensional and strength stability at elevated temperatures account for the almost universal use of materials in T5 tempers for pistons and other engine parts. Some applications demand combinations of strength, toughness, and dimensional stability that cannot be met by heat treating to T5-, T6-, or T8-type tempers. For these applications, T7-type tempers are developed by solution heat treating, quenching in a medium that provides a moderate cooling rate, and then precipitation heat treating at a temperature higher than those used to develop T5-, T6-, and T8-type tempers. Heat treating to T7-type tempers results in lower strength than that of material in T6- or T8-type tempers, develops high ductility and toughness, and carries precipitation far enough to minimize further precipitation during service.

Stress Relief

Immediately after being quenched, most aluminum alloys are nearly as ductile as they are in the annealed condition. Consequently, it is often advantageous to stress relieve parts by working the metal immediately after quenching. Numerous attempts also have been made to develop a thermal treatment that will remove, or appreciably reduce, quenching stresses. Normal precipitation heat-treating temperatures are generally too low to provide appreciable stress relief. Exposure to higher temperatures (at which stresses are relieved more effectively) results in lower properties. However, such treatments are sometimes utilized when even moderate reduction of residual stress levels is important enough so that some sacrifice in mechanical properties can be accepted. The T7 temper for castings is a typical example of this kind of treatment.

Mechanical Stress Relief. Deformation consists of stretching (bar, extrusions, and plate) or compressing (forgings) the product sufficiently to achieve a small but controlled amount (1 to 3%) of plastic deformation. If the benefits of mechanical stress relieving are needed, the user should refrain from reheat treating.

Figure 28 illustrates the beneficial effect of 3% permanent deformation in compression on a large forging.

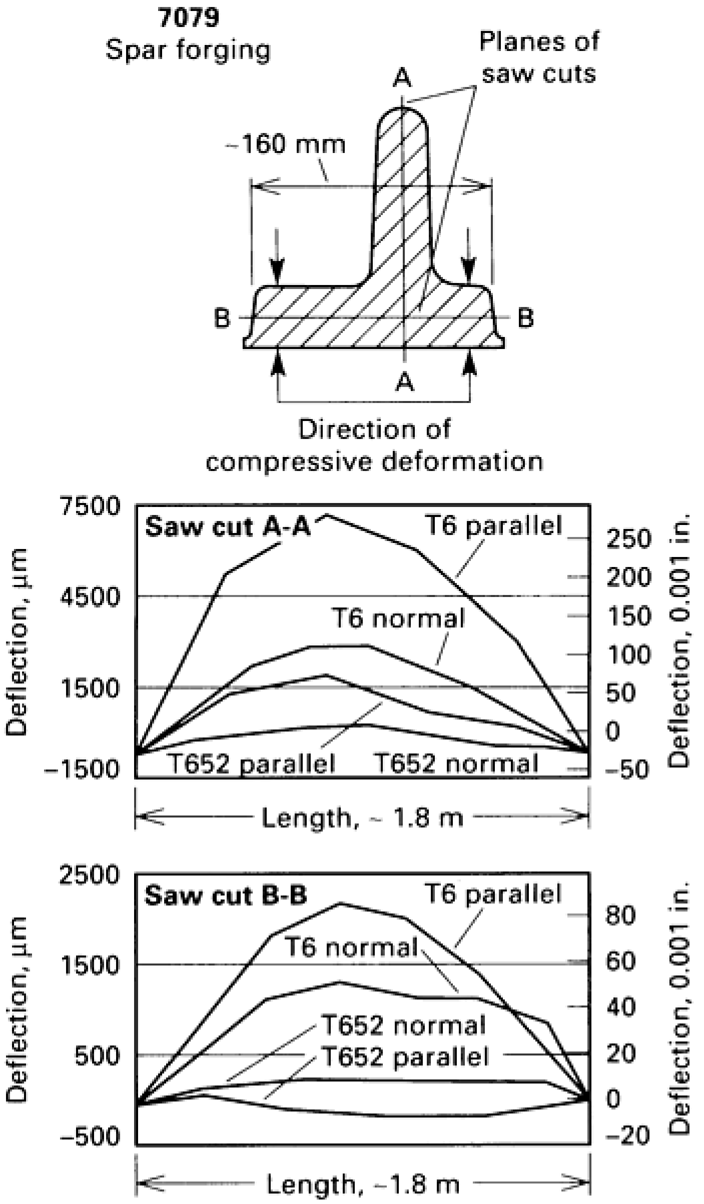


Fig. 28 Effect of 3% permanent deformation in compression (T652 treatment) on distribution of stress in a large forging. Parallel and normal refer to warpage directions with respect to the plane of the saw cut.

These methods are most readily adaptable to mill and forge shop products and require equipment of greater capacity than that found in most manufacturing plants. Application of these methods to die forgings and extrusions usually requires construction of special dies and jaws. Stretching generally is limited to material of uniform cross section; however, it has been applied successfully to stepped extrusions and to a 3 by 14 m (10 by 47 ft) aircraft wing skin roll-tapered to a thickness range of 7.1 to 3.2 mm (0.280 to 0.125 in.).

Specific combinations of the supplemental digits are used to denote the tempers produced when mechanical deformation is used primarily to relieve residual stresses induced during the quenching operation. For products stress relieved by stretching, the digits 51 follow the basic T*x* designation (T451, for example). For products stress relieved by compressive deformation, the supplementary digits are 52.

An additional digit is added to designations for extrusions: an added zero specifies that the product has not been straightened after final stretching; an added one indicates that straightening may have been performed after final stretching.

Effect of Precipitation Heat Treating on Residual Stress. The stresses developed during quenching from solution heat treatment are reduced during subsequent precipitation heat treatment. The degree of relaxation of stresses is highly dependent upon the time and temperature of the precipitation treatment and the alloy composition. In general, the precipitation treatments used to obtain the T6 tempers provide only modest reduction in stresses, ranging from about 10 to 35%. To achieve a substantial lowering of quenching stresses by thermal stress relaxation, higher-temperature treatments of the T7 type are required. These treatments are used when the lower strengths resulting from overaging are acceptable.

Other thermal stress-relief treatments, known as subzero treatment and cold stabilization, involve cycling of parts above and below room temperature. The temperatures chosen are those that can be readily obtained with boiling water and mixtures of dry ice and alcohol--namely, 100 and -73 °C (212 and -100 °F)--and the number of cycles ranges from one to five. The maximum reduction in residual stress that can be effected by these techniques is about 25%. The maximum effect can be obtained only if the subzero step is performed first, and immediately after quenching from the solution-treating temperature while yield strength is low. No benefit is gained from more than one cycle.

A 25% reduction in residual stress is sometimes sufficient to permit fabrication of a part that could not be made without this reduction. However, if a general reduction is needed, as much as 83% relief of residual stress is possible by increasing the severity of the uphill quench--that is, more closely approximating the reverse of the coolingrate differential during the original quench. This may be accomplished by a patented process that involves extending the subzero step to -195 °C (-320 °F) and then very rapidly uphill quenching in a blast of live steam (Fig. 29). The rate of reheating is extremely critical, and therefore, to ensure proper application of the steam blast, a special fixture usually is required for each part.

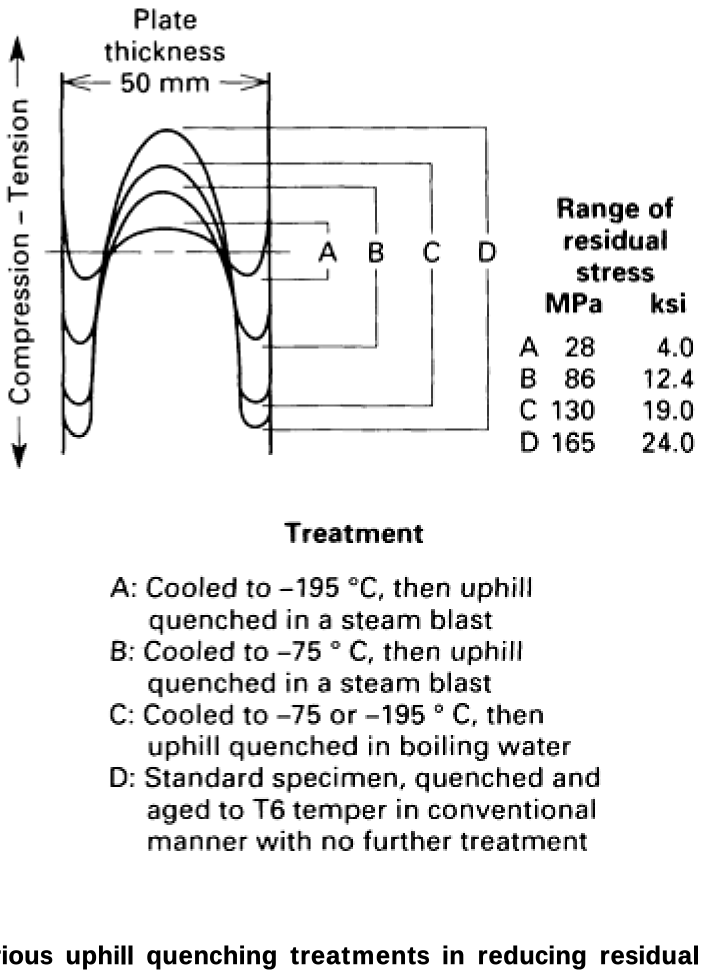
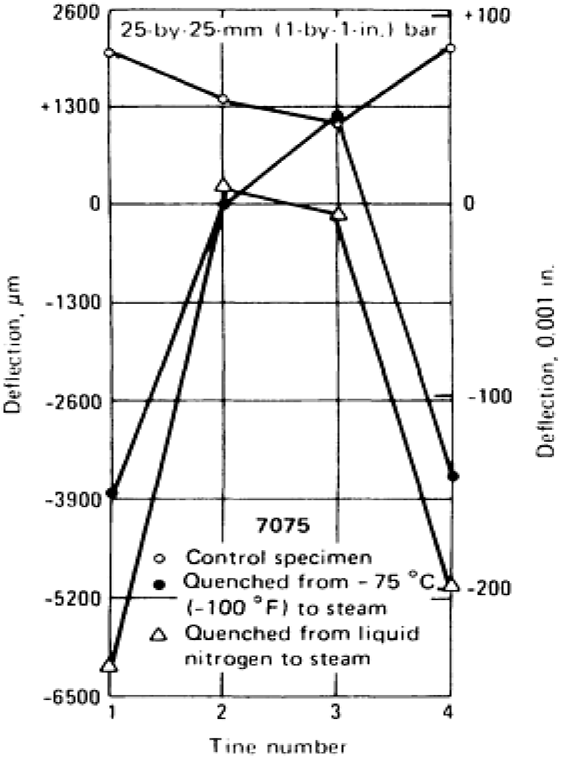
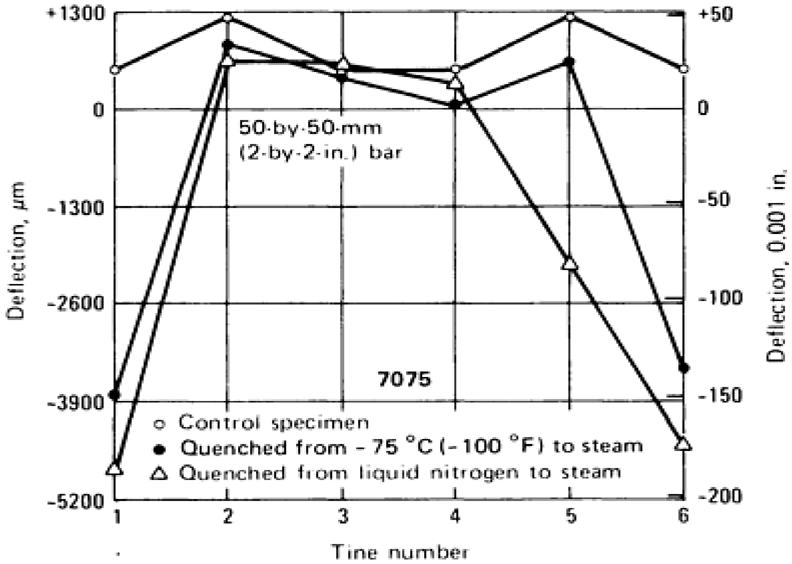
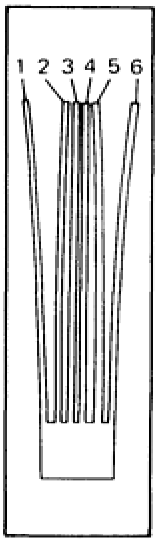


Fig. 29 Effectiveness of various uphill quenching treatments in reducing residual quenching stresses in 2014 plate. Note: uphill quenching treatments (single-cycle only) were applied from $\frac{1}{2}$ to $1\frac{1}{2}$ h after quenching from the recommended solution-treating temperature. All specimens were aged to the T6 temper after uphill quenching.

This process will not solve all problems of warpage in machining. It may reduce warpage internally but increase warpage of the extreme outer layers, although in the opposite direction (Fig. 30). Also, the effect of the altered residual-stress pattern on performance must be evaluated carefully for each part. This is particularly important for parts subjected to cyclic loading or exposed to corrosive environments such as marine atmospheres, especially if the process is introduced after the start of production and original performance tests are not repeated. Further disadvantages are the cost and hazard involved in handling liquid nitrogen and live steam.


25-by-25-mm (1-by-1-in.) bar
2600
+1300
0
-1300
-2600
-3900
-5200
-6500
+100
0
-100
-200
Deflection, μm
Deflection, 0.001 in.
7075
○ Control specimen
● Quenched from − 75 °C (−100 °F) to steam
△ Quenched from liquid nitrogen to steam
1
2
3
4
Tine number


+1300
0
-1300
-2600
-3900
-5200
+50
0
-50
-100
-150
-200
50-by-50-mm
(2-by-2-in.) bar
Deflection, μm
Deflection, 0.001 in.
7075
○ Control specimen
● Quenched from − 75 °C (−100 °F) to steam
△ Quenched from liquid nitrogen to steam
1
2
3
4
5
6
Tine number


1 2 3 4 5 6

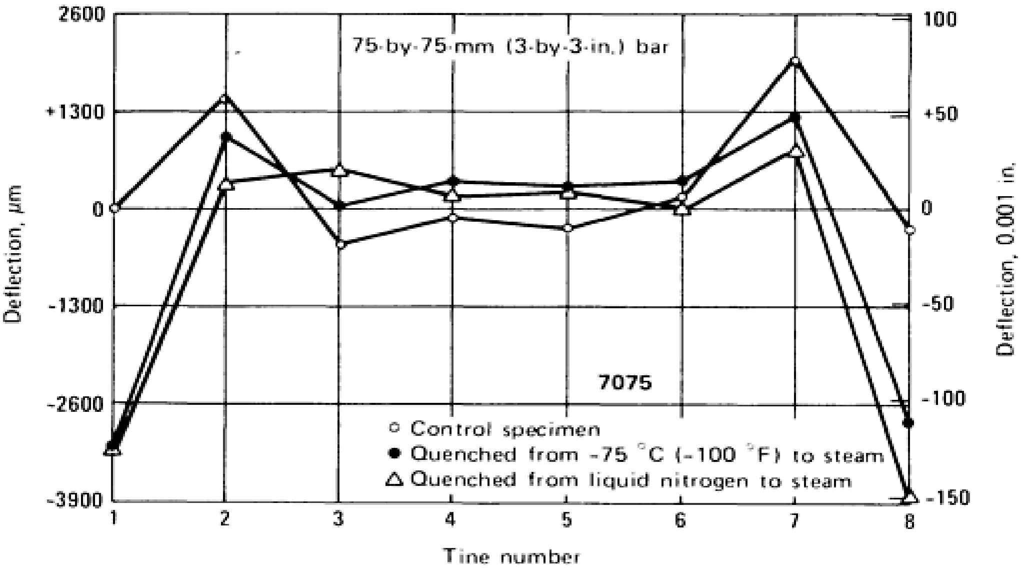

2600
+1300
0
-1300
-2600
-3900
100
+50
0
-50
-100
-150
75-by-75-mm (3-by-3-in.) bar
Deflection, μm
Deflection, 0.001 in.
7075
○ Control specimen
● Quenched from −75 °C (−100 °F) to steam
△ Quenched from liquid nitrogen to steam
1
2
3
4
5
6
7
8
Tine number

Fig. 30 Effect of uphill quenching on deflection of tines. Six-tine specimen was machined from 50 by 50 mm (2 by 2 in.) bar. Similar specimens machined from 25 by 25 mm (1 by 1 in.) and 75 by 75 mm (3 by 3 in.) bars had four and eight tines, respectively.

Effects of Reheating

The precipitation characteristics of aluminum alloys must be considered frequently during evaluation of the effects of reheating on mechanical properties and corrosion resistance. Such evaluations are necessary for determining standard practices for manufacturing operations, such as hot forming and straightening, adhesive bonding, and paint and dry-film lubricant curing, and for evaluating the effects of both short-term and long-term exposure in elevated temperatures in service.

The stage of precipitation that exists in an alloy at the time of reheating plays a significant role in the effects of reheating. Consequently, it is extremely dangerous to reheat material in a solution heat-treated temper without first carefully testing the effects of such reheating. In one such test, 2024-T4 sheet was found to be very susceptible to intergranular corrosion when subjected to a 15-min drying operation at 150 °C (300 °F) during the first 8 h after quenching; no susceptibility was evident when the same drying operation was performed more than 16 h after quenching. In another test, 7075-W (0.2 to 600 h) bar and plate were reheated for hot forming at 175 °C (350 °F) for 20 min. Strengths after aging to the T6 temper were 10 to 15% lower than those for standard 7075-T6. In contrast, similar reheating of T6 material for up to 1 h at 175 °C (350 °F) produced no detrimental effect.

If reheating is performed on material in the W or T4 condition, its effect can be estimated from families of precipitation heat-treating curves such as those presented in Fig. 22(a), 22(b), 22(c), and 22(d). Such curves can also be used for reheating of precipitation heat-treated material at the precipitation heat-treating temperature. For reheating at other temperatures, other data may be needed (Fig. 31). The heat-treating and reheating curves may be used as the bases for limitations on reheating (Table 9).

Table 9 Reheating schedules for wrought aluminum alloys

The schedules given in this table normally will not decrease strength more than 5%.

Alloy and temper	Reheating time at a temperature of:						
	150 °C (300 °F)	**165 °C (325 °F)**	**175 °C (350 °F)**	**190 °C (375 °F)**	**205 °C (400 °F)**	**220 °C (425 °F)**	230 °C (450 °F)
2014-T4	(a)	(a)	(a)	(a)	(a)	(a)	**(a)**
2014-T6	2-50 h	8-10 h	2-4 h	$\frac{1}{2}$-1 h	5-15 min	(b)	**(b)**
2024-T3, 2024-T4	(a)	(a)	(a)	(a)	(a)	(a)	**(a)**
2024-T81, 2024-T86	20-40 h	. . .	2-4 h	1 h	$\frac{1}{2}$ h	15 min	**5 min**

7075-T6, 7178-T6	**10-12 h**	**1-2 h**	**1-2 h**	**$\frac{1}{2}$-1 h**	**5-10 min**	(b)	(a)

(a) Reheating not recommended.

(b) Bring to temperature

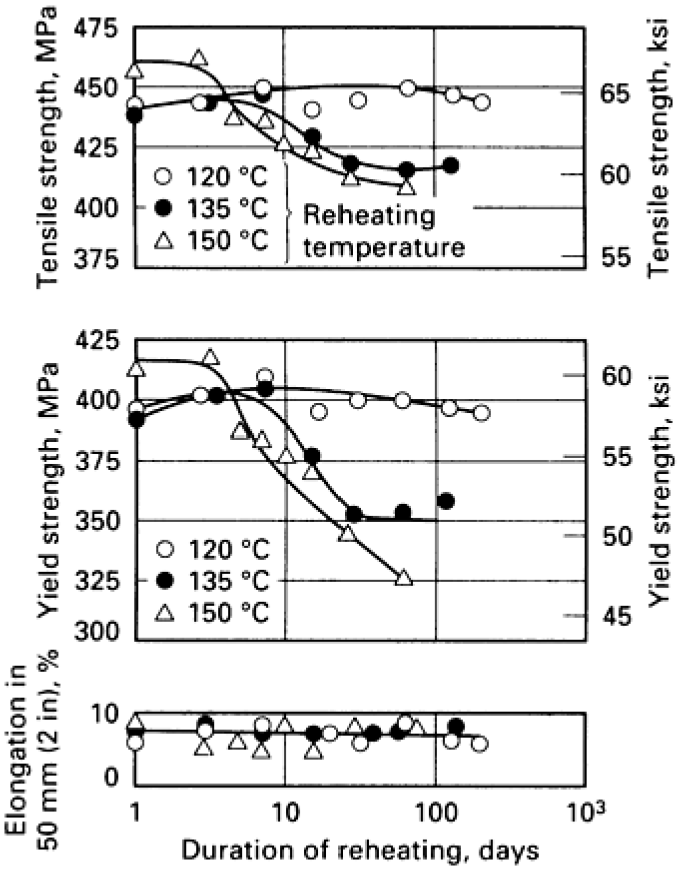


Fig. 31 Effects of reheating on tensile properties of alclad 2024-T81 sheet

Annealing

Annealing treatments employed for aluminum alloys are of several types that differ in objective. Annealing times and temperatures depend on alloy type as well as on initial structure and temper.

Full Annealing. The softest, most ductile, and most workable condition of both non-heat-treatable and heat-treatable wrought alloys is produced by full annealing to the temper designated "O." Strain-hardened products in this temper normally become recrystallized, but hot-worked products may remain unrecrystallized. In the case of heat-treatable alloys, the solutes are sufficiently thoroughly precipitated to prevent natural age hardening. A higher maximum temperature than that used for stress-relief annealing, controlled cooling to a lower temperature, and additional holding time at the lower temperature generally are employed.

For both heat-treatable and non-heat-treatable aluminum alloys, reduction or elimination of the strengthening effects of cold working is accomplished by heating at a temperature from about 260 to about 440 °C (500 to 825 °F). The rate of softening is strongly temperature-dependent; the time required to soften a given material by a given amount can vary from hours at low temperatures to seconds at high temperatures.

If the purpose of annealing is merely to remove the effects of strain hardening, heating to about 345 °C (650 °F) will usually suffice. If it is necessary to remove the hardening effects of a heat treatment or of cooling from hot-working temperatures, a treatment designed to produce a coarse, widely spaced precipitate is employed. This usually consists of soaking at 415 to 440 °C (775 to 825 °F) followed by slow cooling (28 °C/h, or 50 °F/h, max) to about 260 °C (500 °F). The high diffusion rates that exist during soaking and slow cooling permit maximum coalescence of precipitate particles and result in minimum hardness.

As a result of this treatment, only partial precipitation occurs in 7*xxx* alloys, and a second treatment (soaking at 230 ±6 °C, or 450 ± 10 °F, for 2 h) is required. When the need arises for small additional improvements in formability, cooling at 28 °C/h (50 °F/h) should be extended to 230 °C (450 °F), and the material should be soaked at 230 °C for 6 h. The effects of eliminating or prolonging the 230 °C second step on the ductility of 7075-O sheet are compared with the standard treatment in Table 10.

Table 10 Effects of annealing treatments on ductility of 7075-O sheet

Annealing treatment	**Elongation in tension[(a)], % in 50 mm (2 in.) for thickness of:**			**Bend angle[(b)], degrees, for thickness of:**		Elongation in bending[(c)], % in 50 mm (2 in.) for thickness of:	
	0.5 mm (0.020 in.)	**1.6 mm (0.064 in.)**	**2.6 mm (0.102 in.)**	**1.6 mm (0.064 in.)**	**2.6 mm (0.102 in.)**	**1.6 mm (0.064 in.)**	2.6 mm (0.102 in.)
Treatment 1[(d)]	12	12	12	82	73	48	**50**
Treatment 2[(e)]	14	14	14	91	76	58	**57**
Treatment 3[(f)]	**16**	**16**	**. . .**	**92.5**	**84**	**56**	**60**

(a) Uniform elongation of gridded tension specimens.

(b) Bend angle at first fracture.

(c) Elongation in bend test for 1.3 mm (0.05 in.) gage spanning fracture.

(d) Soak 2 h at 415 ± 14 °C (775 ± 25 °F); furnace cool to 260 °C (500 °F) at 30 °C/h (50 °F/h); air cool.

(e) Soak 2 h at 425 °C (800 °F), air cool; soak 2 h at 230 °C (450 °F), air cool.

(f) Soak 1 h at 425 °C (800 °F); furnace cool to 230 °C (450 °F) at 30 °C/h (50 °F/h); soak 6 h at 230 °C (450 °F), air cool

In annealing, it is important to ensure that the proper temperature is reached in all portions of the load; therefore, it is common to specify a soaking period of at least 1 h. The maximum annealing temperature is moderately critical; it is advisable not to exceed 415 °C (775 °F), because of oxidation and grain growth. The heating rate can be critical, especially for alloy 3003, which usually requires rapid heating for prevention of grain growth. Relatively slow cooling, in still air or in the furnace, is recommended for all alloys to minimize distortion. Typical annealing conditions used for some alloys in common use are listed in Table 11.

Table 11 Typical full annealing treatments for some common wrought aluminum alloys

These treatments, which anneal the material to the O temper, are typical for various sizes and methods of manufacture and may not exactly describe optimum treatments for specific items.

Alloy	**Metal temperature**		Approximate time at temperature, h
	°C	**°F**	
1060	345	650	[a]
1100	345	650	[a]
1350	345	650	[a]
2014	415[b]	775[b]	**2-3**
2017	415[b]	775[b]	**2-3**
2024	415[b]	775[b]	**2-3**
2036	385[b]	725[b]	**2-3**
2117	415[b]	775[b]	**2-3**
2124	415[b]	775[b]	**2-3**
2219	415[b]	775[b]	**2-3**
3003	415	775	[a]
3004	345	650	[a]
3105	345	650	[a]
5005	345	650	[a]
5050	345	650	[a]
5052	345	650	[a]
5056	345	650	[a]
5083	345	650	[a]

5086	345	650	[(a)]
5154	345	650	[(a)]
5182	345	650	[(a)]
5254	345	650	[(a)]
5454	345	650	[(a)]
5456	345	650	[(a)]
5457	345	650	[(a)]
5652	345	650	[(a)]
6005	415[(b)]	775[(b)]	**2-3**
6009	415[(b)]	775[(b)]	**2-3**
6010	415[(b)]	775[(b)]	**2-3**
6053	415[(b)]	775[(b)]	**2-3**
6061	415[(b)]	775[(b)]	**2-3**
6063	415[(b)]	775[(b)]	**2-3**
6066	415[(b)]	775[(b)]	**2-3**
7001	415[(c)]	775[(c)]	**2-3**
7005	345[(d)]	650[(d)]	**2-3**
7049	415[(c)]	775[(c)]	**2-3**
7050	415[(c)]	775[(c)]	**2-3**
7075	415[(c)]	775[(c)]	**2-3**
7079	415[(c)]	775[(c)]	**2-3**

7178	415[c]	775[c]	**2-3**
7475	415[c]	775[c]	**2-3**
Brazing sheet			
No. 11 and 12	345	650	[a]
No. 21 and 22	345	650	[a]
No. 23 and 24	**345**	**650**	[a]

(a) Time in the furnace need not be longer than necessary to bring all parts of the load to appealing temperature. Cooling rate is unimportant.

(b) These treatments are intended to remove the effects of solution treatment and include cooling at a rate of about 30 °C/h (50 °F/h) from the annealing temperature to 260 °C (500 °F). Rate of subsequent cooling is unimportant. Treatment at 345 °C (650 °F), followed by uncontrolled cooling, may be used to remove the effects of cold work or to partly remove the effects of heat treatment.

(c) These treatments are intended to remove the effects of solution treatment and include cooling at an uncontrolled rate to 205 °C (400 °F) or less, followed by reheating to 230 °C (450 °F) for 4 h. Treatment at 345 °C (650 °F), followed by uncontrolled cooling, may be used to remove the effects of cold work or to partly remove the effects of heat treatment.

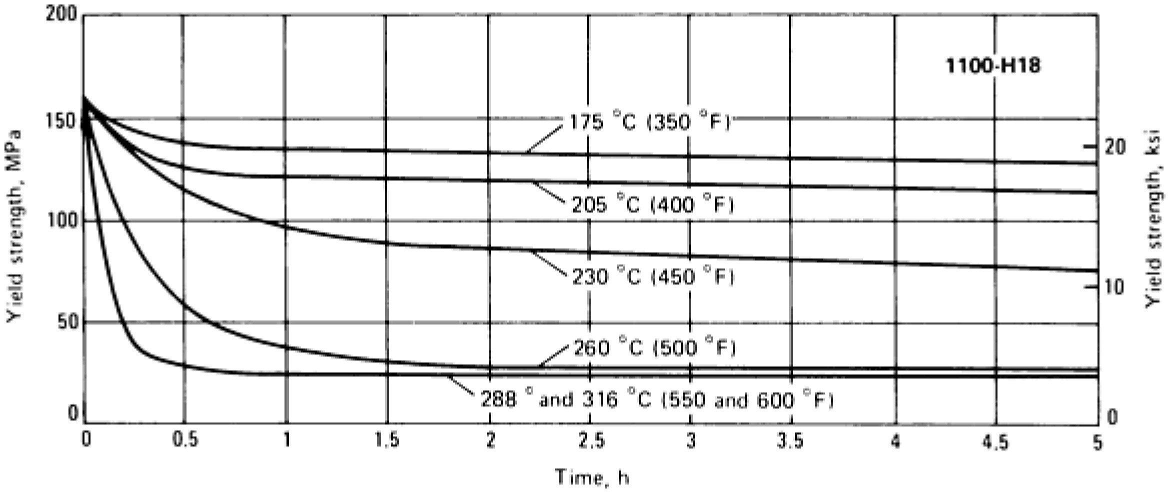
(d) Cooling rate to 205 °C (400 °F) or below is less than or equal to 30 °C/h (50 °F/h).

Products that can be heated and cooled very rapidly, such as wire, are annealed by continuous processes that require a total heating and cooling time of only a few seconds. Continuous annealing of coiled sheet is accomplished in a total time of a few minutes. For these extremely rapid operations, maximum temperature may exceed 440 °C (825 °F).

Although material annealed from the precipitation-hardened condition usually has sufficient ductility for most forming operations, this ductility often is slightly lower than that of material that has not been subjected to prior heat treatment--that is, material annealed at the producing source. Therefore, when maximum ductility is required, annealing of a previously heat-treated product is sometimes unsuccessful.

Partial Annealing. Annealing of cold-worked non-heat-treatable wrought alloys to obtain intermediate mechanical properties (H2-type tempers) is referred to as partial annealing or recovery annealing. Temperatures used are below those that produce extensive recrystallization, and incomplete softening is accomplished by substructural changes in dislocation density and rearrangement into cellular patterns (polygonization). Bendability and formability of an alloy annealed to an H2-type temper generally are significantly higher than those of the same alloy in which an equal strength level is developed by a final cold-working operation (H1-type temper). Treatments to produce H2-type tempers require close control of temperature to achieve uniform and consistent mechanical properties.

Figure 32 shows changes in yield strength as functions of temperature and time for sheet of two non-heat-treatable alloys (1100 and 5052) initially in the highly cold-worked condition (H18 temper). From these curves, it is apparent that, by selection of appropriate combinations of time and temperature, mechanical properties intermediate to those of cold-worked and fully annealed material can be obtained. It is also evident that yield strength depends much more strongly on temperature than on time of heating.



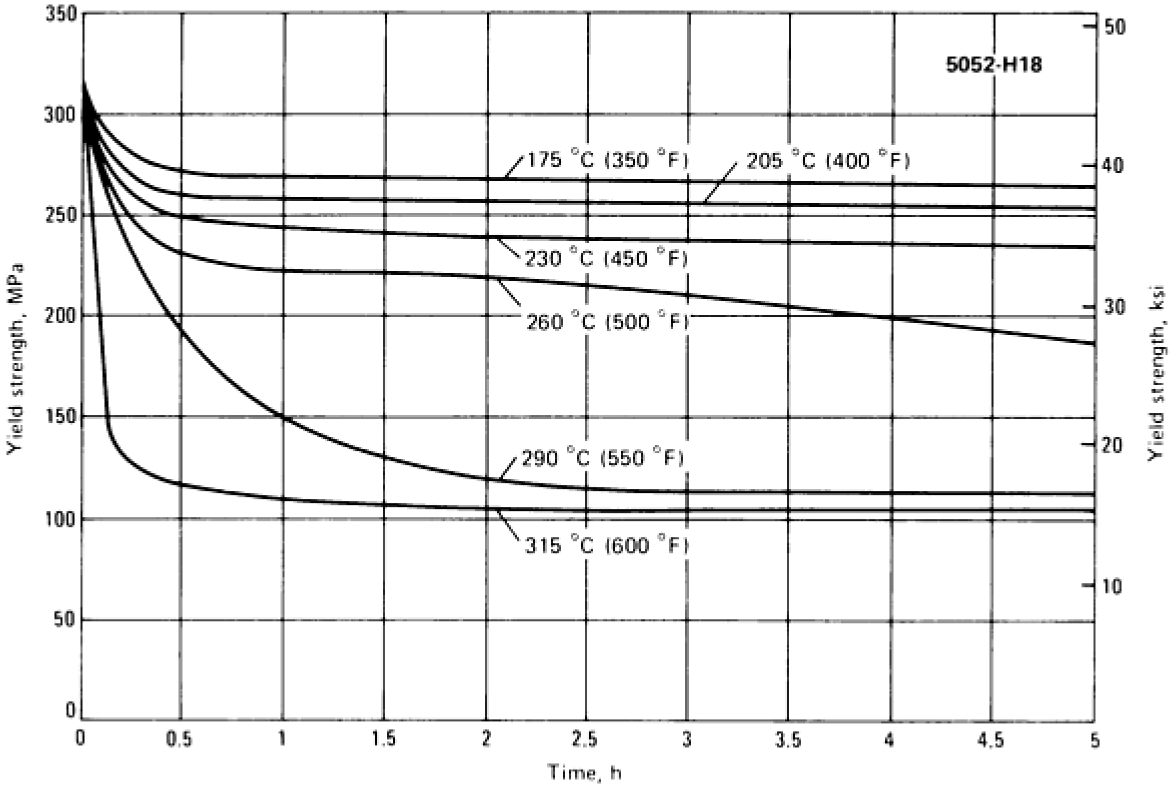


Fig. 32 Representative isothermal annealing curves for alloys 1100-H18 and 5052-H18

Stress-Relief Annealing. For cold-worked wrought alloys, annealing merely to remove the effects of strain hardening is referred to as stress-relief annealing. Such treatments employ temperatures up to about 345 °C (650 °F), or up to 400 ± 8 °C (750 ± 15 °F) for 3003 alloy, and cooling to room temperature. No appreciable holding time is required. Such treatment may result in simple recovery, partial recrystallization, or full recrystallization. Age hardening may follow stress-relief annealing of heat-treatable alloys, however, because a concentration of soluble alloying elements sufficient to cause natural aging remains in solid solution after such treatments.

A special form of stress-relief temper is used for heat-treatable alloy products that subsequently will be inspected ultrasonically. The product is heated to its normal solution heat-treating temperature, then cooled in still air to room temperature. This temper is referred to as the O1 temper.

Controlled-Atmosphere Annealing and Stabilizing. Aluminum alloys that contain even very small amounts of magnesium will form a surface magnesium oxide unless the atmosphere in the annealing furnace is free of moisture and oxygen. Examples include alloy 3004, which is used for cooking utensils, and alloys of the 5*xxx* series.

Another problem that control of the annealing atmosphere helps to overcome or avoid is oil staining by oil-base roll lubricants that do not burn off at lower annealing temperatures. If the oxygen content of the furnace atmosphere is kept very low during such annealing, the oil will not oxidize and stain the work.

Temperature control for full and partial annealing is somewhat more critical than for stress-relief annealing; the temperatures and times specified are selected to produce recrystallization and, in the case of heat-treatable alloys, a precipitate of maximum size; for this the cooling rate must be closely controlled. Even allowing the load to cool in the furnace may result in an excessively high rate. Similarly, lowering the furnace-control instrument by 28 °C (50 °F) each hour may produce stepped cooling, which is not satisfactory for severe forming operations. For maximum softening, a continuous cooling rate of not more than 28 °C/h (50 °F/h) is recommended.

Annealing of castings for 2 to 4 h at temperatures from 315 to 345 °C (600 to 650 °F) provides the most complete relief of residual stresses and precipitation of the phases formed by the excess solute retained in solid solution in the as-cast condition. Such annealing treatments provide maximum dimensional stability for service at elevated temperatures. The annealed temper is designated "O." (This temper was designated "T2" prior to 1975.)

Grain Growth

Many of the aluminum alloys in common use are subject to grain growth during solution treatment or annealing. This phenomenon can occur during or after recrystallization of material that has been subjected to a small critical amount of prior cold work. It is usually manifested by surface roughening during subsequent fabrication operations and frequently results in rejections for appearance or functional reasons. Less frequently, some deterioration of mechanical properties is encountered, and this is undesirable regardless of surface-roughening effects.

Degree of susceptibility to grain growth varies with alloy, structure, and chemical-composition variation, and from one product form to another. The critical range of cold work is ordinarily about 5 to 15%. Usually, temperatures of 400 °C (750 °F) and above must be reached before grain growth occurs, but some growth has been encountered at temperatures as low as 345 °C (650 °F). Grain growth that occurs during initial recrystallization is more a function of composition, structure, and degree of cold work than of temperature per se; temperatures in excess of 455 °C (850 °F) in common alloys can lead to secondary-recrystallization grain-growth problems. The common symptom indicating moderately large-grain material is roughening or "orange peel" on the external surfaces of bends. Severe growth of grains to fingernail size and larger sometimes is evident in parts made from annealed (O temper) material by stretch forming and then thermal treating or similar operations. This type of grain growth often is detected during subsequent anodizing, etching, and chemical milling operations.

Cracking during welding or brazing is another characteristic which may indicate that severe grain growth has occurred. In such instances, cracks propagate along grain boundaries that provide little obstruction to their progress.

If the surface roughening is objectionable from either an appearance or a functional aspect, the desirability of surface-smoothing operations, such as sanding or buffing, must be evaluated. If reductions in mechanical properties are suspected, these must be established by test and evaluated in relation to the anticipated service.

In one application, a part that had been made by stretch forming O-temper 2 mm (0.080 in.) sheet and heat treating exhibited significantly lower tensile and yield strengths in portions where severe grain growth had occurred than in portions having normal grain size:

Test	Grain structure	Tensile strength	Yield strength

	structure	MPa	ksi	MPa	ksi
Transverse					
1	Coarse	265	38.5	247	**35.8**
2	Coarse	263	38.2	241	**35.0**
3	Fine	311	45.1	261	**37.8**
Longitudinal					
1	Coarse	259	37.6	243	**35.3**
2	Coarse	269	39.0	245	**35.6**
3	**Fine**	**305**	**44.2**	**270**	**39.1**

In other similar investigations, no detrimental effects have been discovered, and in many cases such parts have served satisfactorily in critical applications.

When a grain-growth problem is discovered, it is too late to change the condition of the parts in question, but several possible methods are available for preventing recurrence of the difficulty. The simplest of these is relieving the causative stress by interjecting a stress-relief anneal into the manufacturing sequence immediately prior to the solution-treating or full-annealing cycle in which the grain growth occurred. This approach is usually successful and practical. Another possibility is to adjust the amount of stress present in the part immediately prior to the critical heat treatment so that the stress level is outside the critical range. This may be done by adding a cold-working operation before forming, such as pre-stretching of blanks, or by forming in multiple stages with a stress-relief anneal before each stage.

A third method that is sometimes successful consists of increasing the heating rate during the critical heat treatment by reducing the size of furnace loads or by changing from an air furnace to a salt bath. In one application, severe grain growth was found during bending of alloy 1100 rectangular tubing. The roughening of the inside surfaces of the parts, which occurred during forming of the large-grain material, impaired their functioning as radar waveguides. Investigation disclosed that, to minimize handling marks, the material was procured in the strain-hardened (H14) temper and was stress-relief annealed at 345 °C (650 °F) immediately prior to forming. Grain growth occurred during annealing as a result of the moderate amount of cold work introduced at the mill. The problem was eliminated by changing the stress-relieving operation to a 5-min heating period in an air furnace operating at 540 °C (1000 °F). The explanation advanced for the success of this treatment was that, due to the rapid heating rate, the temperature of the material was raised through the recrystallization range for the less severely cold-worked grains before the critically cold-worked grains had time to grow appreciably.

Heating Equipment and Accessories

The general methods for heat treating aluminum alloys include the use of molten salt baths, air-chamber furnaces, and induction heaters. The choice of heating equipment depends largely on the alloy and the configuration of the parts to be processed. The type of heat treatment can also influence the choice of heating equipment. For example, both molten salt baths and air-chamber furnaces are suitable for solution treating of aluminum alloys, while induction heating requires additional analysis to define the proper temperature range for solution treatment. Induction methods can provide high heating rates, which affect transformation behavior (see, for example, the section "Nonequilibrium Melting" in this article).

Molten salt baths and air-chamber furnaces both have advantages and disadvantages in solution heat treatments, as discussed below. Oil- and gas-fired furnaces, in designs that allow the products of combustion to come in contact with the work, are usually unsatisfactory because they promote high-temperature oxidation.

Salt baths heat the work faster (see Table 2) than air furnaces, provided that the amount of work introduced at any one time is controlled to prevent the temperature from falling below the desired range. If the temperature is permitted to fall below the minimum limit, much of the advantage of the salt bath is lost, because of the necessity for reheating the large mass of salt.

Salt baths are also more readily adapted to the introduction, at any time, of small amounts of work requiring different soaking periods. (Economical utilization of air furnaces usually dictates accumulation of a large load of parts of similar thickness before charging.) Also, the buoyant effect of the salt reduces distortion during heating, and the large reservoir of heat facilitates temperature control and uniformity.

Salt bath operation entails special house-keeping requirements. Dragout is costly and unsightly. Because residual salt on parts may result in corrosion, all salt must be completely removed, including that from crevices and blind holes. In addition, salt residue from the quench water must be kept to a minimum by a constant water overflow or by providing a fresh-water rinse for all parts after quenching. When these provisions are impractical, corrosion can be inhibited by adding 14 g ($\frac{1}{2}$ oz) of sodium or potassium dichromate to each 45 kg (100 lb) of the molten salt.

Precautions. Molten salt baths are potentially hazardous and require special precautions. Operators must be protected from splashing and dripping of the hot salt. Because heated nitrates are powerful oxidizing agents, they must never by allowed to come in contact with combustibles and reducing agents, such as magnesium and cyanides. Most authorities advise against inserting aluminum alloys containing more than a few percent of magnesium into molten nitrate. To avoid exposure of personnel to nitrous fumes produced during decomposition of nitrates, good ventilation is essential.

When molten nitrates are being used, the possibilities of explosions resulting from both physical and chemical reactions must be avoided. The former result from rapid expansion of gases entrapped beneath the surface of the bath. Hence, parts entering the bath must be clean and dry; they must also be free of pockets or cavities that contain air or other gases. Chemical-reaction explosions result from rapid breakdown of the nitrates due to overheating or reaction with the pot material. Stainless steel pots (preferably of type 321 or 347) are more resistant to scaling than those made of carbon steel or cast iron and therefore present a lower probability of local overheating. Sludge or sediment accumulations in bottom-heated pots can also lead to local overheating. Overheat controls are essential to ensure against temperatures exceeding 595 °C (1100 °F).

It is vitally important that water be kept away from a nitrate tank. In controlling a nitrate fire, do not use water or any fire extinguisher containing water. The best extinguisher is dry sand, a supply of which should be kept near the tank.

Extra sacks of salt should be stored in a dry place, distant from the tank. If the fresh salt being added to the bath is even slightly damp, it should be added very slowly or when the bath is frozen.

Air furnaces are used more widely than salt baths because they permit greater flexibility in operating temperature. When production schedules and the variety of alloys requiring heat treatment necessitate frequent changes in temperature, the time and cost of adjusting the temperature of a large mass of salt makes the use of an air furnace almost mandatory. However, waiting periods are often required to allow the walls of air furnaces to stabilize at the new temperature before parts are introduced. Otherwise, parts may radiate heat to colder walls or absorb radiant heat from hotter walls, and the temperature indicated by the control instrument will not reflect actual metal temperature in the usual manner. Air furnaces are also more economical when the product mix includes a few rather large parts; holding the temperature of a large volume of salt in readiness for an occasional large part is far more expensive than heating an equal volume of air.

Induction heating with either solenoid (longitudinal-flux) coils or transverse-flux coils provides an efficient method for in-line heating of flat-rolled products (particularly strip). Solenoid coils create a longitudinal flux, which can produce efficient heating for thicker and/or lower resistivity materials. Solenoid coils can also be used efficiently in the heating of thinner magnetic material (see, for example, steel below the Curie temperature in Table 12).

Table 12 Frequency selection for induction heating with a longitudinal-flux coil and a transverse-flux coil

Material	Minimum part thickness, mm (in.), for a frequency of:				
	60 Hz	**200 Hz**	**1 kHz**	**3 kHz**	10 kHz
Solenoid (longitudinal-flux) coil					
Steel below Curie temperature	>38 (1.5)	13 (0.5)	5 (0.2)	2.3 (0.09)	**1 (0.04)**
Steel above Curie temperature	>175 (7.0)	100 (4.0)	43 (1.7)	25 (1.0)	**13 (0.5)**
Brass	>50 (2.0)	28 (1.1)	13 (0.5)	7 (0.28)	**4 (0.16)**
Aluminum	>38 (1.5)	22 (0.85)	9 (0.375)	5 (0.2)	**3 (0.12)**
Transverse-flux coil					
Aluminum	>5 (0.2)	1.3 (0.05)	0.25 (0.01)	0.08 (0.003)	**0.04 (0.0016)**
Brass	>10 (0.4)	2.5 (0.1)	0.5 (0.02)	0.15 (0.006)	**0.08 (0.0032)**
Steel	**>50 (2.0)**	**13 (0.5)**	**2.5 (0. 1)**	**0.9 (0.035)**	**0.5 (0.020)**

For several nonferrous materials (aluminum, copper, brass), however, efficiency and power factors with solenoid coils are significantly lower than for ferrous materials. Therefore, transverse-flux coils are ideally suited for heating nonferrous materials, because transverse-flux lines do not exhibit the degree of current cancellation associated with longitudinal flux lines. This aspect of transverse-flux coils improves efficiency and also permits the use of lower frequencies (Table 12). This reduces the capital equipment costs, and where it shifts from requiring RF frequencies, the power source conversion efficiency is also significantly improved. Aluminum, brass, copper, and austenitic stainless steel strip lines are ideally suited for transverse-flux heating. Each of these materials often requires in-line processes like partial or full annealing or solution heat treating to provide necessary mechanical properties for subsequent finishing operations.

Transverse-flux induction heating offers several benefits for in-line strip heating and has been known for many years. However, it requires specially designed iron-cored laminated inductor coils and tighter control of the power, strip handling, and process parameters. Frequency selection is dictated by the resistivity and thickness of the material, while power requirements depend on the production rates, the specific heat, and the processing temperatures for a given material. Figure 33 shows typical power source requirements for transverse-flux heating of aluminum strip.

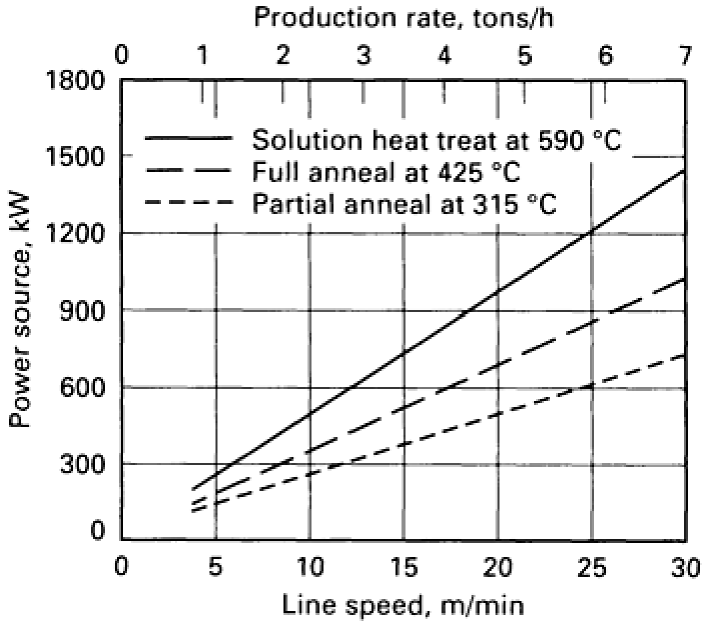


Fig. 33 Power requirement for transverse-flux induction heating of aluminum strip 1 mm (0.04 in.) thick and 1270 mm (50 in.) wide. Source: Ref 9

Reference cited in this section

9. G.F. Bobart, *J. Heat Treat.,* Vol 6 (No. 1), 1988, p 47-52

Furnace Temperature Control

The importance of close temperature control in solution treating has been noted in the previous section on solution treating. Each control zone of each furnace should contain at least two thermocouples. One thermocouple, with its instrument, should act as a controller, regulating the heat input; the other should act independently as a safety cutoff, requiring manual reset if its set temperature (usually the maximum of the specified range) is exceeded during the solution-treating cycle.

Safety cutoffs are mandatory for salt baths to guard against explosions and often have paid for themselves in air furnaces by saving a load of parts or even the furnace itself. It is important, however, that they be tested periodically (by deliberately overshooting the empty furnace) to guard against "frozen" corroded contacts resulting from prolonged periods of idleness.

At least one of the instruments for each zone should be of the recording type, and both instruments should have restricted scales--for instance, 400 to 600 °C (750 to 1110 °F), rather than 0 to 600 °C (32 to 1110 °F). This is required for maximum accuracy because manufacturers' guarantees are specified in terms of percent of scale.

In the placement of instruments, exposure to extremes in ambient temperature, humidity, vibration, dust, and corrosive fumes should be avoided. Ambient temperatures between 5 and 50 °C (40 and 120 °F) are satisfactory, but temperature changes of 6 °C/h (10 °F/h) or more should be avoided. It is also essential that instruments and thermocouple circuits be shielded from electromagnetic fields commonly associated with the leads of high-amperage furnace heating elements.

Temperature-sensing elements must be capable of responding more rapidly to temperature changes than the materials being processed. Therefore, thermocouple wire diameter should not exceed $1\frac{1}{2}$ times the thickness of the minimum-gage material to be heat treated, and should in no case exceed 14 gage. Thermocouples for salt baths should be enclosed in suitable protection tubes. Air-furnace thermocouples should be installed in open-end protection tubes, with the thermocouple junction extending sufficiently beyond the tube to prevent any loss in sensitivity.

Temperature-sensing elements should be located in the furnace work chamber, not in ducts and plenums, and should be as close as possible to the working zone. Specification MIL-H-6088C restricts distance between the sensing element and the working zone to a maximum of 100 mm (4 in.). The safety-cutoff thermocouple should be located to reflect the highest temperature in the working zone. The control thermocouple should be located in a position where it will read a temperature approximately halfway between the hottest and coldest temperatures.

Probe Checks. After the temperature-measurement equipment is properly installed, it must be checked frequently for accuracy. This is accomplished by inserting a calibrated probe thermocouple into the furnace adjacent to each furnace thermocouple and comparing its reading on a calibrated test potentiometer with that indicated by the furnace instrument. Correction factors should be applied after each probe check, but if the correction required exceeds ±3 °C (±5 °F), the source of the deviation should be corrected. MIL-H-6088 recommends that this check be made weekly, but many operators make the check as frequently as once each shift.

Temperature-Uniformity Surveys. In controlling the temperature of parts that are being heat treated it must first be determined that the temperature indicated by the furnace instruments truly represents the temperature of the nearby air or salt. Second, the uniformity of temperature within the working zone must be shown to be within a range of 11 °C, or 20 °F (6 °C, or 10 °F, for precipitation heat treatment of alloy 2024). This is accomplished by measuring the temperature at several test locations, using calibrated test thermocouples and a calibrated test potentiometer, and reading furnace instruments nearly simultaneously. MIL-H-6088 recommends monthly surveys with one test location per 1.1 m^3, or 40 ft^3 (0.7 m^3, or 25 ft^3, for air furnaces on initial survey), but with a minimum of nine test locations distributed as shown in Fig. 34. Despite the large size of some furnaces, rather surprising temperature uniformities have been reported. In one instance the initial survey of an air furnace measuring 12.5 by 1.2 by 3.0 m (41 by 4 by 10 ft) showed maximum temperature variations of +1.7, -1.1 °C (+3, -2 °F). When a partition 0.3 m (1 ft) thick was lowered, converting the furnace to two chambers 6.1 by 1.2 by 3.0 m (20 by 4 by 10 ft) each, the spread was +1.1, -0.6 °C (+2, -1 °F) in one section and +0.6, -1.1 °C (+1, -2 °F) in the other.

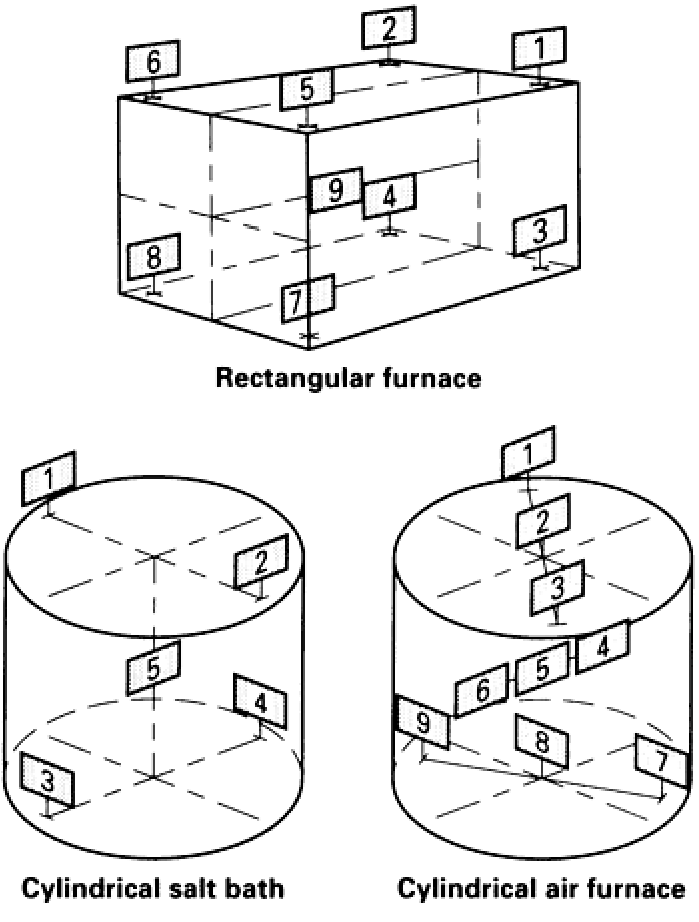


Fig. 34 Location of thermocouples for surveying temperature uniformity in the working zones of air furnaces and salt baths

For each furnace load, one thermocouple (the "cold" couple) should be placed in the coldest area of the furnace and another (the "hot" couple) in the hottest area. In addition to these two thermocouples, a load thermocouple should be installed. The load couple should be of approximately the same gage as the sheet or other product being heat treated. If heavy plate, forgings, or castings are being heat treated, a similar discarded item should be used at the controlling load couple. The thermocouple should be placed in a drilled hole and packed to hold it firmly in place during the heat-treating cycle. In some instances, the items being heat treated can be used as the load couples. The thermocouples can be placed in holes drilled in areas that will be removed in making the finished article.

It is important that items of different thicknesses--1 mm (0.040 in.) sheet and 25 mm (1 in.) plate, for example--not be heat treated in the same furnace load.

In salt baths, uniformity surveys usually are made by holding a probe thermocouple in each location until thermal equilibrium is reached; in air furnaces, a mock heat-treating cycle is required. First, the air furnace is stabilized at the test temperature. Then a rack containing the test thermocouples is inserted into the furnace. By using multiple switches or a multipoint recording instrument, all test thermocouples and furnace instruments are read every 5 min. As the temperature approaches the test range, it is advisable to increase the frequency of readings to detect possible overshooting. After thermal equilibrium is reached, readings should be continued until the recurrent temperature pattern is established.

Surveys of salt baths generally are considered acceptable whether they are made while the bath is empty or filled with work. It is controversial whether surveys of air furnaces should be made with or without a load. Undoubtedly, recovery overshoots are most likely to occur with a very light load and would not be detected if a heavier load were used. Certainly, if all loads are essentially alike, surveys should be made with typical loads. With widely varying loads, the optimum approach is to make several surveys initially, including one with an empty furnace, and then to make succeeding surveys with an empty furnace to ensure against changes in furnace characteristics. If any changes are made in the furnace that might affect temperature distribution, such as repair of vanes or louvers, several surveys should be repeated.

Another aspect of the problem of temperature control in air furnaces is the necessity of ensuring that the temperature of the parts is the same as that of the surrounding air. Furnace components whose temperature differs from the air temperature must be suitably shielded to prevent radiation to or from the parts being heat treated. In a furnace used for solution heat treating of rivets, unshielded heating elements have been known to produce part temperatures as much as 20 °C (35 °F) higher than the control temperature, resulting in eutectic melting and cracking. In two other instances, reradiation through inadequate shielding produced a radiation effect of as much as 11 °C (20 °F). One of these problems was solved by painting the shield with reflective aluminum paint and the other by adding a 13 mm ($\frac{1}{2}$ in.) thick layer of asbestos to the 1.6 mm ($\frac{1}{16}$ in.) stainless steel shield.

Furnace-wall temperatures that differ appreciably from the temperature of the parts also must be avoided. Consequently, when the operating temperature of an air furnace is changed, waiting periods are required after the furnace instrument indicates stability, to allow the furnace walls to stabilize at the new temperature. The magnitude of this limitation is directly proportional to the efficiency of the furnace as an insulated chamber, but possibilities of such radiation should be recognized even in thin-wall furnaces.

Radiation effects are potentially dangerous because they often cannot be detected by ordinary thermocouples. Specially prepared radiation panels with thermocouples attached are used, and their readings are compared with adjacent free thermocouples. These panels normally are made of material of the same gage as the thinnest parts to be heat treated and should have a single surface area of about 650 cm^2 (100 $in.^2$). A thermocouple is attached to the center of the panel by welding or peening. In order to detect the maximum effect, panel surfaces should be darkened so that their emissivity is at least as high as that of any material to be processed. During the test, the panel surfaces should be parallel to the suspected source or recipient of radiation. As an example of the number of panels required, several aerospace companies specify one panel for every 1.5 linear meters (5 linear feet) of furnace wall.

Instrument Calibration. All instruments and thermocouples must be accurately calibrated, and it is essential that the calibrations be traceable directly to the National Bureau of Standards. The chain of traceability should consist of not more than four links for sensing elements and three links for measuring elements. To illustrate, if the article calibrated by the National Bureau of Standards is called a primary standard, then the chain of traceability of measuring elements should consist of primary standard, test potentiometer, and furnace instrument. Similarly, the chain for sensing elements should consist of primary standard, secondary standard, test thermocouple, and furnace thermocouple. Every effort should be

made to ensure that the temperature indicated by the furnace instruments is as close as possible to the actual temperature. To achieve this, it is necessary to apply correction factors obtained during calibration to the next lower echelon of accuracy. Even then, if all errors inherent in the chain are in the same direction, a considerable difference will exist between the measured and actual temperatures. Therefore, it is advisable to operate as close to the mean of the desired range as possible.

Dimensional Changes during Heat Treatment

In addition to the completely reversible changes in dimensions that are simple functions of temperature change and are caused by thermal expansion and contraction, dimensional changes of more permanent character are encountered during heat treatment. These changes are of several types, some of mechanical origin and others caused by changes in metallurgical structure. Changes of mechanical origin include those arising from stresses developed by gravitational or other applied forces, from thermally induced stresses or from relaxation of residual stresses. Dimensional changes also accompany recrystallization, solution, and precipitation of alloying elements.

Solution Heat Treatment. Distortion as a result of creep during solution heat treatment should be avoided by proper loading of parts in baskets, racks, or fixtures, or by provision of adequate support for long pieces of plate, rod, bar, and extrusions heat treated in horizontal roller hearth furnaces. Sheet is provided with air-pressure support in continuous heat-treating furnaces to avoid scratching, gouging, and distortion. If parts are to be solution heat treated in fixtures or racks made of materials (such as steel) with coefficients of thermal expansion lower than that of the aluminum being treated, allowance should be made for this differential expansion to ensure that expansion of the aluminum is not restricted. Straightening immediately after solution heat treating may be preferable to fixturing.

Solution of phases formed by major alloying elements causes volumetric expansion or contraction, depending on the alloy system, and this may have to be taken into account in heat treatment of long pieces. For example, solution heat treatment and quenching of alloy 2219 causes lengthwise contraction of about 2 mm/m (0.002 in./in.). Solution heat treatment and quenching of alloys of the 7*xxx* series is accompanied by lengthwise expansion--about 0.6 mm/m (0.0006 in./in.) for alloy 7075 rod or plate.

Quenching. The most troublesome changes in dimensions and shape are those that occur during quenching or that result from stresses induced by quenching. Due to its nonuniform cooling, quenching may produce warpage or distortion, particularly in thin material and in thin sections of parts that contain variations in thickness. For thick-section products or parts, changes in external shape may be small because of rigidity, but the interior-to-surface temperature gradients that form with rapid cooling create residual stresses; these stresses normally are compressive at the surfaces and tensile in the interior.

As previously discussed, warpage or distortion of thin-section material can be reduced by using a quenching medium that provides slower cooling; however, cooling must be sufficient to produce the required properties. Slower quenching can also reduce the magnitude of residual stresses in thicker parts or pieces, as shown in Fig. 9 for cylindrical specimens of alloy 6151 quenched in cold or boiling water. Stress range (maximum tensile stress plus maximum compressive stress) for a cylinder with a radius of 89 mm (3.5 in.) is about 205 MPa (30 ksi) when the cylinder is quenched in cold water but less than 70 MPa (10 ksi) when it is quenched in boiling water. The effects of average cooling rate through the temperature range from 400 to 290 °C (750 to 550 °F) on longitudinal stress ranges developed in alloy 2014 cylinders 75 mm (3 in.) in diameter are shown in Fig. 35.

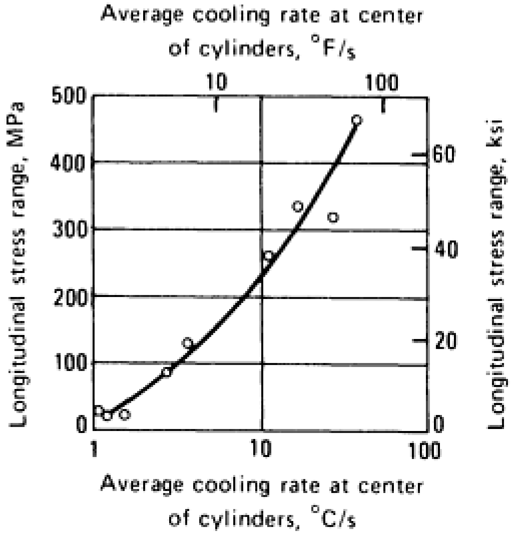


Fig. 35 Effect of quenching rate on longitudinal stress ranges in alloy 2014-T4 cylinders quenched in various media. Cylinders were 75 mm (3 in.) in diameter by 230 mm (9 in.) long. Cooling rate was measured from 400 to 290 °C (750 to 555 °F). Stress range is maximum tensile stress plus maximum compressive stress.

High stresses induced by rapid quenching generally are reduced only modestly by the precipitation heat treatments used to produce T6- or T8-type tempers. Consequently, for the alloys that require rapid cooling to develop the properties of these tempers, those incorporating mechanical stress relief (T*x*51, T*x*52) usually are specified when substantial metal must be removed to produce final shapes. Other T8-type tempers, such as T86 and T87, also have low residual stress as a result of the stretching required to produce them.

Heat Treatments for Precipitation and Stabilization. The most significant dimensional changes associated with precipitation heat treatments and stabilizing heat treatments arise from concurrent dilution of the solid solution (which changes lattice parameter) and formation of precipitate. Changes in density and specific volume resulting from these changes in metallurgical structure are the reverse of those caused by solution of the alloy phases. However, because the strongest tempers are those in which the precipitate is present in nonequilibrium transition forms, the amount of change during precipitation heat treatment does not totally compensate for the previous (and opposite) change that occurred during solution heat treatment. Most of the heat-treatable alloys expand (grow) during precipitation heat treatment. Exceptions are alloys of the 7*xxx* wrought series and the 7*xx*.0 casting series, which exhibit contraction.

In alloys of the 2*xxx* series, the amount of growth decreases with increasing magnesium content. Thus, growth of about 1.5 mm/m (0.0015 in./in.) can be expected during precipitation heat treatment of alloy 2219-T87, about 0.5 mm/m (0.005 in./in.) for treatment of alloy 2014-T6 and less than 0. 1 mm/m (0.0001 in./in.) for treatment of alloy 2024-T851. Alloys 7050 and 7075, on the other hand, contract about 0.3 mm/m (0.0003 in./in.) on precipitation heat treating from the W temper to the T6 temper and about 0.7 mm/m (0.0007 in./in.) on treating from the W temper to the T73 temper.

Stabilizing T7-type treatments cause greater amounts of growth than the T5-, T6-, or T8-type treatments for the same alloys. This increased growth is associated either with formation of increased amounts of transition precipitates or with transformation of transition precipitates to equilibrium phases.

Dimensional Stability in Service

Dimensional stability of heat-treated parts in service depends on alloy, temper, and service conditions. Of the latter, excluding mechanical conditions such as applied loads, the most important is service temperature range relative to the range in which precipitation occurs. Residual stresses constitute another source of dimensional changes. Stress relief minimizes changes due to residual stresses, and most mill products usually are supplied in tempers that include stress relief. Potential dimensional change as a result of further precipitation in parts that operate at elevated temperatures is minimized for wrought products by use of T7-type stabilizing treatments and for castings by use of T5-type treatments. However, components of high-precision equipment, such as instruments for aerospace guidance systems and optical and

telescopic devices, may require special supplementary treatments during manufacture to further reduce stresses or subsequent precipitation. (These treatments are discussed below, under "Stability of Precision Equipment.")

The T3- and T4-type tempers are the least stable dimensionally because of possible precipitation in service. Alloys 2024 and its variants have the smallest dimensional change in aging; the total change from the quenched to the average state is of the order of 0.06 mm/m (0.00006 in./in.), less than the change due to a temperature variation of 3 °C (5 °F). These alloys therefore can be used in the T3- and T4-type tempers, except for precision equipment. For all other alloys, T6- or T8-type tempers should be used, because in these tempers all the alloys have good dimensional stability.

Stability of Precision Equipment. Proper maintenance of high-precision devices, such as gyros, accelerometers, and optical systems, requires use of materials in which dimensional changes from metallurgical instability are limited from 10 μm/m (10 μin./in.). Several laboratory investigations and considerable practical experience have shown that wrought alloys 2024 and 6061 and casting alloy 356.0 are well suited and generally preferred for such applications. Dimensional changes were no greater than 10 μm/m when alloys 2024-T851 and -T62, 6061-T651 and -T62, and 356.0-T51, -T6, and -T7 were tested for more than a year at room temperature and for several months at 70 °C (160 °F), and then the same alloys were tested with repeated thermal cycling between 20 and -70 °C (68 and -94 °F).

Because stresses applied or induced by acceleration in such devices generally are not high, strength levels lower than those of the highest-strength tempers frequently are satisfactory. To increase precision of machining to intended dimensions, as well as to promote maximum stability, it is common practice to apply additional thermal treatments for stress relief and precipitation of 1 to 2 h at temperatures of 175 to 205 °C (350 to 400 °F) after rough machining. These additional treatments sometimes are repeated at successive stages of processing, and even after final machining. In addition, it has been claimed that one or two cyclic treatments consisting of cooling to -100 °C (-150 °F), holding for 2 h, heating to 232 to 240 °C (450 to 465 °F) and again holding for 2 h can improve dimensional stability of 356-T6 castings.

Quality Assurance

Quality-assurance criteria that heat-treated materials must meet always include minimum tensile properties and, for certain alloys and tempers, adequate fracture toughness and resistance to detrimental forms of corrosion (such as intergranular or exfoliation attack) or to stress-corrosion cracking. All processing steps through heat treatment must be carefully controlled to ensure high and reliable performance.

Tensile Tests. In general, the relatively constant relationships among various properties allow the use of tensile properties alone as acceptance criteria. The minimum guaranteed strength is ordinarily that value above which it has been statistically predicted with 95% probability that 99% or more of the material will pass. The inherent variability within lots and among specimens from a given piece is shown in Fig. 36. Testing provides a check for evidence of conformance; process capability and process control are the foundations for guaranteed values.

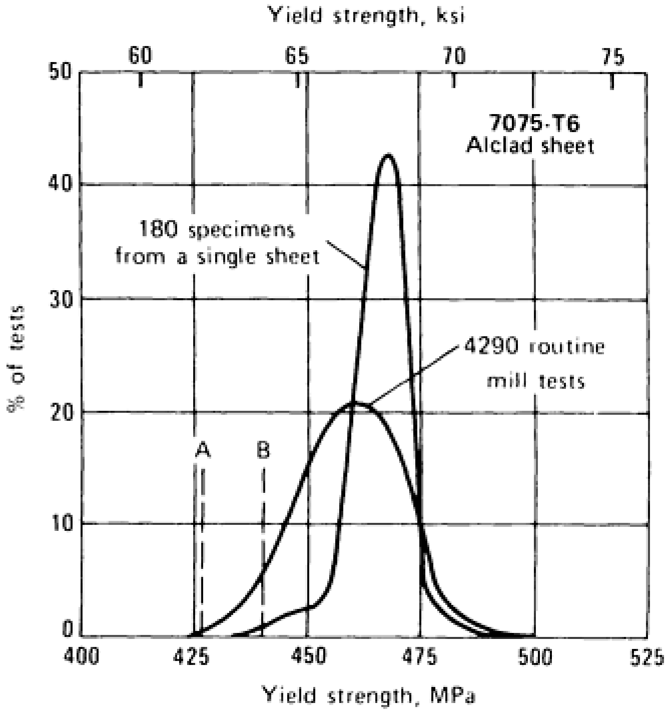


Fig. 36 Comparison of distribution of yield strength in heat-treated 7075-T6 clad sheet product with distribution in a single sheet. A is 95% probability that not more than 1% of all material will fall below this value; B is 95% probability that not more than 10% of all material will fall below this value. (A and B refer only to curve representing 4290 routine mill tests.)

Published minimum guaranteed values are applicable only to specimens cut from a specific location in the product, with their axes oriented at a specific angle to the direction of working as defined in the applicable procurement specification. In thick plate, for example, the guaranteed values apply to specimens taken from a plane midway between the center and the surface, and their axes parallel to the width dimension (long transverse). Different properties should be expected in specimens taken from other locations, or in specimens whose axes were parallel to thickness dimension (short transverse). However, the specified "referee" locations and orientations do provide a useful basis for lot-to-lot comparisons, and constitute a valuable adjunct to other process-control measures.

Tensile tests can be used to evaluate the effects of changes in the process, provided specimens are carefully selected. A variation in process that produces above-minimum properties on test specimens, however, is not necessarily satisfactory. Its acceptability can be judged only by comparing the resulting properties with those developed by the standard process on similarly located specimens. Finally, variations in heat-treating procedure are likely to affect the relationships among tensile properties and other mechanical properties. In applications where other properties are more important than tensile properties, the other properties should be checked also.

Hardness tests are less valuable for acceptance and rejection of heat-treated aluminum alloys than they are for steel. Nevertheless, hardness tests have some utility for process control. Typical hardness values for various alloys and tempers are given in Table 13. Figure 37 shows the general relationship between longitudinal tensile strength and hardness for aluminum alloys.

Table 13 Typical acceptable hardness values for wrought aluminum alloys

Acceptable hardness does not guarantee acceptable properties; acceptance should be based on acceptable hardness plus written evidence of compliance with specified heat-treating procedures. Hardness values higher than the listed maximums are acceptable provided that the material is positively identified as the correct alloy.

Alloy and temper	**Product form**[(a)]	Hardness

		HRB	**HRE**	**HRH**	HR15T
2014-T3, -T4, -T42	All	65-70	87-95	. . .	**. . .**
2014-T6, -T62, -T65	Sheet[(b)]	80-90	103-110	. . .	**. . .**
	All others	81-90	104-110	. . .	**. . .**
2014-T61	All	. . .	100-109	. . .	**. . .**
2024-T3	Not clad[(c)]	69-83	97-106	111-118	**82.5-87.5**
	Clad, ≤1.60 mm (0.063 in.)	52-71	91-100	109-116	**80-84.5**
	Clad, >1.60 mm (0.063 in.)	52-71	93-102	109-116	**. . .**
2024-T36	All	76-90	100-110	. . .	**85-90**
2024-T4, -T42[(d)]	Not clad	69-83	97-106	111-118	**82.5-87.5**
	Clad, ≤1.60 mm (0.063 in.)	52-71	91-100	109-116	**80-84.5**
	Clad, >1.60 mm (0.063 in.)	52-71	93-102	109-116	**. . .**
2024-T6, -T62	All	74.5-83.5	99-106	. . .	**84-88**
2024-T81	Not clad	74.5-83.5	99-106	. . .	**84-88**
	Clad	. . .	99-106	. . .	**. . .**
2024-T86	All	83-90	105-110	. . .	**87.5-90**
6053-T6	All	. . .	79-87	. . .	**74.5-78.5**
6061 -T4[(d)]	Sheet	. . .	60-75	88-100	**64-75**
	Extrusions; bar	. . .	70-81	82-103	**67-78**
6061-T6	Not clad, 0.41 mm (0.016 in.)	. . .	. . .	. . .	**75-84**
	Not clad, ≥0.51 mm (0.020 in.)	47-72	85-97	. . .	**78-84**

	Clad	. . .	84-96	. . .	**. . .**
6063-T5	All	. . .	55-70	89-97	**62.5-70**
6063-T6	All	. . .	70-85	. . .	**. . .**
6151-T6	All	. . .	91-102	. . .	**. . .**
7075 -T6, -T65	Not clad[(e)]	85-94	106-114	. . .	**87.5-92**
	Clad: ≤ 0.91 mm (0.036 in.)	. . .	102-110	. . .	**86-90**
	>0.91 ≤ 1.27 mm (>0.036 ≤ 0.050 in.)	78-90	104-110	. . .	**. . .**
	>1.27 ≤ 1.57 mm (>0.050 ≤ 0.062 in.)	76-90	104-110	. . .	**. . .**
	>1.57 ≤ 1.78 mm (>0.062 ≤ 0.070 in.)	76-90	102-110	. . .	**. . .**
	>1.78 mm (0.070 in.)	73-90	102-110	. . .	**. . .**
7079-T6, -T65	All[(e)]	81-93	104-114	. . .	**87.5-92**
7178-T6	Not clad[(f)]	85 min	105 min	. . .	**88 min**
	Clad: ≤ 0.91 mm (0.036 in.)	. . .	102 min	. . .	**86 min**
	>0.91 ≤ 1.57 mm (>0.036 ≤ 0.062 in.)	85 min	. . .	. . .	**. . .**
	>1.57 mm (0.062 in.)	**88 min**	**. . .**	**. . .**	**. . .**

(a) Minimum hardness values shown for clad products are valid for thicknesses up to and including 2.31 mm (0.091 in.); for heavier-gage material, cladding should be locally removed for hardness testing or test should be performed on edge of sheet.

(b) 126 to 158 HB (10 mm ball, 500 kg load).

(c) 100 to 130 HB (10 mm ball, 500 kg load).

(d) Alloys 2024-T4, 2024-T42 and 6061-T4 should not be rejected for low hardness until they have remained at room temperature for at least three days following solution treatment.

(e) 136 to 164 HB (10 mm ball, 500 kg load).

(f) 136 HB min (10 mm ball, 500 kg load)

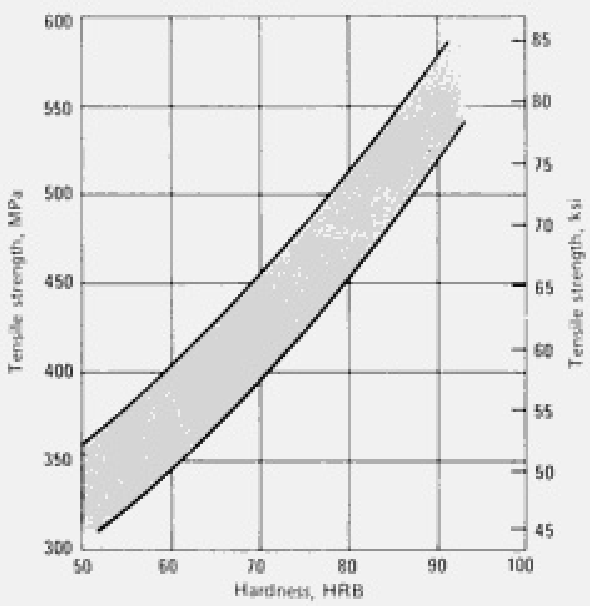


Fig. 37 Tensile strength versus hardness for various aluminum alloys and tempers

Intergranular-Corrosion Test. The extent of precipitation during elevated-temperature aging of alloys 2014, 2219, and 2024 markedly influences the type of corrosion attack and the corrosion resistance. With thin-section products quenched at rates sufficiently rapid to prevent precipitation in the grain boundaries during the quench, short periods of precipitation heat treating produce localized grain boundary precipitates adjacent to the depleted areas, producing susceptibility to intergranular corrosion. Additional heating, however, induces extensive general precipitation within the grains, lowering the corrosion potential differences between the grains and the boundary areas, thus removing the cause of the selective corrosion.

The most common test for susceptibility to intergranular corrosion is carried out as follows:

- Use a specimen that has at least 19 cm^2 (3 $in.^2$) of surface area
- Remove any cladding by filing or etching
- Clean the specimen by immersing it for 1 min in a solution containing 5% concentrated nitric acid and 0.5% hydrofluoric acid at a temperature of 95 °C (200 °F); rinse in distilled water. Immerse for 1 min in concentrated nitric acid at room temperature; rinse in distilled water
- Immerse the specimen for 6 h in a freshly prepared solution containing 57 g of sodium chloride and 10 mL of 30% hydrogen peroxide per liter of water at a temperature of 30 ± 5 °C (86 ± 9 °F). More than one specimen may be corroded in the same container provided that at least 4.6 mL of solution is used for each square centimeter (30 mL/$in.^2$) of specimen surface and that the specimens are electrically insulated from each other
- After the immersion period, wash the specimen with a soft-bristle brush to remove any loose corrosion product. Cut a cross-sectional specimen at least 19 mm ($\frac{3}{4}$ in.) long through the most severely corroded area; mount and metallographically polish this specimen
- Examine the cross-sectional specimen microscopically at magnifications of 100× and 500× both before and after etching with Keller's reagent
- Describe the results of the microscopic examination in terms of the five degrees of severity of

intergranular attack illustrated in Fig. 38

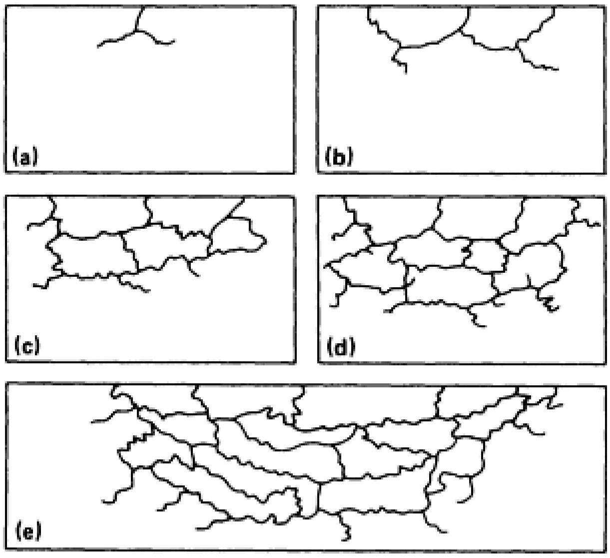


Fig. 38 Five degrees of severity of intergranular attack. Severity of intergranular attack (schematic), as observed microscopically in transverse sections after test for susceptibility to intergranular corrosion. Top of each area shown in surface exposed to corrosive solution

Electrical Conductivity. For control of the corrosion and stress-corrosion characteristics of certain tempers, notably the T73 and T76 types, the materials must meet combination criteria of yield strength plus electrical conductivity. Although these criteria are based on indirect measurements of properties, their validity for ensuring the intended corrosion and stress-corrosion resistance has been firmly established by extensive correlation and testing.

Low tensile strengths may be accompanied by high levels of electrical conductivity, so electrical conductivity is sometimes used as a quality-assurance diagnostic tool. However, because the correlation between strength and electrical conductivity is strongly a function of chemical composition and fabricating practice, use of electrical conductivity is not recommended except for rough screening. This screening must be followed by hardness testing, and then by tensile testing if the hardness tests indicate that the heat treatment was suspect.

Fracture Toughness Indices. Fracture toughness is rarely, if ever, a design consideration in the 1000, 3000, 4000, 5000, and 6000 series alloys. The fracture toughness of these alloys is sufficiently high that thicknesses beyond those commonly produced would be required to obtain a valid test.

Fracture toughness is a meaningful design-related parameter for some conventional high-strength alloys and all the controlled-toughness, high-strength alloys. Conventional aerospace alloys for which fracture toughness minimums may be useful in design include 2014, 2024, 2219, 7075, and 7079. These alloys have toughness levels that are inferior to those of their controlled-toughness counterparts. Consequently, these products are not used in fracture-critical applications, although fracture toughness can be a meaningful design parameter. Fracture toughness is not guaranteed in conventional high-strength alloys.

Fracture toughness quality control and material procurement minimums are appropriate for controlled-toughness, high-strength alloys. The alloys and tempers currently identified as controlled-toughness, high-strength products include:

Alloy	**Condition**	Product form

2048	T8	**Sheet and plate**
2124	T3, T8	**Sheet and plate**
2419	T8	**Sheet, plate, extrusions, and forgings**
7049	T7	**Plate, forgings, and extrusions**
7050	T7	**Sheet, plate, forgings, and extrusions**
7150	T6	**Sheet and plate**
7175	T6, T7	**Sheet, plate, forgings, and extrusions**
7475	**T6, T7**	**Sheet and plate**

The fracture toughness of these alloys and tempers range in measured K_{Ic} values from about 20 MPa$\sqrt{m}$ (18 ksi$\sqrt{in}$) upward. Controlled-toughness alloys are often derivatives of conventional alloys. For example, 7475 alloy is a derivative of 7075 with maximum compositional limits on some elements that were found to decrease toughness.

In products of the newer controlled-toughness high-strength alloys 2090, 2091, 2124, 2224, 2324, 7050, 7149, 7150, 7175, 7475, and 8090, which provide guaranteed levels of fracture toughness, minimum values of the applicable indices, K_{Ic} or K_c, are established by accumulation of statistical data from production lots as a basis for guaranteed minimum values. If the minimum specified fracture toughness value is not attained, the material is not acceptable. Some specifications allow use of less-expensive screening tests (such as the notch tensile or chevron-notched short bar) as a basis for release of high-toughness alloy products. In these instances, correlations between K_{Ic} and the screening test result is used to establish the appropriate notch-yield ratio as a lot-release criterion.

Temper Designations for Heat-Treatable Aluminum Alloys

The temper designations used in the United States for heat-treatable aluminum alloys are part of the system that has been adopted as an American National Standard (ANSI H35.1). Used for all wrought and cast product forms except ingot, the system is based on the sequences of mechanical or thermal treatments, or both, used to produce the various tempers. The temper designation follows the alloy designation and is separated from it by a hyphen. Basic temper designations consist of individual capital letters. Major subdivisions of basic tempers, where required, are indicated by one or more digits following the letter. These digits designate specific sequences of treatments that produce specific combinations of characteristics in the product. Variations in treatment conditions within major subdivisions are identified by additional digits. The conditions during heat treatment (such as time, temperature, and quenching rate) used to produce a given temper in one alloy may differ from those employed to produce the same temper in another alloy.

Designations for the common heat-treated tempers, and descriptions of the sequences of operations used to produce those tempers, are given in the following paragraphs. (For the entire aluminum alloy temper designation system, including designations for non-heat-treatable alloys, see *Properties and Selection: Nonferrous Alloys and Special-Purpose Materials,*Volume 2, *ASM Handbook.*

Basic temper designations for heat-treated conditions include the codes O, W, and T. Other basic temper designations are F (as fabricated) and H (strain hardened).

O, annealed. Applies to wrought products that are annealed to obtain lowest strength temper and to cast products that are annealed to improve ductility and dimensional stability. The O may be followed by a digit other than zero.

W, solution heat treated. An unstable temper applicable to any alloy that naturally ages (spontaneously ages at room temperature) after solution heat treatment. This designation is specific only when the period of natural aging is indicated--for example, W $\frac{1}{2}$h. (See also the discussion of the T*x*51, T*x*52, and T*x*54 tempers, in the section below on subdivision of the T temper.)

T, heat treated to produce stable tempers other than O. Applies to products that are thermally treated, with or without supplementary strain hardening, to produce stable tempers. The T is always followed by one or more digits, as discussed below.

Major Subdivisions of T Temper. In T-type designations, the T is followed by a number from 1 to 10; each number denotes a specific sequence of basic treatments, as described below.

T1, cooled from an elevated-temperature shaping process and naturally aged to a substantially stable condition. Applies to products that are not cold worked after an elevated-temperature shaping process such as casting or extrusion, and for which mechanical properties have been stabilized by room-temperature aging. If the products are flattened or straightened after cooling from the shaping process, the effects of the cold work imparted by flattening or straightening are not recognized in specified property limits.

T2, cooled from an elevated-temperature shaping process, cold worked, and naturally aged to a substantially stable condition. Applies to products that are cold worked specifically to improve strength after cooling from a hot-working process such as rolling or extrusion, and for which mechanical properties have been stabilized by room-temperature aging. The effects of cold work, including any cold work imparted by flattening or straightening, are recognized in specified property limits.

T3, solution heat treated, cold worked, and naturally aged to a substantially stable condition. Applies to products that are cold worked specifically to improve strength after solution heat treatment, and for which mechanical properties have been stabilized by room-temperature aging. The effects of cold work, including any cold work imparted by flattening or straightening, are recognized in specified property limits.

T4, solution heat treated and naturally aged to a substantially stable condition. Applies to products that are not cold worked after solution heat treatment, and for which mechanical properties have been stabilized by room-temperature aging. If the products are flattened or straightened, the effects of the cold work imparted by flattening or straightening are not recognized in specified property limits.

T5, cooled from an elevated-temperature shaping process and artificially aged. Applies to products that are not cold worked after an elevated-temperature shaping process such as casting or extrusion, and for which mechanical properties or dimensional stability, or both, have been substantially improved by precipitation heat treatment. If the products are flattened or straightened after cooling from the shaping process, the effects of the cold work imparted by flattening or straightening are not recognized in specified property limits.

T6, solution heat treated and artificially aged. Applies to products that are not cold worked after solution heat treatment, and for which mechanical properties or dimensional stability, or both, have been substantially improved by precipitation heat treatment. If the products are flattened or straightened, the effects of the cold work imparted by flattening or straightening are not recognized in specified property limits.

T7, solution heat treated and stabilized. Applies to products that have been precipitation heat treated to the extent that they are overaged. Stabilization heat treatment carries the mechanical properties beyond the point of maximum strength to provide some special characteristic, such as enhanced resistance to stress-corrosion cracking or to exfoliation corrosion.

T8, solution heat treated, cold worked, and artificially aged. Applies to products that are cold worked specifically to improve strength after solution heat treatment, and for which mechanical properties or dimensional stability, or both, have been substantially improved by precipitation heat treatment. The effects of cold work, including any cold work imparted by flattening or straightening, are recognized in specified property limits.

T9, solution heat treated, artificially aged, and cold worked. Applies to products that are cold worked specifically to improve strength after they have been precipitation heat treated.

T10, cooled from an elevated-temperature shaping process, cold worked, and artificially aged. Applies to products that are cold worked specifically to improve strength after cooling from a hot-working process such as rolling or extrusion, and for which mechanical properties or dimensional stability, or both, have been substantially improved by precipitation heat treatment. The effects of cold work, including any cold work imparted by flattening or straightening, are recognized in specified property limits.

Other Subdivisions of T Temper Codes for Stress-Relieved Products. When it is desirable to identify a variation of one of the ten major T tempers described above, additional digits, the first (*x*) of which cannot be zero, may be added to the designation.

The following specific sets of additional digits have been assigned to stress-relieved wrought products.

Tx51, stress relieved by stretching. Applies to the following products when stretched to the indicated amounts after solution heat treatment or after cooling from an elevated-temperature shaping process:

Product form	Permanent set, %
Plate	**$1\frac{1}{2}$-3**
Rod, bar, shapes, extruded tube	**1-3**
Drawn tube	**$\frac{1}{2}$-3**

T*x*51 applies directly to plate and to rolled or cold finished rod and bar. These products receive no further straightening after stretching. T*x*51 also applies to extruded rod, bar, shapes, and tubing, and to drawn tubing, when designated as follows:

- T*x*510. Products that receive no further straightening after stretching
- T*x*511. Products that may receive minor straightening after stretching to comply with standard tolerances
- T*x*52. Stress relieved by compressing. Applies to products that are stress relieved by compressing after solution heat treatment, or after cooling from a hot-working process to produce a permanent set of 1 to 5%
- T*x*54. Stress relieved by combining stretching and compressing. Applies to die forgings that are stress relieved by restriking cold in the finish die. (These same digits--and 51, 52, and 54--may be added to the designation W to indicate unstable solution heat-treated and stress-relieved tempers)

Temper designations T42 and T62 have been assigned to wrought products heat treated from the O or the F temper to demonstrate response from the heat treatment described below. Temper designations T42 and T62 also may be applied to wrought products heat treated from any temper by the user when such heat treatment results in the mechanical properties applicable to these tempers.

- *T42.* Solution heat treated from the O or the F temper to demonstrate response to heat treatment and naturally aged to a substantially stable condition
- *T62.* Solution heat treated from the O or the F temper to demonstrate response to heat treatment and

artificially aged

Subdivision of the O Temper. In temper designations for annealed products, a digit following the O indicates special characteristics. For example, O1 denotes that a product has been heat treated according to a time/temperature schedule approximately the same as that used for solution heat treatment, and then air cooled to room temperature, to accentuate ultrasonic response and provide dimensional stability; this designation applies to products that are to be machined prior to solution heat treatment by the user.

Heat Treating of Copper Alloys

Revised by Arthur Cohen, Copper Development Association Inc.

Introduction

HEAT-TREATING PROCESSES that are applied to copper and copper alloys include homogenizing, annealing, stress relieving, solution treating, precipitation (age) hardening, and quench hardening and tempering.

Homogenizing

Homogenizing is a process in which prolonged high-temperature soaking is used to reduce chemical or metallurgical segregation commonly known as coring, which occurs as a natural result of solidification in some alloys. Homogenizing is applied to copper alloys to improve the hot and cold ductility of cast billets for mill processing, and occasionally is applied to castings to meet specified hardness, ductility, or toughness requirements.

Homogenization is required most frequently for alloys having wide freezing ranges, such as tin (phosphor) bronzes, copper nickels, and silicon bronzes. Although coring occurs to some extent in α brasses, α-aluminum bronzes, and copper-beryllium alloys, these alloys survive primary mill processing and become homogenized during normal process working and annealing. Rarely is it necessary to apply homogenization to finished or semifinished mill products.

A characteristic of high cooling rates is the uneven distribution of the alloy elements in the interior of the dendritic microstructure. These differences increase with higher cooling rates and greater differences in composition between melt and solid phase at the onset of crystallization. This difference may be equalized in some alloys by long-time homogenization as a result of diffusion processes taking place in the solid phase.

The time and temperature required for the homogenization process vary with the alloy, the cast grain size, and the desired degree of homogenization. Typical soak times vary from 3 to over 10 h. Temperatures normally are above the upper annealing range, to within 50 °C (90 °F) of the solidus temperature.

Homogenization changes the mechanical properties: ultimate tensile strength, hardness, and yield (proof) strength all slowly decrease, whereas elongation at fracture and necking increase by as much as twice the initial value. Figure 1 shows a typical example of these changes taking place at a homogenizing time of 4 h for alloy C52100, a wrought phosphor bronze alloy containing nominally 92% Cu, 8% Sn, a small amount of phosphorus, and trace amounts of several other elements.

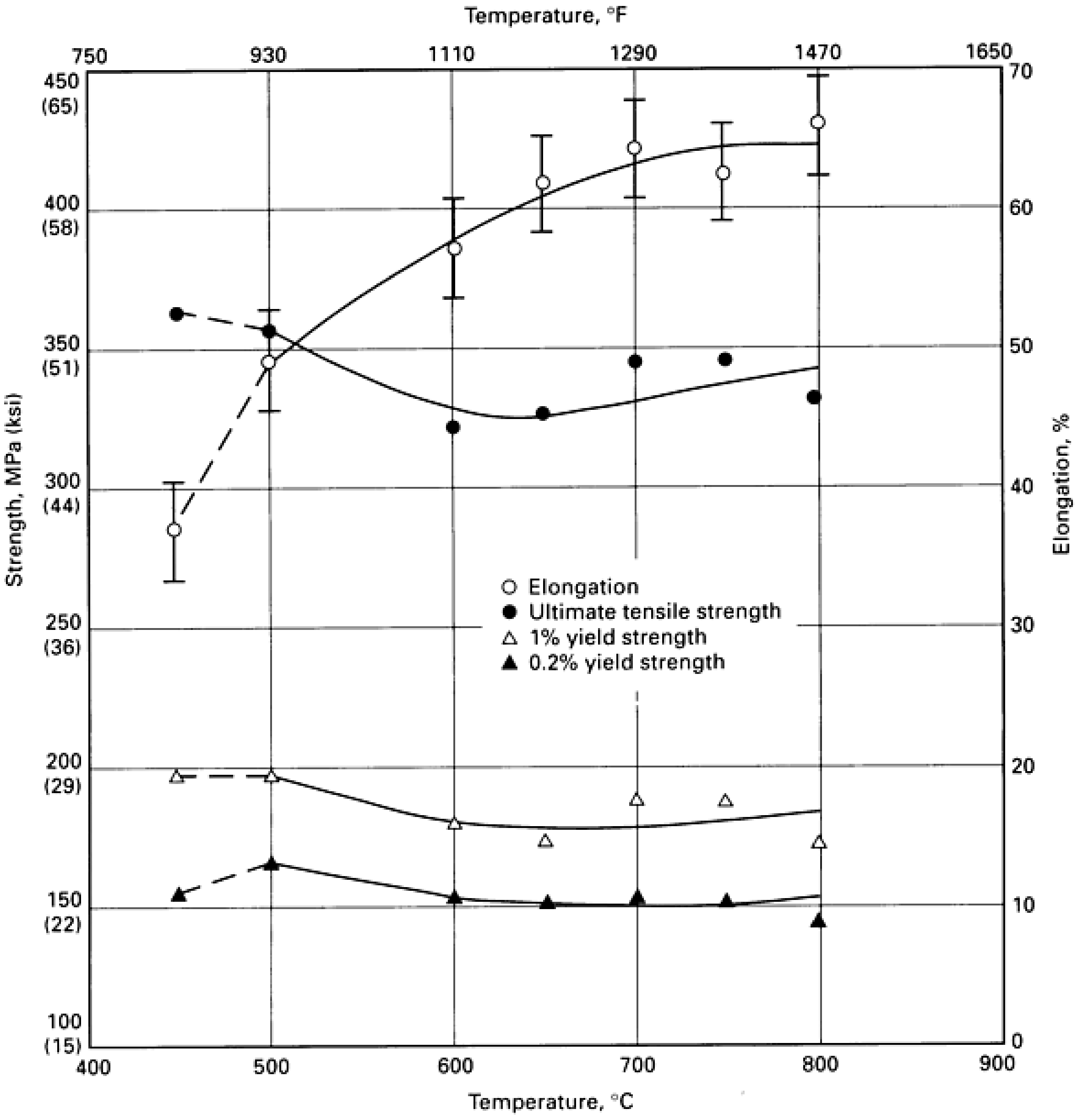


Fig. 1 Effect of annealing temperature on the mechanical properties of an alloy C52100 slab. Annealing time, 4 h

The normal precautions that apply to annealing should be used for the homogenization of any particular alloy. The furnace atmosphere should be selected for the control of both surface and internal oxidation. Where there is appreciable danger of liquefying segregated phases, the materials, particularly castings, should be well supported and heated slowly through the final 100 °C (180 °F).

Typical applications of homogenization are:

- Alloy C71900 (copper-nickel-chromium) billets: 1040 to 1065 °C (1900 to 1950 °F) for 4 to 9 h, to prevent cracks, seams, and excessive wood fiber structure in extrusions
- Alloy C52100 and C52400 (phosphor bronzes, 8 and 10% Sn): 775 °C (1425 °F) for 5 h, to reduce embrittlement in billets and slabs that are to be cold rolled
- Alloy C96400 (cast 70Cu-30Ni): 1000 °C (1830 °F) for 2 h under a protective atmosphere and then cooled to 400 °C (750 °F), followed by air cooling

For the precipitation-hardenable alloys, homogenization may involve a prolonged solution treatment.

Annealing

Annealing is a heat treatment intended to soften and to increase the ductility and/or toughness of metals and alloys. Annealing is applied to wrought products, during and after mill processing, and to castings. The process includes heating, holding, and cooling, and a proper process description should include heating rate, temperature, time at temperature, atmosphere, and cooling rate where each may affect results.

Wrought Products

The annealing of cold-worked metal is accomplished by heating to a temperature that produces recrystallization and, if desirable, by heating beyond the recrystallization temperature to initiate grain growth. Temperatures commonly used for annealing cold-worked coppers and copper alloys are given in Table 1.

Table 1 Annealing temperatures for widely used cold-worked copper and copper alloys

Alloy	**Common name**	Annealing temperature	
		°C	°F
Wrought coppers			
C10100-C10300	Oxygen-free copper	375-650	**700-1200**
C10400-C10700	Oxygen-free silver-bearing copper	475-750	**900-1400**
C10800	Oxygen-free low-phosphorus copper	375-650	**700-1200**
C11000	Electrolytic tough-pitch copper	250-650	**500-1200**
C11100	Electrolytic tough-pitch, anneal-resistant copper	475-750	**900-1400**
C11300, C11400, C11500, C11600	Silver-bearing tough pitch copper	400-475	**750-900**
C12000	Phosphorus-deoxidized copper, low residual phosphorus	375-650	**700-1200**
C12200	Phosphorus-deoxidized copper, high residual phosphorus	375-650	**700-1200**
C12500, C12700, C13000	Fire-refined, tough-pitch copper with silver	400-650	**750-1200**
C14500	Phosphorus-deoxidized, tellurium-bearing copper	425-650	**800-1200**
C14700	Sulfur copper	425-650	**800-1200**

C15500	. . .	475-525	**900-1000**
Wrought copper alloys			
C16200	Cadmium copper	425-750	**800-1400**
C17000, C17200, C17500	Beryllium copper	775-925[(a)]	**1425-1700[(a)]**
C19200	. . .	700-800	**1300-1500**
C19400	. . .	375-650	**700-1200**
C19500	. . .	375-600	**750-1100**
C21000	Gilding metal	425-800	**800-1450**
C22000	Commercial bronze	425-800	**800-1450**
C22600	Jewelry bronze	425-750	**800-1400**
C23000	Red brass	425-725	**800-1350**
C24000	Low brass	425-700	**800-1300**
C26000	Cartridge brass	425-750	**800-1400**
C26800, C27000, C27400	Yellow brass	425-700	**800-1300**
C28000	Muntz metal	425-600	**800-1100**
C31400, C31600	Leaded commercial bronzes	425-650	**800-1200**
C33000, C33500	Low-leaded brass	425-650	**800-1200**
C33200, C34200, C35300	High-leaded brass	425-650	**800-1200**
C34000, C35000	Medium-leaded brass	425-650	**800-1200**
C35600	Extra-high-leaded brass	425-650	**800-1200**
C36000	Free-cutting brass	425-600	**800-1100**

C36500, C36600, C36700, C36800	Leaded Muntz metal	425-600	**800-1100**
C37000	Free-cutting Muntz metal	425-650	**800-1200**
C37700	Forging brass	425-600	**800-1100**
C38500	Architectural bronze	425-600	**800-1100**
C41100	. . .	425-600	**800-1100**
C41300	. . .	425-750	**800-1400**
C42500	. . .	475-750	**900-1400**
C44300, C44400, C44500	Inhibited admiralty brasses	425-600	**800-1100**
C46200, C46400-C46700	Naval brass	425-600	**800-1100**
C48200, C48500	Leaded naval brass	425-600	**800-1100**
C50500	Phosphor bronze	475-650	**900-1200**
C51000, C52100, C52400	Phosphor bronze	475-675	**900-1250**
C53200, C53400, C54400	Free-cutting phosphor bronze	475-675	**900-1250**
C60600, C60800	Aluminum bronze	550-650	**1000-1200**
C61000	Aluminum bronze	615-900	**1125-1650**
C61300, C61400	Aluminum bronze	750-875	**1400-1600**
C61800, C62300-C62500	Aluminum bronze	600-650[b]	**1100-1200[b]**
C61900	. . .	550-800	**1000-1450**
C63000	Aluminum bronze	600-700[c]	**1100-1300[c]**
C63200	Aluminum bronze	625-700[c]	**1150-1300[c]**
C64200	Aluminum bronze	600-700	**1100-1300**

C63800	. . .	400-600	**750-1100**
C65100	Low-silicon bronze	475-675	**900-1250**
C65500	High-silicon bronze	475-700	**900-1300**
C66700	Manganese brass	500-700	**930-1300**
C67000, C67400, C67500	Manganese bronze	425-600	**800-1100**
C68700	Aluminum brass	425-600	**800-1100**
C68800	. . .	400-600	**750-1100**
C70600	Copper nickel, 10%	600-825	**1100-1500**
C71000, C71500	Copper nickel, 20%, Copper nickel, 30%	650-825	**1200-1500**
C72500	. . .	675-800	**1250-1475**
C74500, C75200	Nickel silver	600-750	**1100-1400**
C75400, C75700, C77000	Nickel silver	600-815	**1100-1500**
C78200	Leaded nickel silver	500-620	**930-1150**
Cast copper alloys			
C95300-C95800	**Aluminum bronze castings**	**620-670**	**1150-1225**

(a) Solution-treating temperature; see Table 6 for temperatures for specific alloys.

(b) Cool rapidly (cooling method important in determining result of annealing).

(c) Air cool (cooling method important in determining result of annealing).

Annealing is primarily a function of metal temperature and time at temperature. Except for multiphase alloys, including certain precipitation-hardening alloys, and alloys susceptible to fire cracking, rates of heating and cooling are relatively unimportant. On the other hand, the source and application of heat, furnace design, furnace atmosphere, and shape of the workpiece are important because they affect finish, cost of annealing, and uniformity of results obtained.

The multiplicity of influential variables (such as temperature, time, and furnace load) make it difficult to tabulate a definite annealing schedule that will result in completely recrystallized metal of a specific grain size. The effects of annealing temperature on the tensile strength, elongation, and grain size of hard-drawn (63%) C27000 (yellow brass) wire annealed for 1 h and the effect of annealing time on the grain size of C27000 strip are shown in Fig. 2.

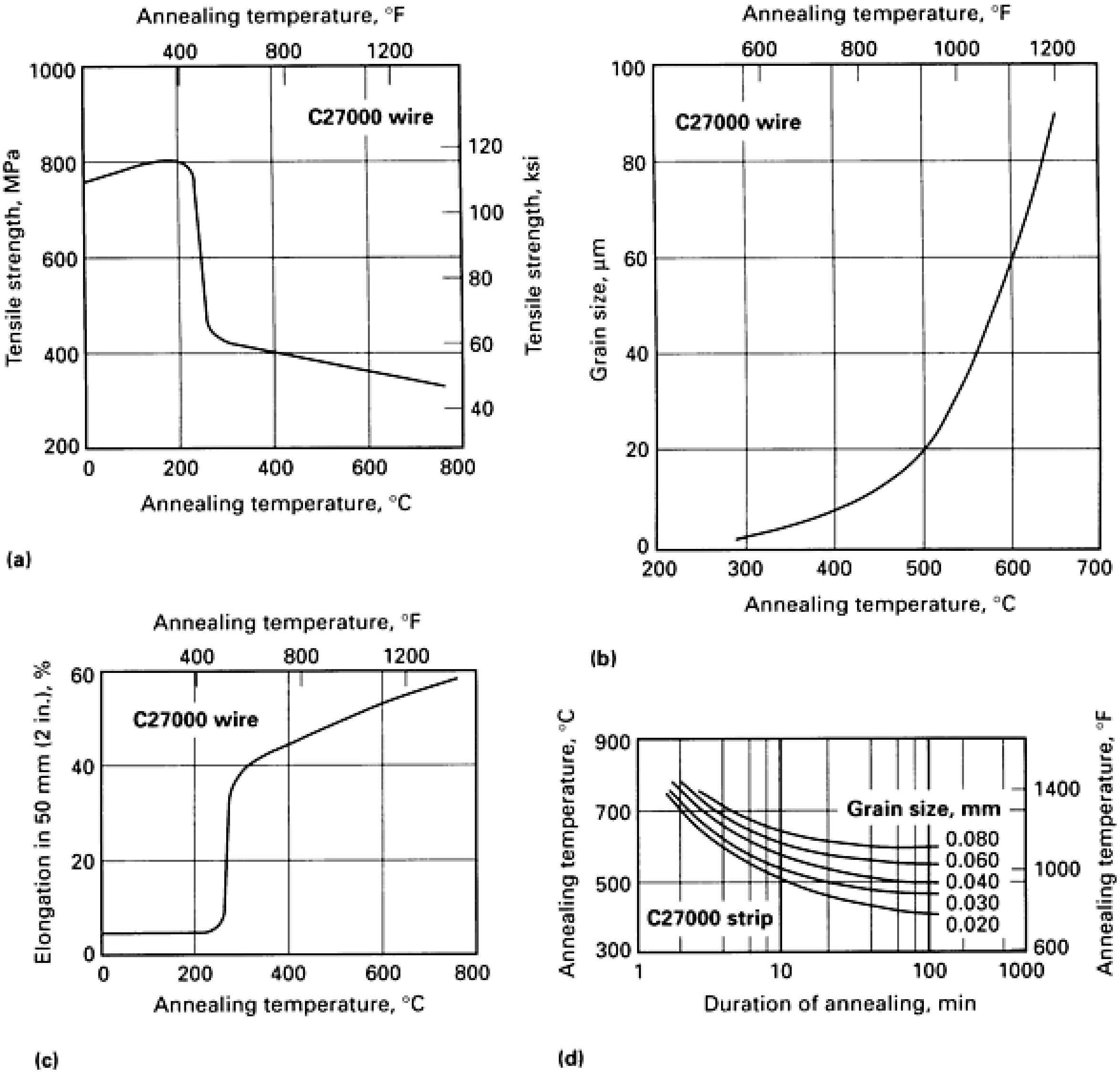


Fig. 2 Effects of annealing temperature and time on characteristics of C27000 wire and strip. Effects of annealing temperature (annealing time, 1 h) on (a) tensile strength, (b) grain size, and (c) elongation of C27000 wire hard drawn 63%. (d) Effect of annealing time on grain size of C27000 strip 1.3 mm (0.050 in.) thick

The annealing response of alloy C26000 (cartridge brass) strip after a reduction of 40.6% by cold rolling is shown in Fig. 3. Time at temperature was 1 h. The actual increases in hardness and tensile properties shown at temperatures below the recrystallization range are typical of alloys such as brasses, nickel silvers, phosphor bronzes, and α-aluminum bronzes. Depending on the individual alloy, these increases are attributable to phenomena of the strain-aging and/or lattice-ordering type.

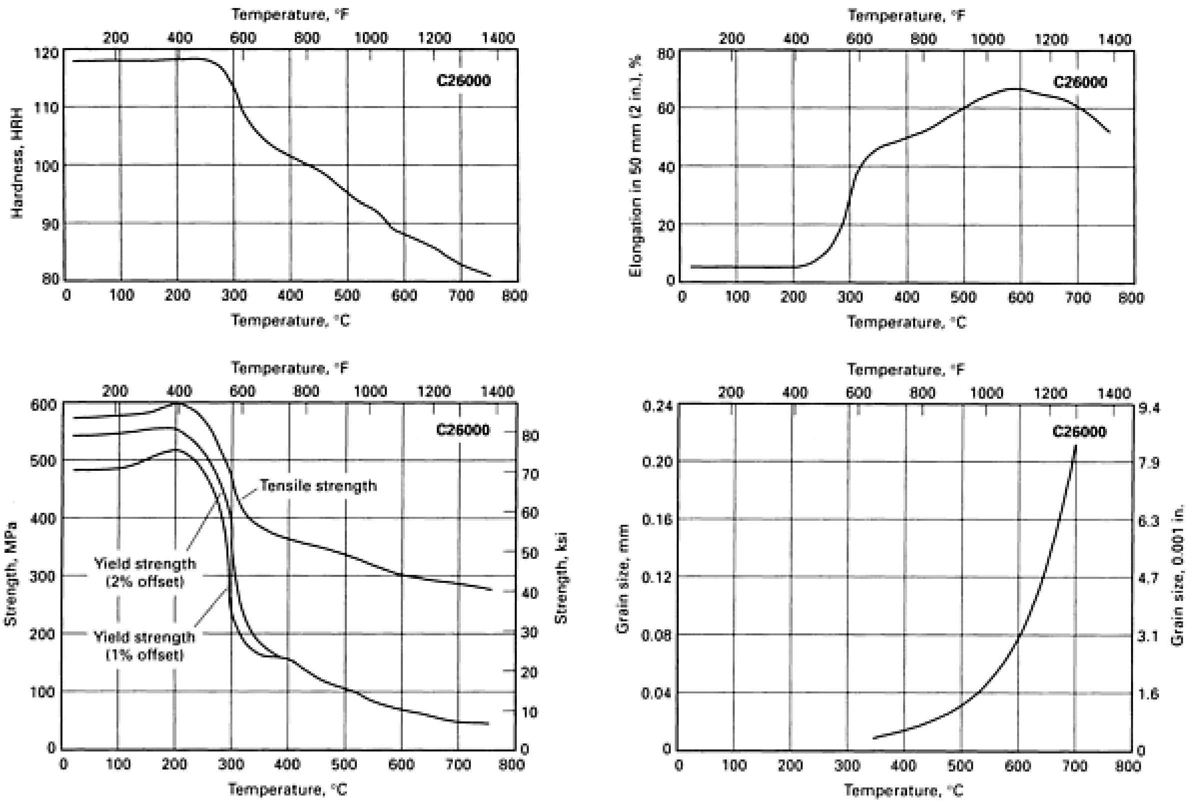


Fig. 3 Annealing data for alloy C26000. Finish rolling reduction 40.6%

Methods of rapid recrystallization have gained importance in heat treatment technology. Softening time can be significantly reduced, compared to conventional annealing processes, by increased heating rates using higher temperatures. However, these heat treat parameters may affect the mechanical properties of the materials.

An increased amount of cold work prior to annealing lowers the recrystallization temperature. The lower the degree of prior deformation, the larger the grain size after annealing. For a fixed temperature and duration of annealing, the larger the original grain size before working, the larger the grain size after recrystallization.

In commercial mill practice, copper alloys are usually annealed at successively lower temperatures as the material approaches the final anneal, with intermediate cold reductions of at least 35% and as high as 50 to 60% in single or multiple passes wherever practicable. The higher initial temperatures accelerate homogenization, and the resulting large grains permit a more economical reduction during the early working operation.

During subsequent anneals, the grain size should be decreased gradually to approximate the final grain size required. This point is usually reached one or two anneals before the final anneal. With such a sequence and with sufficiently severe intermediate reductions, it is possible to produce a uniform final grain size within a lot and from lot to lot.

The grain size and mechanical properties required for further cold working vary considerably with the alloy and with the amount and kind of further cold work to be done. The goal of annealing for cold working is to obtain the optimum combination of ductility and strength. However, when press-drawn parts are to be finished by polishing and buffing, the grain size should be as fine as practicable to keep the surface texture smooth and thus to avoid the need for excessive buffing and the attendant costs. The anneal must be governed by definite specifications and coordinated with cold-working operations to yield the desired finished properties.

Because the annealing of closed strip in tightly wound coils of large weight causes uneven heating in the individual layers corresponding to the direction of heat flow, uneven deep-drawing properties and variations in size may result.

These difficulties led to the development of the continuous-strip furnace (Fig. 4a) through which the material to be annealed passes in a single strip. The annealing temperature for the entire length is dependent only on the furnace temperature and the speed of travel of the strip through the furnace.

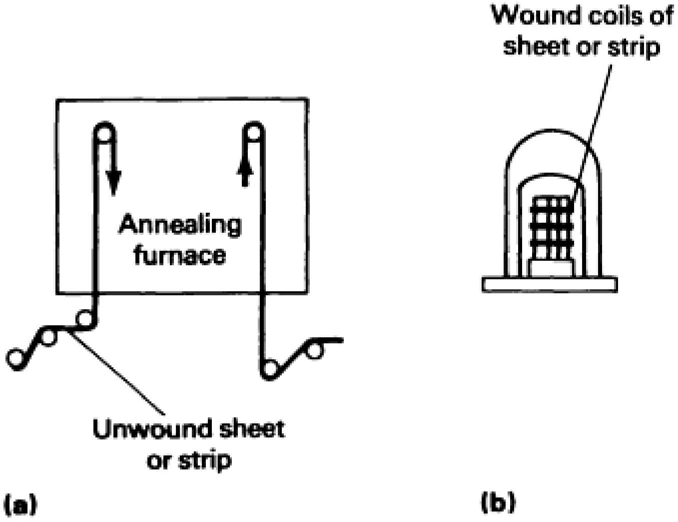


Fig. 4 Types of annealing. (a) Continuous. (b) Batch

The very large surface area with respect to weight permits extremely rapid heating of the metal strip in comparison to previous annealing methods. The annealing time can be measured accurately in seconds by controlling the speed of travel.

Annealing to Specific Properties

Although specific properties are most frequently produced by the controlled cold working of annealed material, there are occasions in which annealing to temper is necessary or advantageous. In the hot rolling of copper alloy plate--particularly plate of large pattern--the finishing temperature may not be consistent or controllable, and varying degrees of work hardening may occur. Also, small quantities and/or odd sizes of required drawn or roll-tempered materials may not be readily available, while appropriate stocks of harder material may be. Thin-gage strip (0.25 mm, or 0.010 in., thick) for radiator fabrication produced by annealing to temper is more closely controlled and more suitable for fabrication than strip in cold-worked tempers. In each case, an anneal is used to alter hardness and tensile properties to levels between those of the hard and fully annealed tempers, with reasonably predictable results. For most copper alloys, the rapid drops in tensile properties and hardness that occur with an increase in temperature in the annealing range necessitate the very close control of the annealing process to produce the desired results. Temperatures used are those in the lower annealing range, with special precautions taken to avoid any overheating. The resultant microstructures may indicate incomplete recrystallization for the harder tempers and grain sizes generally up to 0.025 mm (0.001 in.) for softer tempers. Tensile strengths and hardness levels similar to those of $\frac{1}{8}$, $\frac{1}{4}$, and $\frac{1}{2}$ hard cold-worked tempers can be produced by annealing hard-worked brasses, nickel silvers, and phosphor bronzes. While the yield strength for a given final hardness tends to be lower for alloys annealed to temper than for those cold worked to temper, the fatigue resistance of some phosphor bronze spring materials in annealed $\frac{1}{2}$ hard tempers appears to be superior to that of cold-worked material. Table 2 gives typical properties of annealed-to-temper mill materials. The successful use of annealing to provide specific tempers in mill products requires well-regulated working and annealing schedules designed to produce homogeneous material with controlled grain size, such that the final anneal can produce a uniform result throughout a given lot.

Table 2 Typical properties of copper alloys annealed to temper

Alloy	**Common name**	**Annealed temper**	**Tensile strength**	Approximate hardness, HR30T

		Standard designation	Former designation	MPa	ksi	hardness, HR30T
C26000	Cartridge brass	O81	$\frac{1}{4}$ hard	340-405	49-59	**43-51**
		O82	$\frac{1}{2}$ hard	395-460	57-67	**56-66**
C51100, C53200, C53400, C54400	Phosphor bronze	O82	$\frac{1}{2}$ hard	380-485	55-70	**57-73**
C75200	Nickel silver	O81	$\frac{1}{4}$ hard	400-495	58-72	**49-67**
		O82	$\frac{1}{2}$ **hard**	**455-550**	**66-80**	**62-72**

General Precautions

For best results in annealing copper and copper alloys, the precautions discussed below should be observed.

Sampling and Testing. Test specimens must represent the extreme conditions of the furnace load. For copper alloys that do not contain grain-growth inhibitors, the best and most accurate test for the extent of annealing is the size of the average grain. Grain size is usually the basis for acceptance or rejection of the material. This determination requires special equipment not always available in the plants of consumers or fabricators. For convenience in testing, Rockwell-type hardness testers are used to approximate the grain size; ASTM specifications correlate Rockwell hardness with grain size values for many copper alloys.

Effect of Pretreatment. Because the amount of cold working and the anneal prior to cold working greatly affect the results of annealing after cold working, any schedule that is set up must take this pretreatment into account. Once a schedule has been established, both the anneal and the pretreatment must be adhered to for consistent results.

Effect of Time. In most furnaces, there is an appreciable difference between the temperature of the metal and that of the furnace. Consequently, time in the furnace greatly affects the final temperature of the metal. For a fixed anneal and furnace temperature, time must vary with the type of work load.

Oxidation should be held to a minimum to reduce the loss of metal and the cost of pickling and to improve surface finish. In some instances, specially prepared atmospheres are used to produce a bright annealed material. Usually the control of furnace atmosphere also results in better furnace economy.

Effect of Lubricants. Lubricants on metal to be annealed may cause staining that is difficult to remove. Regardless of the type of furnace or the article to be annealed, it is advisable to eliminate as much of the lubricant as possible before the metal is heated by degreasing or washing.

Hydrogen Embrittlement. When copper that contains oxygen (tough-pitch copper) is to be annealed, the hydrogen in the furnace atmosphere must be kept to a minimum. This reduces the embrittlement caused by the combination of the hydrogen in the atmosphere with the oxygen in the copper, forming water vapor under pressure and resulting in minute porosity in the metal. For temperatures lower than about 480 °C (900 °F), the hydrogen content of the atmosphere preferably should not exceed 1%, and as the temperature is increased, the hydrogen content should approach 0.

Impurities. Occasionally, it is difficult to obtain proper grain growth by annealing under standard conditions that previously have resulted in the desired grain size. This difficulty may sometimes be traced to impurities in the alloy.

Loading. It usually is inadvisable to anneal a variety of different sizes or kinds of material in the same charge because of the different rates of heating and the resulting final metal temperatures.

Fire cracking occurs when some alloys that contain residual stresses are heated too rapidly. Leaded alloys are particularly susceptible to fire cracking. The remedy is to heat slowly until the stresses are relieved. Special types of cold deformation, such as springing (flexing or reeling through a straightener), aid considerably in preventing fire cracking by inducing countervailing mechanical stresses.

Thermal shock or fatigue takes place when rapid and extreme changes in temperatures occur. Stresses that result in thermal shock are influenced by thermal expansion, thermal conductivity, strength, toughness, the rate of temperature change, and the condition of the material. Brasses containing lead, lead and tin, or lead and certain impurities including bismuth or tellurium may be hot short. If they are repeatedly subjected to extreme temperature changes, they may be subject to thermal shock, especially if highly stressed in tension on the surface.

Cooling. Alpha brasses containing less than 70% copper may contain some β phase that is formed during casting or during heat treatment above 600 °C (1110 °F), especially if the metal section is massive. Quenching rapidly will entrap the β phase in the brass. Slow cooling will permit the time and temperature to convert the β to the α phase.

Sulfur Stains. Excessive sulfur in the fuel or lubricant will cause discoloration of the metal; red stains appear on yellow brass, and black or reddish-brown stains on copper-rich alloys.

Castings

Annealing is applied to castings of some duplex alloys, such as manganese bronzes and aluminum bronzes, in order to correct the effects of mold cooling. The extremely slow cooling of sand and plaster castings, or the rapid cooling of permanent mold or die castings, can produce microstructures resulting in hard hardness and/or low ductility and occasionally inferior corrosion resistance. Typical annealing treatments for castings are in the range of 580 to 700 °C (1075 to 1300 °F) for 1 h at temperature. For aluminum bronzes, rapid cooling by water quenching or high-velocity air is advisable.

Stress Relieving

Stress relieving is a process intended to relieve internal stress in materials or parts without appreciably affecting their properties. Stress-relieving heat treatments are applied to wrought or cast copper and copper alloys as one means of accomplishing this objective.

During the processing or fabrication of copper or copper alloys by cold working, strength and hardness increase as a result of plastic strain. Because plastic strain is accompanied by elastic strain, residual stresses remain in the resultant product. If allowed to remain in sufficient magnitude, residual surface tensile stresses can result in stress-corrosion cracking of material in storage or service, unpredictable distortion of material during cutting or machining, and hot cracking of materials during processing, brazing, or welding. In brasses that contain more than 15% Zn, stress-corrosion cracking, or "season cracking," can occur if sufficient amounts of residual tensile stress and trace amounts of atmospheric ammonia are present. Other copper alloys, such as cold-worked aluminum bronzes and silicon bronzes, may also suffer stress-corrosion cracking under more severe environments.

Although mill practice for stress relief frequently involves mechanical means such as flexing, cross-roll straightening, or shot peening, stress-relief heat treatments are employed for some tubular products and odd shapes. Thermal stress relief is also used for formed parts and fabrications made by material users. It is important to recognize that thermal stress relief reduces residual stress by eliminating part of the residual elastic strain, whereas mechanical stress relief merely redistributes residual stress into a less detrimental pattern.

Stress-relief heat treatments are carried out at temperatures below those normally used for annealing. Typical process stress-relieving temperatures for selected coppers and copper alloys are given in Table 3 (wrought products) and Table 4 (cast products). Temperatures for the treatment of cold-formed or welded structures are generally 50 to 110 °C (90 to 200 °F) higher than the temperatures in Table 3. In the case of the weld repair of ship propellers, for example, care must be

exercised to prevent the buildup of excessive residual stresses in the weld zone because such stresses may lead to accelerated corrosion attack. Current propeller repair specifications require post-weld treatment for the aluminum and manganese bronze weldments. Heat treatment of the aluminum bronze at 565 or 650 °C (1050 to 1200 °F) imparts the best overall corrosion resistance to the heat-affected zone. Manganese bronze weldments are not susceptible to stress-corrosion cracking when subjected to yield stress loading in flowing seawater. Heat treatment in the range of 200 to 540 °C (400 to 1000 °F) does not significantly change the tensile, corrosion-fatigue, or general corrosion properties of manganese bronze.

Table 3 Typical stress-relieving temperatures for wrought coppers and copper alloys

Copper or copper alloy number	**Name**	Stress-relief temperature for						
		Sheet and strip		**Rod and wire**			Tube[d]	
		Flat products[a] °C (°F)	**Parts °C (°F)**	**Rod[b] °C (°F)**	**Wire[c] °C (°F)**	**Parts °C (°F)**	**Tube[e] °C (°F)**	Parts °C (°F)
Coppers								
C11000	Electrolytic tough-pitch	180 (355)	180 (355)	180 (355)	180 (355)	180 (355)	. . .	**. . .**
C12000	Phosphorus deoxidized DLP	. . .	. . .	. . .	. . .	. . .	220 (430)	**200 (390)**
C12200	Phosphorus deoxidized DHP	. . .	. . .	. . .	. . .	. . .	240 (465)	**220 (430)**
C14200	Phosphorus deoxidized DPA	. . .	. . .	. . .	. . .	. . .	260 (500)	**240 (465)**
Copper alloys								
C21000	Gilding, 95%	275 (525)	275 (525)	. . .	. . .	. . .	. . .	**. . .**
C22000, C22600	Commercial bronze and jewelry bronze	275 (525)	275 (525)	300 (570)	260 (500)	275 (525)	. . .	**. . .**
C23000	Red brass, low brass	275 (525)	275 (525)	300 (570)	260 (500)	275 (525)	330 (625)	**275 (525)**
C26000	Cartridge brass	260 (500)	260 (500)	290 (555)	250 (480)	260 (500)	320 (610)	**260 (500)**
C27000	Yellow brass, 65%	260 (500)	260 (500)	290 (555)	250 (480)	260 (500)	290 (555)	**260 (500)**

C31400	Leaded commercial bronze	. . .	. . .	300 (570)	260 (500)	275 (525)	. . .	**. . .**
C33000, C33200	High- and low-leaded brasses	. . .	. . .	. . .	. . .	. . .	320 (610)	**260 (500)**
C33500	Low-leaded brasses	. . .	. . .	290 (555)	250 (480)	260 (500)	. . .	**. . .**
C34000, C35000	Medium-leaded brasses	260 (500)	260 (500)	. . .	. . .	. . .	. . .	**. . .**
C35300, C35600, C36000, C37700	Leaded, free-cutting, and forging brasses	. . .	. . .	290 (555)	250 (480)	260 (500)	. . .	**. . .**
C43000	. . .	275 (525)	275 (525)	300 (570)	260 (500)	275 (525)	. . .	**. . .**
C43400	. . .	275 (525)	275 (525)	. . .	. . .	. . .	. . .	**. . .**
C44300-C44500	Admiralty brasses	. . .	. . .	. . .	. . .	. . .	320 (610)	**260 (500)**
C46200, C46400-C46700	Naval brasses	. . .	. . .	290 (555)	250 (480)	260 (500)	. . .	**. . .**
C51000	Phosphor bronze A	275 (525)	275 (525)	300 (570)	260 (500)	275 (525)	. . .	**. . .**
C52100	Phosphor bronze C	. . .	. . .	300 (570)	260 (500)	275 (525)	. . .	**. . .**
C54400	Phosphor bronze B-2	. . .	. . .	300 (570)	. . .	275 (525)	. . .	**. . .**
C65100, C65500	Silicon bronzes	. . .	. . .	300 (570)	275 (525)	275 (525)	. . .	**. . .**
C68700	Aluminum brass, arsenical	. . .	. . .	. . .	. . .	. . .	330 (625)	**290 (555)**
C69700	. . .	. . .	. . .	360 (680)	360 (680)	360 (680)	. . .	**. . .**
C70600	Copper nickel, 10%	420 (790)	420 (790)	. . .	. . .	. . .	480 (895)	**420 (790)**

C71500	Copper nickel, 30%	460 (860)	460 (860)	. . .	. . .	. . .	520 (970)	**460 (860)**
C73500	. . .	380 (715)	380 (715)	400 (750)	350 (660)	380 (715)	. . .	**. . .**
C74500	Nickel silver, 65-10	. . .	. . .	340 (645)	290 (555)	320 (610)	. . .	**. . .**
C75200	Nickel silver, 65-18	380 (715)	380 (715)	. . .	. . .	. . .	. . .	**. . .**
C75400	Nickel silver, 65-15	. . .	. . .	400 (750)	350 (660)	380 (715)	. . .	**. . .**
C75700	Nickel silver, 65-12	. . .	. . .	350 (660)	300 (570)	340 (645)	. . .	**. . .**
C77000	**Nickel silver, 55-18**	**340 (645)**	**340 (645)**	**. . .**	**. . .**	**. . .**	**. . .**	**. . .**

Note: Annealing time is 1 h with the exception of tube.

(a) Extra hard.

(b) $\frac{1}{2}$ hard.

(c) Spring.

(d) Annealing time for tube is 20 min.

(e) Hard drawn

Table 4 Typical stress-relieving temperatures for cast copper alloys

Copper alloy number	Temperature	
	°C	°F
C81300-C82200	260	**500**
C82400-C82800	200	**390**

C83300-C84800	260	**500**
C95200-C95800	315	**600**
C96600-C97800	260	**500**
C99300	**510**	**950**

Note: Time is 1 h per 25 mm (1 in.) of section thickness except for copper alloy C99300, for which it is 4 h per 25 mm (1 in.).

From a practical standpoint, higher-temperature/shorter-time treatments are preferable. However, to guarantee the preservation of mechanical properties, lower temperatures and longer times are sometimes necessary. The optimum cycle produces adequate stress relief without adversely affecting properties. As shown in Fig. 2, some alloys may undergo slight increases in property values during stress-relief heat treatment.

To detect the presence of significant residual stress and to evaluate the effectiveness of stress-relieving treatments, samples of material may be tested with mercurous nitrate solutions, as described in ASTM B 154. This test method is an accelerated test for detecting the presence of residual (internal) stresses, which might result in failure of individual parts in storage or in service due to stress-corrosion cracking. It is not intended for testing assemblies of fabricated parts from mill products. Because of the hazards of mercurous salts, tests in high concentrations of moist ammonia have also been used. Warping of rod or tube during longitudinal saw slitting has also been used as a crude field test for residual stress.

Hardening

Copper alloys that are hardened by heat treatment are of two general types: those that are softened by high-temperature quenching and hardened by lower-temperature precipitation heat treatments, and those that are hardened by quenching from high temperatures through martensitic-type reactions. Alloys that harden during low-to-intermediate-temperature treatments following solution quenching include precipitation-hardening, spinodal-hardening, and order-hardening types. Quench-hardening alloys comprise aluminum bronzes, nickel-aluminum bronzes, and a few special copper-zinc alloys. Usually quench-hardened alloys are tempered to improve toughness and ductility and reduce hardness in a manner similar to that used for alloy steels.

Low-Temperature-Hardening Alloys

For purposes of comparison, Table 5 lists examples of the various types of low-temperature-hardening alloys, as well as typical heat treatments and attainable property levels for these alloys. Additional details are given in the three subsections below.

Table 5 Typical heat treatments and resulting properties for several low-temperature-hardening alloys

Alloy	**Solution-treating temperature**[(a)]		**Aging treatment**			**Hardness**	Electrical conductivity, % IACS[(b)]
			Temperature		**Time, h**		
	°C	**°F**	**°C**	**°F**			
Precipitation hardening							
C15000	980	1795	500-	930-	3	30 HRB	**87-95**

			550	1025			
C17000, C17200, C17300	760-800	1400-1475	300-350	575-660	1-3	35-44 HRC	**22**
C17500, C17600	900-950	1650-1740	455-490	850-915	1-4	95-98 HRB	**48**
C18000[(c)], C81540	900-930	1650-1705	425-540	800-1000	2-3	92-96 HRB	**42-48**
C18200, C18400, C18500, C81500	980-1000	1795-1830	425-500	800-930	2-4	68 HRB	**80**
C94700	775-800	1425-1475	305-325	580-620	5	180 HB	**15**
C99400	885	1625	482	900	1	170 HB	**17**
Spinodal hardening							
C71900	900-950	1650-1740	425-760	800-1400	1-2	86 HRC	**4-4**
C72800	**815-845**	**1500-1550**	**350-360**	**660-680**	**4**	**32 HRC**	**. . .**

(a) Solution treating is followed by water quenching.

(b) International Annealed Copper Standard.

(c) Alloy C18000 (81540) must be double aged, typically 3 h at 540 °C (1000 °F) followed by 3 h at 425 °C (800 °F) (U.S. Patent 4,191,601) in order to develop the higher levels of electrical conductivity and hardness.

Precipitation-Hardening Alloys. Most copper alloys of the precipitation-hardening type find use in electrical and heat conduction applications. Therefore the heat treatment must be designed to develop the necessary mechanical strength and electrical conductivity. The resulting hardness and strength depend on the effectiveness of the solution quench and the control of the precipitation (aging) treatment. It should be noted that the terms age hardening and aging are used in heat-treating practice as substitutes for the term precipitation hardening or a spinodal hardening. Copper alloys harden by elevated-temperature treatment rather than ambient-temperature (natural) aging, as in the case of some aluminum alloys. As dissolved atoms proceed through the coagulation, coherency, and precipitation cycle in the quenched alloy lattice, hardness increases, reaches a peak, and then decreases with time. Electrical conductivity increases continuously with time until some maximum is reached, normally in the fully precipitated condition. The optimum condition generally preferred results from a precipitation treatment of temperature and duration just beyond those that correspond to the hardness aging peak. Cold working prior to precipitation aging tends to improve heat-treated hardness. In the case of lower-strength wrought alloys such as C18200 (copper-chromium) and C15000 (copper-zirconium), some heat-treated hardness may be sacrified to attain increased conductivity, with final hardness and strength being enhanced by cold working. Two

precipitation treatments are necessary in order to develop maximum electrical conductivity and hardness in alloy C18000 (copper-nickel-silicon-chromium) because of two distinct precipitation mechanisms.

Certain guidelines can be used to diagnose problems encountered in producing desired properties in precipitation-hardening alloys:

Problem	Diagnosis
Low hardness	**Solution temperature too low; solution quench delayed or cooling rate too low; aging temperature too low and/or time too short (underaging) or temperature too high and/or time too long (overaging)**
Low hardness; low conductivity	**Inadequate solution treatment and/or underaging**
Low hardness; high conductivity	**Inadequate solution treatment and/or overaging**
High hardness; low conductivity	**Underaging; contaminated material**

When precipitation hardening is performed at the mill, further treatment following the fabrication of parts is not required. However, it may be desirable to stress relieve parts in order to remove stresses induced during fabrication, particularly for highly formed cantilever-type springs and intricate, machined shapes that require maximum resistance to relaxation at moderately elevated temperatures.

Spinodal-Hardening Alloys. Alloys that harden by spinodal decomposition are hardened by a treatment similar to that used for precipitation-hardening alloys. The soft, ductile spinodal structure is generated by a high-temperature solution treatment followed by quenching. The material can be cold worked or formed in this condition. A lower-temperature spinodal-decomposition treatment, commonly referred to as aging, is then used to increase the hardness and strength of the alloy. Spinodal-hardening alloys are basically copper-nickel alloys with chromium or tin additions. The hardening mechanism is related to a miscibility gap in the solid solution and does not result in precipitation. The spinodal-hardening mechanism does result in the chemical segregation of the α crystal matrix on a very fine (Ångström) scale and requires the use of the electron microscope to discern the metallographic effects. Because no crystallographic changes take place, spinodal-hardening alloys retain excellent dimensional stability during hardening.

Order-Hardening Alloys. Certain alloys, generally those that are nearly saturated with an alloying element dissolved in the α phase, undergo an ordering reaction when highly cold worked material is annealed at a relatively low temperature. Alloys C61500, C63800, C68800, and C69000 are examples of copper alloys that exhibit this behavior. Strengthening is attributed to the short-range ordering of the dissolved atoms within the copper matrix, an ordering which greatly impedes the motion of dislocations through the crystals.

The low-temperature order-annealing treatment also acts as a stress-relieving treatment, which raises yield strength by reducing stress concentrations in the lattice at the focuses of dislocation pileups. As a result, order-annealed alloys exhibit improved stress-relaxation characteristics.

Order annealing is done for relatively short times at relatively low temperatures, generally in the range from 150 to 400 °C (300 to 750 °F). Because of the low temperature, no special protective atmosphere is required. Order hardening is frequently done after the final fabrication step to take full advantage of the stress-relieving aspect of the treatment, especially where resistance to stress relaxation is desired.

Quench Hardening and Tempering

Quench hardening and tempering (also referred to as quench and temper hardening) is used primarily for aluminum bronze and nickel-aluminum bronze alloys, and occasionally for some cast manganese bronze alloys with zinc equivalents of 37 to 41%. Aluminum bronzes with 9 to 11.5% Al, as well as nickel-aluminum bronzes with 8.5 to 11.5% Al, respond in a practical way to quench hardening by a martensitic-type reaction. Generally alloys higher in aluminum content are too susceptible to quench cracking, whereas those with lower aluminum contents do not contain enough high-temperature β phase to respond to quench treatments.

Heat-Treating Equipment

Although basic furnace design is similar for all copper alloys, consideration must be given to the annealing temperature range and method of cooling. Solid-solution alloys that do not precipitation harden are usually annealed at temperatures below 760 °C (1400 °F) and may be cooled at any convenient rate. Precipitation- or spinodal-hardenable alloys are solution treated at temperatures up to 1040 °C (1900 °F) and require rapid quenching to ambient temperatures.

Batch-type atmosphere furnaces (Fig. 4b) may be heated electrically or by oil or gas. When nonexplosive atmospheres are used, electrically heated furnaces permit the atmosphere to be introduced directly into the work chamber.

Furnaces that are heated by gas or oil and that employ protective atmospheres sometimes have a muffle to contain the atmosphere and protect the work from the direct fire of the burners.

A properly constructed and safely operated muffle that prevents the infiltration of air by maintaining positive pressure is always required when explosive atmospheres, such as hydrogen, are used.

When protective atmospheres are used during annealing, the work must be cooled in the atmosphere almost to room temperature to prevent surface scale or discoloration. Metal temperatures above 65 °C (150 °F) in air may result in light tarnishing. If some degree of surface oxidation and discoloration can be tolerated, direct-natural-gas-fired furnaces may be used. The products of combustion from the gas-air burners are controlled to yield reducing combustion products similar in composition to manufactured protective atmospheres. Parts annealed in reducing atmospheres developed by the control of the furnace air-to-gas ratio require cleaning to restore luster.

Continuous atmosphere furnaces (Fig. 4(a) and 5) offer versatility for solution heat treating a wide variety of products. Usually, the furnace consists of a vestibule that provides a seal for the atmosphere and in some instances preheats the work, a heating chamber of sufficient length to ensure complete solution treating, and a cooling or quenching chamber that also serves as an atmosphere seal.

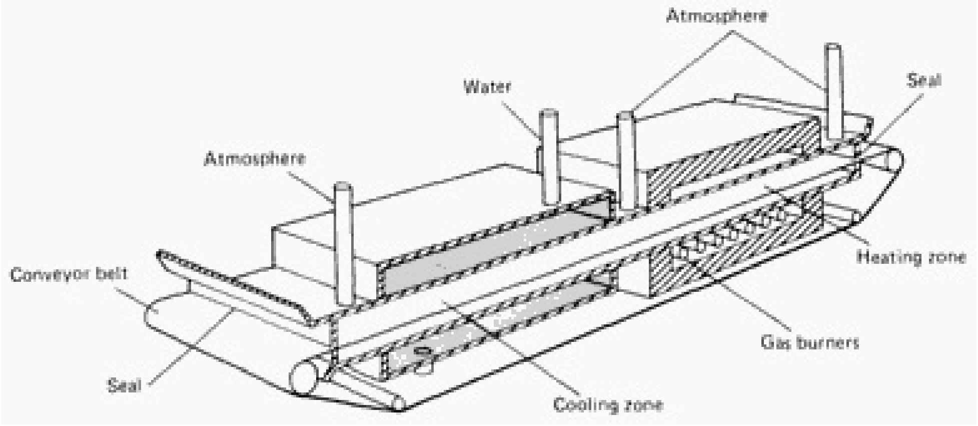


Fig. 5 Continuous conveyor furnace for heat treating copper alloys in a controlled atmosphere

Because the work is usually conveyed at a fixed rate through the furnace, moderate temperature gradients are less harmful than in batch furnaces. When long heating chambers are required, the furnace may be divided into more than one

temperature-controlled heating zone. It is practical to develop a high temperature in the entrance zone to facilitate the heating of the work to the desired temperature. The cooling chamber may be either a long tunnel through which cool, protective atmosphere is circulated or a water-quench zone supplied with a protective atmosphere.

Products such as stampings, machined shapes, castings, and small assemblies are conveyed through the furnace on an endless belt or conveyor chain. Long sections such as tubing, bar, and flat products, or heavy sections that permit stacking on trays, may be conveyed on a roller hearth. In rolling-mill operations, the product is uncoiled at the entrance of the furnace and pulled through the furnace by terminal equipment at the exit end; thus, there are no moving parts within the furnace. For wire products, either annealing is carried out in bell furnaces, with the wire reel wound, or in-line resistance annealing is performed upon exit of the product from the drawing machine prior to reel winding.

Salt Baths. Molten neutral salts may be used for the annealing, stress relieving, solution heat treating, or aging of copper alloys. The composition of the salt mixture depends on the temperature range required. For heating between 705 and 870 °C (1300 and 1600 °F), mixtures of sodium chloride and potassium chloride are commonly used. Various mixtures of barium chloride with sodium and potassium chlorides are used for a wider temperature range (595 to > 1095 °C, or 1100 to > 2000 °F). The latter mixtures are compatible with each other and are commonly used in multiple-furnace operations when it is advantageous to preheat the work in one mixture at a low temperature and then transfer the work to a high-temperature bath. The least common neutral salts are mixtures of calcium chloride, sodium chloride, and barium chloride. They have an operating temperature range of 540 to 870 °C (1000 to 1600 °F) but usually are operated between 540 and 650 °C (1100 and 1200 °F).

The sodium chloride-carbonate mixtures (not true neutral salts) are used between 595 and 925 °C (1100 and 1700 °F), primarily for annealing. For operating temperatures below 540 °C (1000 °F), the only practical mixtures are the nitrate-nitrite salts. Cyanide-base salts have limited application for heating copper alloys. Although copper is soluble in cyanide, these salts can be used, with caution, when a very bright finish is required.

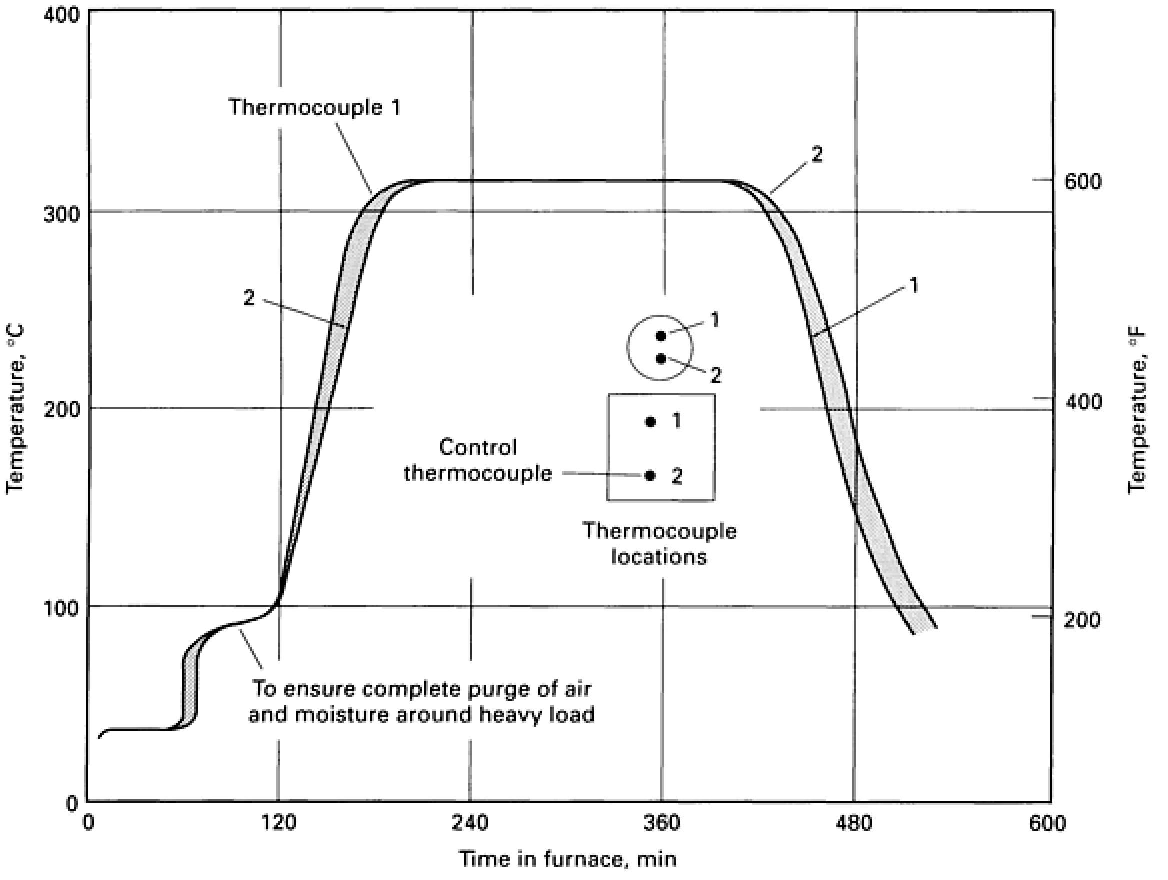
None of the above salt mixtures can be used for the solution treating of standard beryllium-copper alloys because of intergranular attack, pitting, or discoloration.

Aging and stress-relieving operations require furnace equipment that can be controlled to within 3 °C (5 °F) throughout the work zone. Unless cleaning after heating is permissible, it may be necessary to use controlled-atmosphere or vacuum equipment.

Because of the necessity for close temperature control, forced-convection (recirculating-air) and salt bath furnaces are commonly used for aging and stress relieving. Forced-convection furnaces may be of the box, bell, or pit type. Each is equipped with a fan that recirculates the constant-temperature atmosphere over the work. When forced-convection furnaces are fired by gas or oil and protective atmosphere or vacuum is used, the work must be contained in a properly operating muffle chamber or retort to seal off all products of combustion and to prevent air infiltration. Temperature variations and heating and cooling times are compared in the example below.

Example 1: Comparison of Atmosphere Furnaces and Salt Bath Treatment.

A comparison was made of temperature variations in a bell furnace and in a pit retort furnace during the heat treating of small, flat springs made of beryllium copper (see Fig. 6). Both furnaces were rated at 30 kW. The load in each furnace weighed 90 kg (200 lb) and contained 55,000 to 60,000 springs. An exothermic gas, produced by a generator using an air-to-gas ratio of 6.75:1 (capacity, 10 m^3/h, or 350 ft^3/h), was used as the protective atmosphere. The composition of the atmosphere was 6.5% CO, 6% CO_2, 10% H_2, rem N_2, dew point was 2 °C (35 °F) after refrigeration (18 to 21 °C, or 65 to 70 °F, as generated).


Thermocouple 1
2
2
1
1
2
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2
Control
thermocouple
Thermocouple
locations
To ensure complete purge of air
and moisture around heavy load
Temperature, °C
Temperature, °F
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200
400
600
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120
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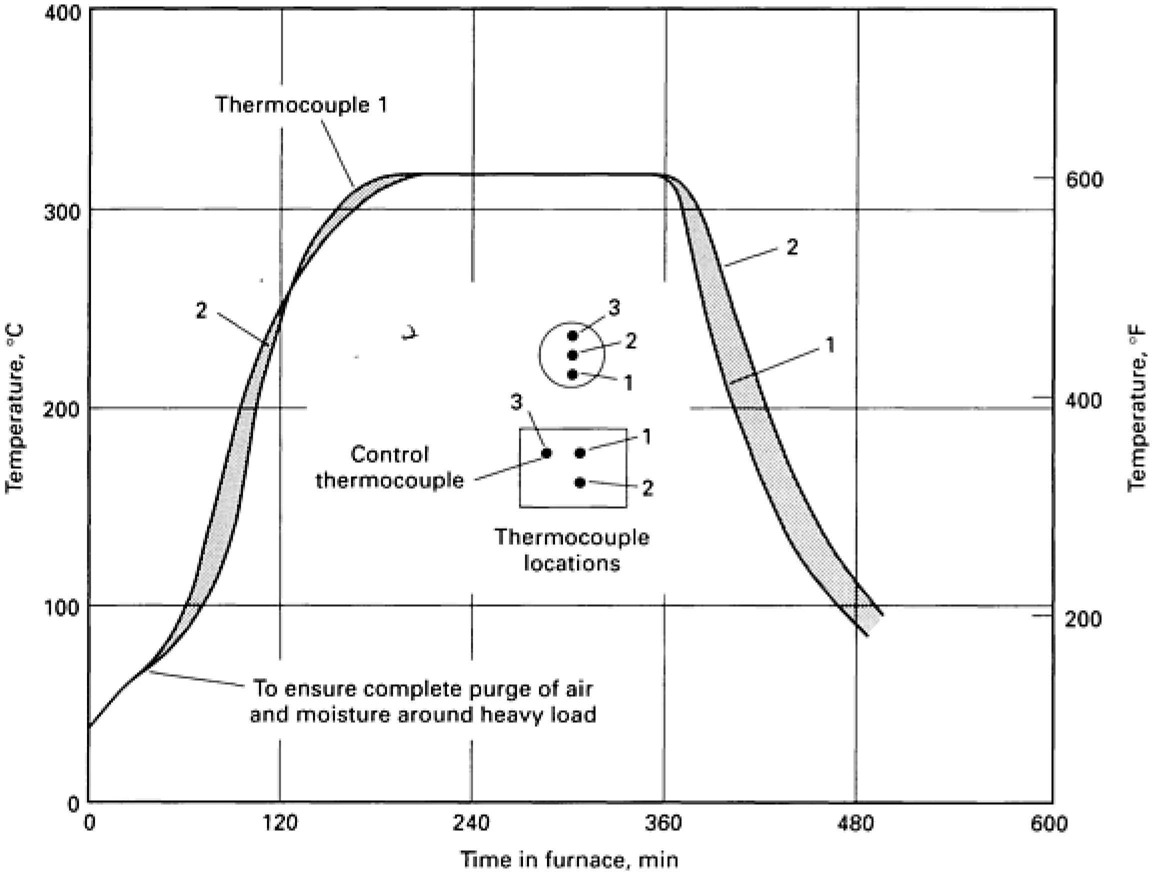
360
480
600

(a)


Thermocouple 1
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To ensure complete purge of air
and moisture around heavy load
Temperature, °C
Temperature, °F
Time in furnace, min
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100
200
300
400
200
400
600
0
120
240
360
480
600

(b)

Fig. 6 Temperature variations in two types of furnaces (Example 1). (a) Bell furnace. (b) Retort furnace

Salt baths can reduce total furnace time by up to 30%, compared to that required with atmosphere furnaces (Fig. 7). Salt baths are particularly valuable when the age-hardening time is of short duration and when the precise control of time at the aging temperature is required.

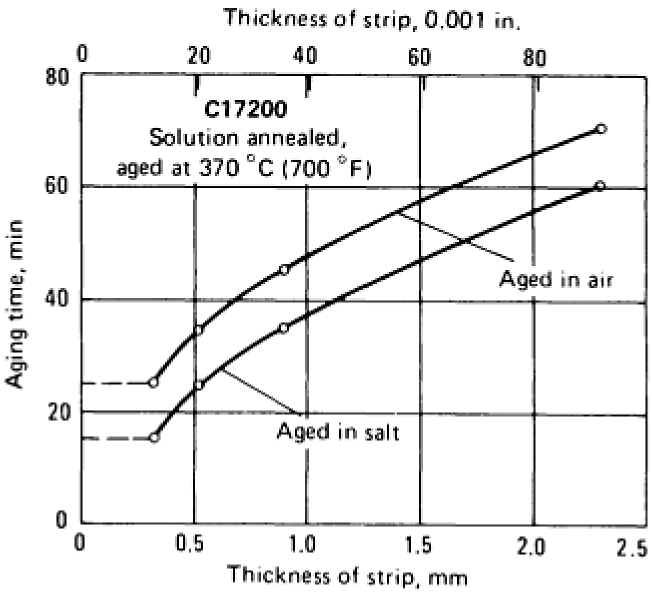


Fig. 7 Effect of metal thickness and heating medium on aging time required to develop maximum strength in C17200 strip

Commercially available nitrate-nitrite salt mixtures (40 to 50% sodium nitrate, remainder sodium or potassium nitrite) that melt at 143 °C (290 °F) are used for aging and stress relieving. All material to be heated in salt should be properly cleaned and dried before being immersed in the molten salt; any organic substance (such as oil or grease) will react violently with the nitrate-nitrite salt.

Protective Atmospheres

The selection of protective atmospheres for heat treating copper and copper alloys is influenced by the temperature used in the heat-treating process.

Heating above 705 °C (1300 °F). An exothermic atmosphere is the least expensive protective atmosphere for the heat treatment of copper alloys. The air-to-gas ratio is adjusted to produce a combusted gas that contains 2 to 7% H for use in muffle furnaces operating at 705 to 995 °C (1300 to 1825 °F). This atmosphere is used successfully for solution treating alloys such as beryllium coppers, chromium coppers, zirconium coppers, and copper-nickel-silicon alloys.

Usually, combusted gases are dried with a surface cooler, using tap water to keep the water-to-hydrogen ratio reducing throughout the heating and cooling cycle. It may be necessary to lower the dew point further by refrigerating the gas. If the furnace atmosphere is not sufficiently reducing, or if the muffle leaks air, a subscale, or internal oxidation of the hardening elements below the surface of the metal, results. Subscale formation can occur rapidly above 845 °C (1550 °F) if the atmosphere becomes oxidizing.

Dissociated ammonia is used primarily for annealing and brazing operations. The gas is very flammable and can explode if air enters the furnace while at an elevated temperature or if the furnace is improperly purged before reaching the elevated temperature.

Dissociated ammonia can be partly or completely burned with air to reduce cost and flammability. The hydrogen content can be controlled within a range of 1 to 24%, the remainder being nitrogen saturated with water vapor. Water must be removed to maintain a reducing atmosphere.

Hydrogen is highly reducing to copper oxide at elevated temperatures and is recommended for elevated-temperature bright annealing and brazing.

Commercial hydrogen contains about 0.2% O, which, if not removed, may cause internal oxidation of the reactive alloying elements in the copper.

When mixed with air, hydrogen is explosive at elevated temperature. Therefore, the furnace must be purged before being heated to high temperature, and air must not enter the furnace.

Heating below 705 °C (1300 °F). Combusted gas (lean exothermic atmosphere) is the most widely used protective atmosphere for the anneal of copper and copper alloys. Because of its low sulfur content, natural gas is the preferred fuel for the production of combusted gas. The air-to-gas ratio is adjusted to produce a hydrogen content of 0.5 to 1%. Combusted gas is dried before entering the furnace to prevent discoloration and staining of the metal by water vapor during the cooling cycle.

Steam is the most economical atmosphere for protecting copper alloys during annealing. Although the annealed metal is not as bright as when heated in a combusted-fuel-gas atmosphere, it is satisfactory for some applications. For products such as tightly wound coils of strip, steam can be used during the heating cycle, and combusted fuel gas can be used during cooling.

Inert gases, dissociated ammonia burned with air, and vacuum are more expensive and are not in common use for the annealing of copper alloys. A major disadvantage of vacuum is that heating and cooling are slow because heat is transferred by radiation only.

Copper-Beryllium Alloys

Because the solid solubility of beryllium in an α-copper matrix decreases as the temperature is lowered, beryllium-copper alloys are precipitation hardenable. Heat treatment typically consists of solution annealing, followed by precipitation hardening. Table 6 gives recommended schedules for the solution treating and precipitation hardening of the five major copper-beryllium alloys that are produced in wrought form. Optimum mechanical and physical properties for specific applications can be attained by varying these schedules, but the temperatures and times given in this table constitute the most conventional practice and typically provide maximum tensile strength. In addition, better age hardening characteristics can be obtained if the material is cold worked after the solution anneal.

Table 6 Solution treating and precipitation hardening of copper-beryllium alloys

Alloy	**Solution**[a]			Aging treatment		
	Temperature		**Time**[b] **h**	**Temperature**		Time, h
	°C	**°F**		**°C**	**°F**	
C17000	775-800	1425-1475	$\frac{1}{2}$-3	300-330	575-625	**1-3**
C17200	775-800	1425-1475	$\frac{1}{2}$-3	300-330	575-625	**1-3**

C17300	775-800	1425-1475	$\frac{1}{2}$-3	300-330	575-625	**1-3**
C17500	900-925	1650-1700	$\frac{1}{2}$-3	455-480	850-900	**1-3**
C17510	**900-925**	**1650-1700**	$\frac{1}{2}$**-3**	**455-480**	**850-900**	**1-3**

(a) All alloys are cooled immediately and rapidly from the solution-treating temperature. Thin sections such as strip can be cooled in circulating atmosphere; heavier sections require water quenching.

(b) Shorter times may be desirable to minimize grain growth, particularly for thin sections.

There is a wide variety of copper-base casting alloys (C81300 through C82800), in addition to the wrought copper-beryllium alloys, that contain beryllium. Appropriate solution-treating and aging schedules for these alloys are dictated by the levels of beryllium and other additives.

Solution Treating

Wrought copper-beryllium alloy mill products are generally supplied solution treated or solution treated and cold worked (Table 7). Material in these conditions can be fabricated without further heat treatment. Thus, solution treating is not typically a part of the fabricating process unless it is necessitated by a special requirement such as softening of the material for additional forming or is used as a salvage operation for parts that have been incorrectly heated for precipitation hardening.

Table 7 Typical conditions of copper-beryllium mill products

Temper	**Description**	Tensile strength before aging	
		MPa	ksi
TB00	Solution treated	480	**70**
TD01	Solution treated and cold worked to $\frac{1}{4}$ hard	550	**80**
TD02	Solution treated and cold worked to $\frac{1}{2}$ hard	625	**91**

In the quenched condition, copper-beryllium alloys are easily fabricated by standard production methods. Strip can be readily blanked, formed, deep drawn, or spun. Rod and bar respond to hot or cold forming, including forging, machining, and swaging. However, even though fully solution-annealed material is the softest form available, better age-hardening properties can be obtained if the material is cold worked after the final solution anneal. Therefore the alloy is often used

in one of the cold-worked tempers shown in Table 7. The selection of a proper temper for a particular application is based on the severity of cold forming and the mechanical property requirements.

Solution-treating temperature limits must be adhered to if optimum properties are to be obtained from the precipitation-hardening treatment. Solution treating below the specified minimum temperature results in insufficient solution of the beryllium-rich phase. This results in lower hardness after precipitation hardening (Fig. 8).

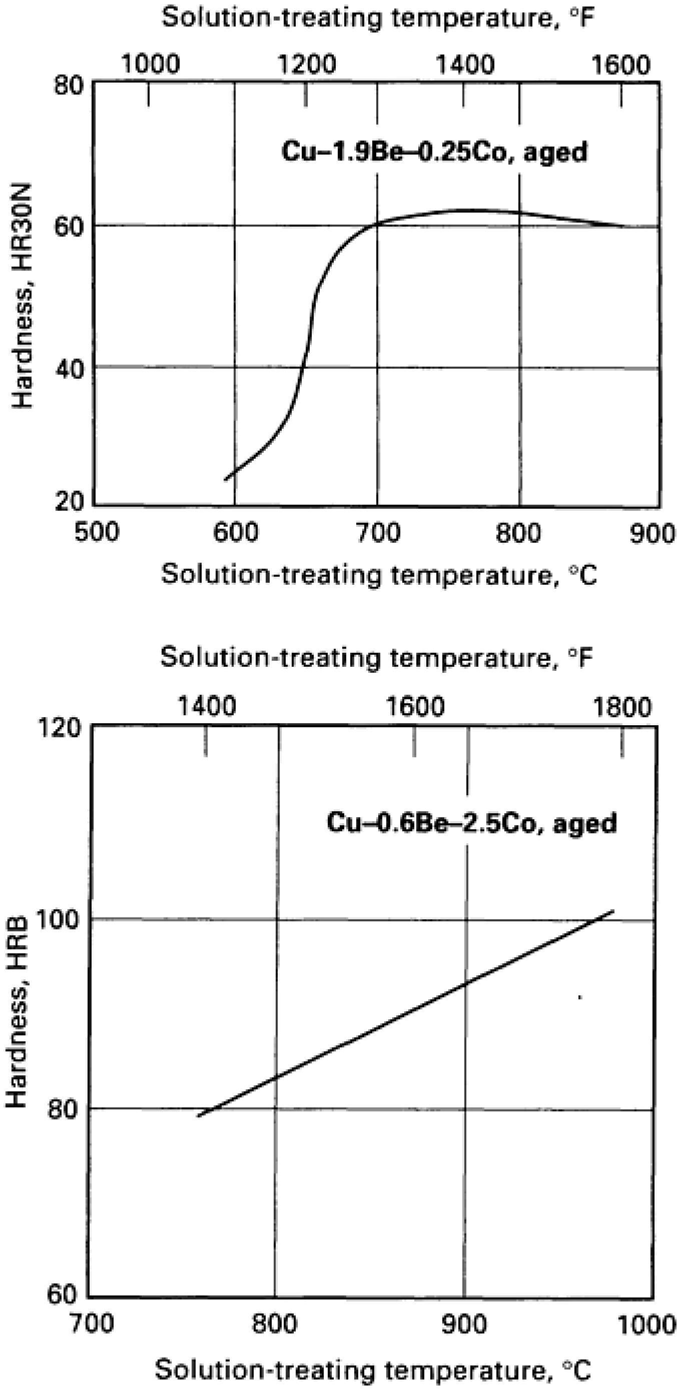


Fig. 8 Effect of solution-treating temperature on hardness of C17200 and C17500 after aging

Also, solution treating must be carefully controlled to produce the desired grain size, dimensional tolerances, and mechanical properties and to prevent oxidation. Exceeding the upper temperature limit causes grain coarsening in wrought material and overheating in wrought and cast materials. A coarse grain size impairs formability; overheating results in a brittle material that does not fully respond to precipitation hardening.

Effect of Solution-Treating Time. The time at the solution-treating temperature depends on the amount of beryllium-rich phase that must be dissolved. Solution of this phase must be complete to produce maximum strength after precipitation hardening.

In cast products, the as-cast structure usually contains a large amount of microsegregation within the dendritic pattern. Therefore, castings must be heated for a length of time sufficient to homogenize the structure. A minimum of 3 h at temperature is recommended for this purpose.

The solution treating of wrought material also removes the effects of cold working and permits additional forming. Some grain growth will occur during softening for additional forming because the solution-treating temperature is above the recrystallization temperature. Therefore, to minimize grain growth, excessive time at temperature must be avoided. It is recommended that wrought alloys be held at temperature 1 h for each inch or fraction of an inch of section thickness. The optimum amount of time for a specific application must be determined by mechanical testing and microscopic examination of the alloy.

Effect of Oxidation. When copper-beryllium alloys are solution treated in air or in an oxidizing atmosphere, two types of oxidation are encountered. A continuous and tenacious oxide surface layer forms on alloys with high beryllium contents. Low-beryllium alloys form a loosely adhering scale and are subject to internal oxidation.

The oxide layer on high-beryllium alloys does not significantly affect the mechanical properties of the precipitation-hardened material, but it is abrasive and causes severe wear of tools and dies if not removed. The oxidation of low-beryllium alloys not only has an abrasive effect, it decreases mechanical properties. This is caused by the surface layer of internal oxidation, which reduces the effective section thickness of the material. For both types of alloys, oxides may be removed by chemical or abrasive cleaning methods.

Quenching is a critical phase of the solution-treating process. Successful treatment requires that the material be quenched immediately, and at the highest possible rate, after being removed from the furnace. Any time lapse during transfer from the furnace to the quenching medium permits some cooling and causes precipitation. Precipitation is rapid at elevated temperatures and its occurrence significantly affects the properties obtained during subsequent precipitation hardening. The maximum allowable delay before quenching depends on the mass of the load, the size of the parts, and the transfer equipment. Mechanical testing and microscopic examination of the structure should be used to evaluate the effectiveness of the quenching operation.

Water quenching is the most common method of retaining the solid-solution condition in both wrought and cast products; however, because of their shape, some castings may crack as the result of the rapid cooling. Such castings may be quenched in oil or forced air; however, the slower cooling rates may cause some precipitation. Thin-gage strip is typically cooled in forced air.

Precipitation Hardening

The cold working of solution-treated copper-beryllium alloys influences the strength attainable through subsequent aging; the greatest response to aging occurs in material in the cold-rolled hard temper. In general, work hardening offers no advantage beyond the hard temper because formability is poor and control of the precipitation-hardening treatment for maximum strength is critical. For some applications, however, wire is drawn to higher levels of cold work prior to precipitation hardening.

Table 8 lists the properties typically specified for mill products of the common copper-beryllium alloys, and Fig. 9 shows the time required to develop maximum tensile strength in one of these alloys aged at various temperatures. The aging times in Fig. 9 vary slightly from those given in Table 8 for the same alloy; the latter are primarily for acceptance-test purposes.

Table 8 Properties and precipitation treatments usually specified for copper-beryllium alloys

Initial condition	Standard aging treatment			Tensile strength		Yield strength[a]		Elongation[b], %	Hardness[c]	Electrical conductivity, % IACS
	Time, h	Temperature								
		°C	°F	MPa	ksi	MPa	ksi			
C17200										
Flat products										
Annealed	None	. . .	. . .	415-540	60-78	195-380	28-55	35-60	45-78 HRB	**17-19**
$\frac{1}{4}$ hard	None	. . .	. . .	515-605	75-88	415-550	60-80	10-40	68-90 HRB	**16-18**
$\frac{1}{2}$ hard	None	. . .	. . .	585-690	85-100	515-655	75-95	10-25	88-96 HRB	**15-17**
Hard	None	. . .	. . .	690-825	100-120	620-770	90-112	2-8	96-102 HRB	**15-17**
Annealed[d]	3	315	600	1140-1345	165-195	965-1205	140-175	4-10	35-40 HRC	**22-25**
Annealed	$\frac{1}{2}$	370	700	1105-1310	160-190	895-1205	130-175	3-10	34-40 HRC	**22-25**
$\frac{1}{4}$ hard[d]	2	315	600	1205-1415	175-205	1035-1275	150-185	3-6	37-42 HRC	**22-25**
$\frac{1}{4}$ hard	$\frac{1}{3}$	370	700	1170-1380	170-200	965-1275	140-185	2-6	36-42 HRC	**22-25**
$\frac{1}{2}$ hard[d]	2	315	600	1275-1485	185-215	1105-1345	160-195	2-5	39-44 HRC	**22-25**
$\frac{1}{2}$ hard	$\frac{1}{4}$	370	700	1240-1450	180-210	1070-1345	155-195	2-5	38-44 HRC	**22-25**
Hard[d]	2	315	600	1310-1575	190-220	1140-1415	165-205	1-4	40-45 HRC	**22-25**

Hard	$\frac{1}{4}$	370	700	1275-1480	185-215	1105-1415	160-205	1-4	39-45 HRC	**22-25**
Rod, bar, plate										
Annealed	None	. . .	. . .	415-585	60-85	185-205	20-30	35-60	45-85 HRB	**17-19**
Hard	None	. . .	. . .	585-895	85-130	515-725	75-105	10-20	88-103 HRB	**15-17**
Annealed[(d)]	3	315	600	1140-1345	165-200	1000-1205	145-175	3-10	36-41 HRC	**22-25**
Hard[(d)]	2	315	600	1205-1550	175-225	1035-1380	150-200	2-5	39-45 HRC	**22-25**
Wire[(e)]										
Annealed	None	. . .	. . .	450-590	65-85	185-240	20-35	35-55	. . .	**17-19**
$\frac{1}{4}$ hard	None	. . .	. . .	620-795	90-115	485-655	70-95	10-35	. . .	**15-17**
$\frac{1}{2}$ hard	None	. . .	. . .	760-930	110-135	620-760	90-110	4-10	. . .	**15-17**
$\frac{3}{4}$ hard	None	. . .	. . .	895-1070	130-155	760-930	110-135	2-8	. . .	**15-17**
Annealed[(d)]	3	315	600	1140-1310	165-190	1000-1205	145-175	3-8	. . .	**22-25**
Annealed	$\frac{1}{2}$	370	700	1105-1310	160-190	930-1205	135-175	3-8	. . .	**22-25**
$\frac{1}{4}$ hard[(d)]	2	315	600	1205-1415	175-205	1105-1310	160-190	2-5	. . .	**22-25**
$\frac{1}{4}$ hard	$\frac{1}{4}$	370	700	1170-1415	170-205	1035-1310	150-190	2-5	. . .	**22-25**
$\frac{1}{2}$ hard[(d)]	$1\frac{1}{2}$	315	600	1310-1480	190-215	1205-1380	175-200	1-3	. . .	**22-25**

$\frac{1}{2}$ hard	$\frac{1}{4}$	370	700	1275-1480	185-215	1170-1380	170-200	1-3	. . .	**22-25**
$\frac{3}{4}$ hard(d)	1	315	600	1345-1585	195-230	1245-1415	180-205	1-3	. . .	**22-25**
$\frac{3}{4}$ hard	$\frac{1}{4}$	370	700	1310-1585	190-230	1205-1415	175-205	1-3	. . .	**22-25**
C17000										
Flat products Annealed	None	. . .	. . .	415-540	60-78	170-365	25-55	35-60	47-78 HRB	**17-19**
$\frac{1}{4}$ hard	None	. . .	. . .	515-605	75-88	310-515	45-75	10-40	68-90 HRB	**16-18**
$\frac{1}{2}$ hard	None	. . .	. . .	585-690	85-100	450-620	65-90	10-25	88-96 HRB	**15-17**
Hard	None	. . .	. . .	690-825	100-120	550-760	80-110	2-8	96-102 HRB	**15-17**
Annealed	3	315	600	1035-1240	150-180	895-1105	130-165	4-10	33-39 HRC	**22-25**
Annealed(d)	3	345	650	1105-1275	160-185	860-1140	125-165	4-10	34-40 HRC	**22-25**
$\frac{1}{4}$ hard	2	315	600	1105-1310	160-190	860-1140	135-170	3-6	34-40 HRC	**22-25**
$\frac{1}{4}$ hard(d)	3	330	625	1170-1345	170-195	895-1170	130-170	3-6	36-41 HRC	**22-25**
$\frac{1}{2}$ hard	2	315	600	1170-1380	170-200	895-1170	145-175	2-5	36-41 HRC	**22-25**
$\frac{1}{2}$ hard(d)	2	330	625	1240-1380	180-200	965-1240	140-180	2-5	38-42 HRC	**22-25**
Hard	2	315	600	1240-1450	180-210	965-1240	155-180	2-5	38-42 HRC	**22-25**

Hard[d]	2	330	625	1275-1415	185-205	1070-1345	155-195	2-5	39-43 HRC	**22-25**
Rod, bar										
Annealed	None	. . .	. . .	415-585	60-85	185-205	20-30	35-60	45-85 HRB	**17-19**
Hard	None	. . .	. . .	585-895	85-130	515-725	75-105	10-20	88-103 HRB	**15-17**
Annealed	3	315	600	1035-1240	150-180	860--1070	125-155	4-10	32-39 HRC	**22-25**
Annealed[d]	3	345	650	1105-1275	160-185	930-1140	135-165	4-10	34-40 HRC	**22-25**
Hard	2	315	600	1140-1380	165-200	930-1140	135-165	2-5	36-41 HRC	**22-25**
Hard[d]	2	345	650	1205-1415	175-205	965-1170	140-170	2-5	38-42 HRC	**22-25**
C17500, C17510										
Rod, bar, plate, flat products										
Annealed	None	. . .	. . .	240-380	35-55	185-205	20-30	20-35	20-43 HRB	**25-30**
Hard	None	. . .	. . .	515-585	75-85	380-550	55-80	3-10	78-88 HRB	**20-30**
Annealed	3	480	900	690-760	100-120	550-690	80-100	10-20	92-100 HRB	**45-60**
Annealed[d]	3	455	850	725-825	105-120	550-725	80-105	8-12	93-100 HRB	**45-52**
Hard	2	480	900	760-860	110-130	690-825	100-120	8-15	95-103 HRB	**45-60**
Hard[d]	**2**	**455**	**850**	**795-930**	**115-135**	**725-860**	**105-125**	**5-8**	**97-104 HRB**	45-52

(a) At 0.2% offset.

(b) In 50 mm (2 in.).

(c) Rockwell B and C hardness values are accurate only if metal is at least 1 mm (0.040 in.) thick.

(d) Heat treatment that provides optimum strength.

(e) For wire diameters greater than 1.3 mm (0.050 in.)

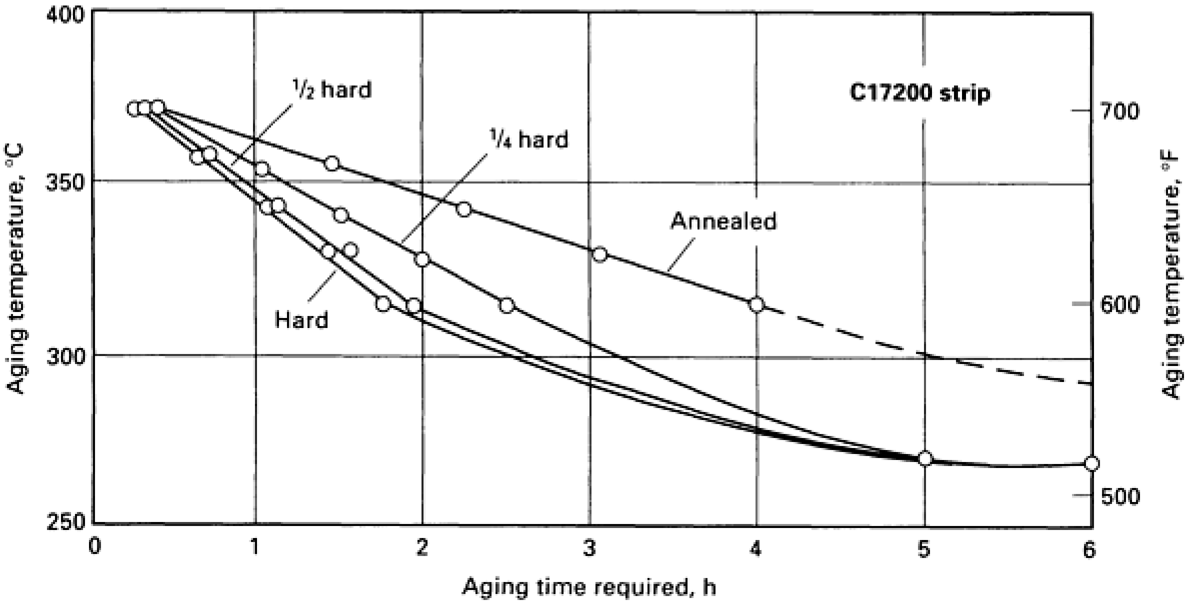


Fig. 9 Time-temperature relationships in aging of C17200 strip, showing aging time required for the development of maximum strength in annealed, $\frac{1}{4}$ hard, $\frac{1}{2}$ hard, and hard C17200 strip aged at various temperatures in a recirculating-air furnace

Special combinations of properties can be obtained by varying either the aging time or the aging temperature. Table 9 shows the age-hardening response from underaging to overaging for cold-rolled material in various tempers. As tensile strength increases, elongation decreases and does not recover substantially with overaging, but electrical conductivity continues to increase. The response of alloy C17200 (1.9Be-0.2Co + Ni) at other aging temperatures within the hardening range (290 to 400 °C, or 550 to 750 °F) are similar to the response at 370 °C (700 °F), but the corresponding time cycles vary. Recommended precipitation-hardening cycles for solution-treated copper-beryllium castings are given in Table 10.

Table 9 Effects of special precipitation-hardening treatments on mechanical properties and electrical conductivity of Cu-1.9Be strip

Initial condition	Aging Temperature			Tensile strength		Yield strength(a)		Elongation(b), %	Electrical conductivity, % IACS	Fatigue, strength(c)		Modulus of elasticity	
	Time, min	Temperature											
		°C	°F	MPa	ksi	MPa	ksi			MPa	ksi	GPa	10^6 psi

Alloy C17200													
Annealed	None	. . .	. . .	465	67.5	250	36	49	18.0	205	30	115	**16.5**
	5	370	700	855	124	695	101	18	19.5	. . .	. . .	120	**17.5**
	15	370	700	1195	173	1055	153	10	22.0	. . .	. . .	125	**18.0**
	30	370	700	1260	182.5	1060	153.5	6	23.0	. . .	. . .	125	**18.0**
	60	370	700	1240	180	1055	153	5	25.5	255	37	130	**18.5**
	120	370	700	1195	173.5	1040	151	6	26.0	. . .	. . .	130	**18.5**
	240	370	700	1150	167	980	142	6	26.5	. . .	. . .	130	**19.0**
$\frac{1}{4}$ hard	None	. . .	. . .	570	82.5	485	70.5	21	17.0	220	32	115	**17.0**
	5	370	700	1115	162	945	137	9	18.5	. . .	. . .	125	**18.0**
	15	370	700	1250	181	1115	162	6	20.5	. . .	. . .	130	**18.5**
	30	370	700	1290	187	1125	163.5	4	23.5	290	42	130	**18.5**
	60	370	700	1230	178.5	1060	154	3	25.5	. . .	. . .	130	**18.5**
	120	370	700	1185	172	1000	145	4	26.5	. . .	. . .	130	**19.0**
	240	370	700	1155	167.5	970	141	6	27.0	. . .	. . .	130	**19.0**
$\frac{1}{2}$ hard	None	. . .	. . .	605	87.5	555	80.5	17	16.0	230	33	115	**17.0**
	3	370	700	1010	146.5	885	128	11	18.0	230	33	125	**18.0**
	5	370	700	1280	186	1110	161	3	21.0	295	43	125	**18.0**

	15	370	700	1310	190	1175	170.5	2	23.0	305	44	130	**18.5**
	30	370	700	1325	192.5	1180	171	2	24.5	305	44	130	**18.5**
	60	370	700	1280	185.5	1105	160	2	25.0	295	43	130	**18.5**
	120	370	700	1200	174	1040	150.5	3	26.0	275	40	130	**18.5**
	240	370	700	1185	172	1035	150	3	27.0	275	40	130	**19.0**
	420	370	700	1010	146.5	860	125	10	27.0	200	29	130	**19.0**
Hard	None	. . .	. . .	730	106	690	100	5	15.0	270	39	120	**17.5**
	5	370	700	1300	188.5	1125	163	3	18.0	. . .	. . .	125	**18.0**
	15	370	700	1360	197	1195	173	2	21.0	. . .	. . .	130	**18.5**
	30	370	700	1310	190	1170	170	1	24.5	315	46	130	**19.0**
	60	370	700	1295	188	1105	160	1	26.5	. . .	. . .	130	**19.0**
	120	370	700	1240	180	1090	158	2	27.5	. . .	. . .	130	**19.0**
	240	370	700	1215	176	1055	153	2	27.5	. . .	. . .	130	**19.0**
Alloy C17500													
Annealed	None	. . .	. . .	350	51	170	25	30	25	. . .	. . .	110	**16.3**
	120	425	800	805	117	625	91	14	44	. . .	. . .	135	**19.3**
	120	455	850	835	121	675	98	14	48	. . .	. . .	140	**20.0**
	120	480	900	805	116.5	625	91	14	48	215	31	140	**20.0**

	120	510	950	795	115	600	87	16	48.5	. . .	. . .	140	**20.0**
Hard	None	. . .	. . .	440	63.5	425	61.5	2	27.8	. . .	. . .	125	**18.3**
	120	425	800	985	142.5	860	125	11	44.0	. . .	. . .	140	**20.0**
	120	455	850	915	133	800	116	13	45.0	. . .	. . .	140	**20.0**
	120	480	900	850	123	760	110.5	13	47.5	250	36	140	**20.0**
	120	**510**	**950**	**800**	**116**	**705**	**102**	**12**	**49.0**	**. . .**	**. . .**	**140**	**20.0**

(a) At 0.2% offset.

(b) In 50 mm (2 in.).

(c) 10^7 cycles

Table 10 Recommended precipitation-hardening schedules and resulting properties for solution-treated copper-beryllium castings

Alloy	**Solution treatment**			**Aging treatment**			**Tensile strength**		**Yield strength**[a]		**Elongation**[b], **%**	**Hardness**	Electrical conductivity, % IACS
	Temperature		**Time, min**	**Temperature**		**Time, min**							
	°C	**°F**		**°C**	**°F**		**MPa**	**ksi**	**MPa**	**ksi**			
C81300	980-1010	1800-1850	60	480	900	120	365	53	250	36	11	89 HB[c]	**60**
C81700	900-925	1650-1700	60	455	850	180	635	92	470	68	8	217 HB[d]	**48**
C81800	900-925	1650-1700	60	480	900	180	705	102	515	75	8	92 HRB	**45**
C82000	900-925	1650-1700	180	480	900	180	690	100	515	75	8	195 HB[d]	**45**

C82100	900-925	1650-1700	60	455	850	180	635	92	470	68	8	217 HB[(d)]	**48**
C82200	900-925	1650-1700	60	445-455	835-850	120	655	95	515	75	8	96 HRB	**45**
C82400	785-850	1450-1560	60	345	650	180	1035	150	965	140	1	34 HRC	**25**
C82500	785-800	1450-1475	60	345	650	180	1105	160	795	115	1	40 HRC	**20**
C82600	785-800	1450-1475	60	345	650	180	1105	160	1035	150	1	40 HRC	**19**
C82700	785-800	1450-1475	180	345	650	180	1070	155	895	130	0	39 HRC	**20**
C82800	**785-800**	**1450-1475**	**60**	**345**	**650**	**180**	**1140**	**165**	**1000**	**145**	**1**	**42 HRC**	**18**

(a) At 0.2% extension under load.

(b) In 50 mm (2 in.).

(c) 500 kg load.

(d) 3000 kg load

Effect of Temperature. The close control of temperature is critical in the conventional aging of copper-beryllium alloys. As indicated by the data in Tables 8 and 9, a change in temperature affects the time required for the development of maximum properties. Also, the higher temperatures can result in lower property values. Normal commercial control of ±6 °C (±10 °F) is adequate for temperatures in the range from 315 to 370 °C (600 to 700 °F).

Problems involving temperature usually arise when test data are translated into production control data. A strip specimen of the material tested at the mill may just meet the minimum specification requirements; however, when the fabricator heat treats a large mass of parts made of the same material, tests may indicate properties below the minimum requirements. The low properties may result from heat treating too large a mass of parts relative to the capacity of the furnace, inadequate time at the proper temperature, or the use of a higher temperature to gain production speed or to obtain fixture conformity when the parts are in fixtures.

Effect of Grain Size. The effect of grain size on the properties of heat-treated material is less significant for copper-beryllium alloys than for solid-solution alloys such as brass and phosphor bronze. The relatively high temperatures required for solution treating copper-beryllium alloys usually override the effects of cold work and time at temperature. Low solution-treating temperatures will result in a fine grain size, but, if the temperature is too low to dissolve the beryllium-rich phase, the response to aging will be affected adversely and the benefits obtained from the fine grain size will be nullified. For this reason, grain sizes below about 0.015 mm (0.0006 in.) are not practical for most beryllium-

copper products, regardless of dimensions. With normal commercial practice, and depending on the product, the grain size of solution-treated material will range from about 0.015 to 0.060 mm (0.6 to 2.4 mils).

Fixturing for Close Tolerances. Excellent dimensional accuracy can be achieved by properly supporting beryllium-copper parts during aging. Usually, overaging is necessary to hold close tolerances. Fixture design should be based on certain principles:

- Fixtures should be of minimum weight
- Excessive clamping pressure should be avoided, to prevent stripping of clamping-screw threads and warping of fixtures
- Parts should be held only at critical locations
- A maximum number of parts should be held by a minimum number of clamping screws
- Design should minimize warping of the fixture, maximizing its service life
- When the configuration of the part permits, the fixture should be designed so that parts can be stacked. Often parts having no more than two planes can be stacked (see Fig. 10), provided that no burrs are present

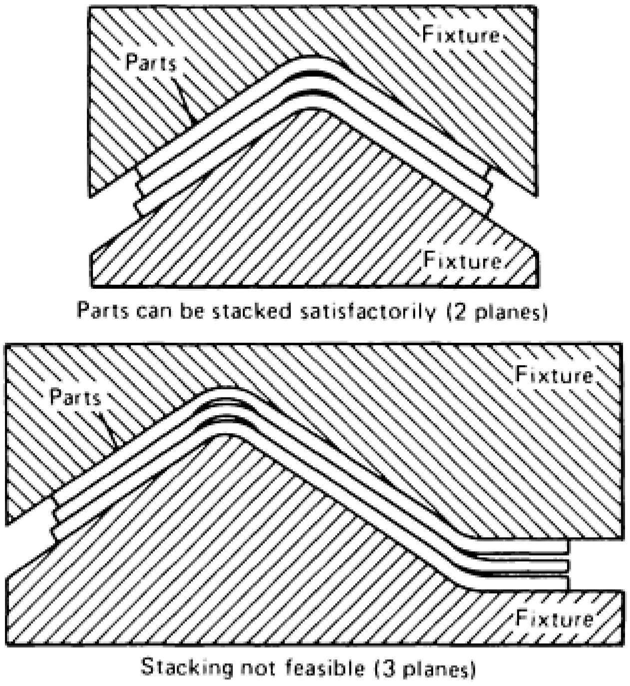


Fig. 10 Parts that can and those that cannot be stacked in fixtures for the control of dimensional tolerances during aging

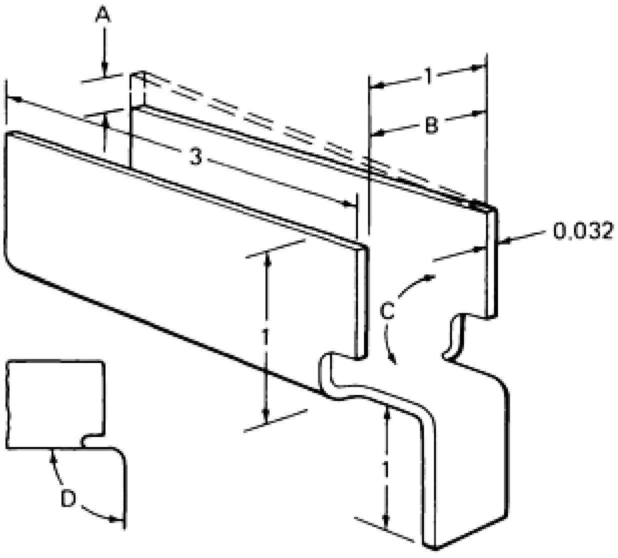
An understanding of the behavior of beryllium-copper alloys during the hardening treatment is helpful in the design and use of fixtures for parts with a controlled gap or opening. These may be U-shaped parts, circular parts, or clips of various designs. During heating for hardening, the material will move in the direction in which it was plastically formed or elastically deflected. If both conditions occur before hardening, movement due to the elastic effect will prevail. These phenomena may be illustrated by the examples below.

Example 2: Reduction in Dimensional Variation with Fixturing.

A comparison was made of the dimensional variations that occurred during the aging of solenoid guides heated as loose pieces and as fixtured pieces. The fixture that was used supported, with adequate pressure, all inside and outside surfaces of the part. Although the total cost of aging the guides as fixtured pieces was nearly two and a half times the cost of aging them as loose pieces (total cost per piece, based on the aging of 100 000 pieces per year), a significant improvement (reduction) in dimensional variation was achieved by the use of fixtures (Table 11).

Table 11 Dimensional variations in beryllium-copper solenoid guides aged with and without fixtures (Example 2)

Dimension	Dimensional variation(a)	
	Loose pieces	Fixtured pieces
A(b)	$\leq \frac{3}{16}$ in.	$\frac{1}{32}$ **in. max**
B	$-\frac{1}{8}$ to $\frac{1}{16}$ in.	**±0.010 in.**
C	-4 to 2°	$\pm\frac{1}{2}$ °
D	**-4 to 2°**	$\pm\frac{1}{2}$ °



(a) Assuming no deviations from the die operation.

(b) Twist in 3 in.

Example 3: Fixturing and Aging Procedure for Dimensional Control of a Beryllium-Copper Spring Clip.

Spring clips like the one shown in Fig. 11 were press formed to a slightly undersized inside diameter (24.9 to 25.2 mm, or 0.980 to 0.990 in.) so that they would fit snugly on a mandrel 25.4 ± 0.03 mm (1 ± 0.001 in.) in diameter. However, during aging for $\frac{1}{2}$ h at 350 °C (660 °F), the metal moved in the direction of elastic deflection, which caused the clips to be loose on the mandrel. Because precipitation hardening of beryllium-copper is a cumulative time-temperature reaction, the hardening treatment can be interrupted. Therefore, the clips (without being placed on the mandrel) were partially aged

for 5 min at 350 °C (660 °F) (decreasing the original dimension to 24.8 to 25.0 mm, or 0.975 to 0.985 in.) and then were placed on the mandrel and aged at the same temperature for the remaining 25 min.

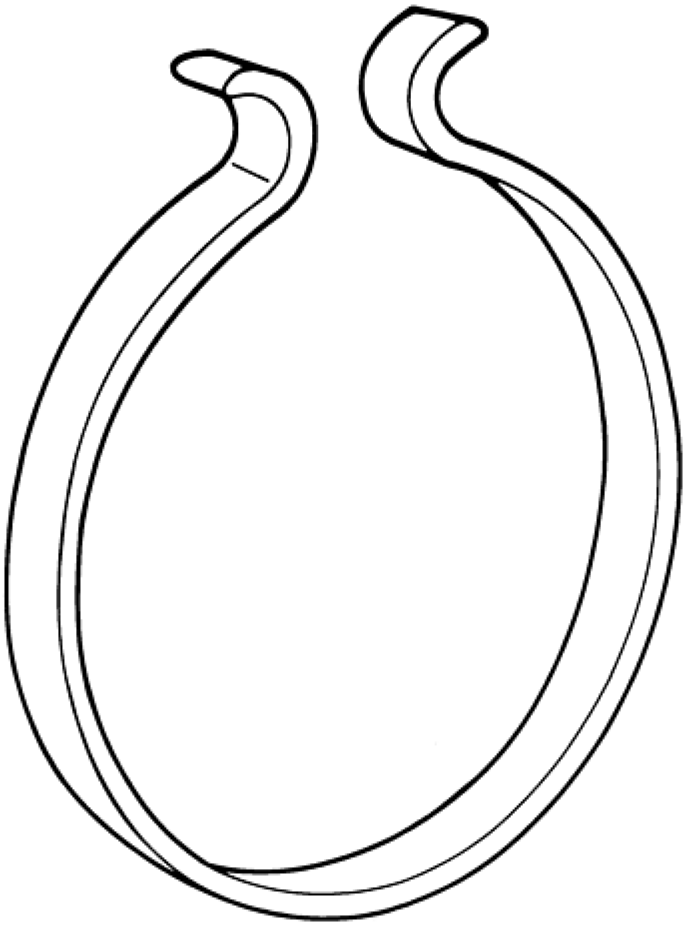


Fig. 11 Spring clip representing a type of beryllium-copper part that should be partially aged without a fixture and then placed on a mandrel for final aging, for control of diameter

Following this aging treatment, none of the clips was larger than the diameter of the mendrel; the actual final dimension was governed by the time and temperature of aging, that is, by the amount of stress relief that occurred.

Interrupted Aging. The selection of the time and temperature for the first step of the interrupted aging sequence (Example 3, above) is important but not critical. If the time is inadequate, the direction of movement will not be established; if excessive, there will be insufficient time for heating the parts on the fixture to allow enough stress relief for close conformity. Usually the duration of the preliminary treatment should be about 15% of the total aging time. Allowance must be made for the mass effect of the load on the time required for it to reach furnace temperature. Also, interrupted aging procedures can be used to restrict increases in the outside diameters of various parts.

Inspection and Quality Control. In most instances, the completeness of aging can be verified by hardness testing. Exceptions are the tension testing of specimens taken from large parts and simulated service testing to determine elastic performance. Figure 12 is an example of variations observed from tensile testing.

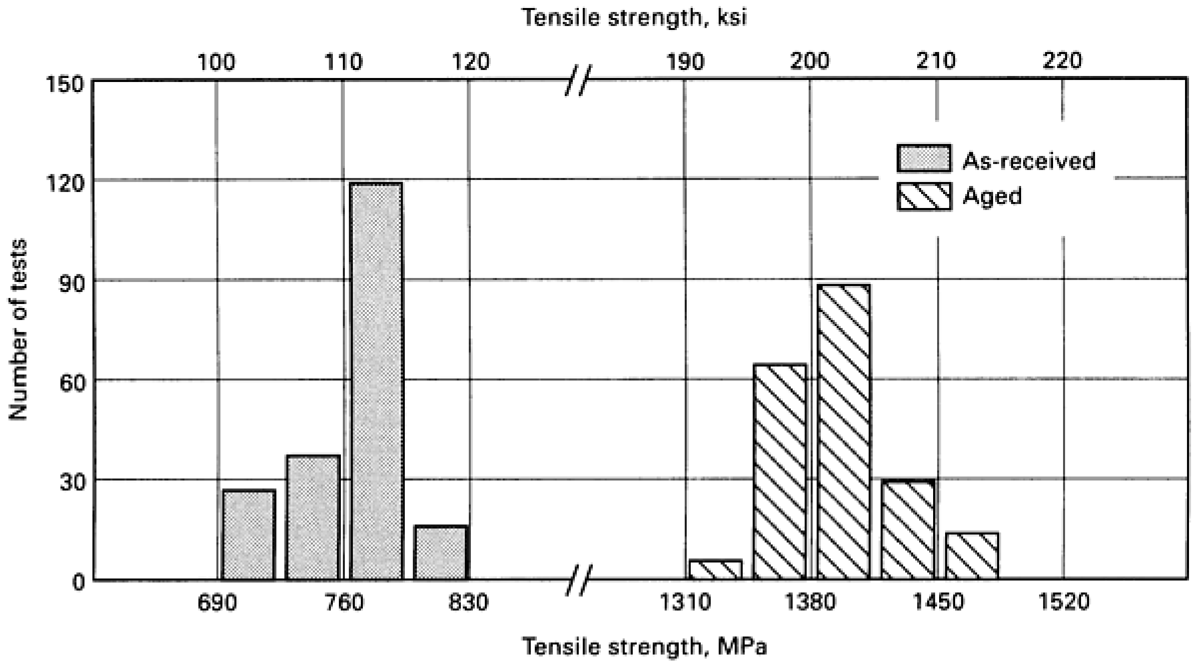


Fig. 12 Variation in tensile strength of hard C17200 strip after aging. The strip was 0.17 to 0.19 mm (0.0065 to 0.0075 in.) thick and was aged 3 h at 315 °C (600 °F). The number of tests of each group was 200.

Hardness measurements should always be made using the method and load most suitable for the thickness of the material and the normal level of hardness expected. Table 12 indicates suggested methods for testing various thicknesses of a hardened beryllium-copper alloy. Variations obtained with heat-treated parts and with strip are presented in the examples below.

Table 12 Suggested methods for measuring the hardness of heat-treated C17200

Thickness		Hardness test method	Load, kg
mm	in.		
0.03-0.08	0.001-0.003	Diamond pyramid	**0.2**
0.08-0.38	0.003-0.015	Diamond pyramid	**0.5**
0.38-0.51	0.015-0.020	Rockwell superficial 15N	**15**
0.51-1.02	0.020-0.040	Rockwell superficial 15N	**30**

Example 4: Hardness Variations in Beryllium-Copper Springs.

Terminal springs made of a beryllium-copper alloy of the composition 0.8 to 1% Be, 0.85% (max) Ni + Co + Fe, 3% (max) Zn + Sn were solution annealed and then aged for 5 h at 343 ± 6 °C (650 ± 10 °F) in a batch-type recirculating-air furnace (Fig. 13). The furnace load consisted of 280,000 pieces. Hardness tests were conducted on specimens of strip

material representative of the parts. Specifications required a hardness of 70 to 75 HRI5N. Results of hardness tests on 41 production lots within a 3-month period are presented in Fig. 13.

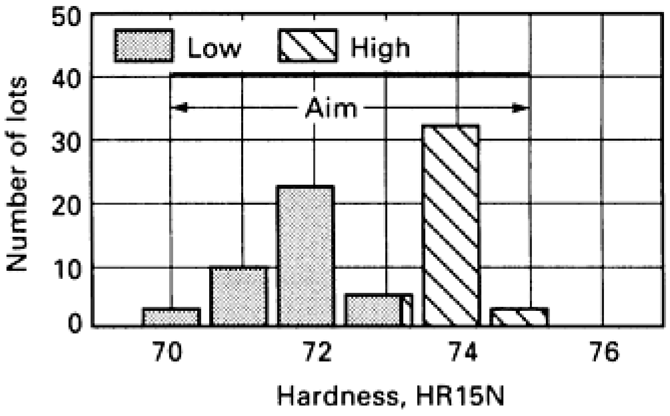


Fig. 13 Variation in hardness for 41 lots of heat-treated beryllium-copper terminal springs tested over a three-month period. High and low values in each lot are plotted.

Example 5: Hardness Variations in a Beryllium-Copper Spring Receptacle.

Spring contact receptacles stamped from $\frac{1}{4}$ hard beryllium-copper strip (alloy C17200) were aged in a salt bath at 300 °C (575 °F) for 30 min. The salt pot, 915 × 840 × 760 mm (36 × 33 × 30 in.), contained 1090 kg (2400 lb) of nitrate-nitrite salt (see Fig. 14).

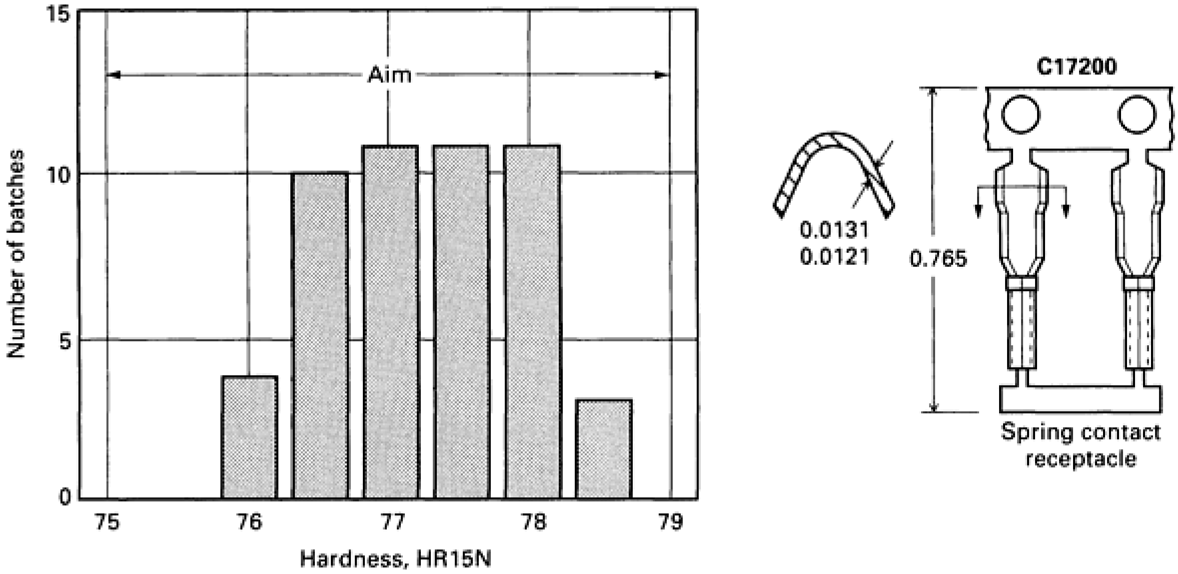


Fig. 14 Variation in hardness for 50 batches of aged spring contact receptacles stamped from $\frac{1}{4}$ hard C17200 strip

A strip of about 1000 of these parts was wound onto a birdcage reel 265 mm (10 $\frac{1}{2}$ in.) in diameter and 305 mm (12 in.) wide. Each receptacle weighed about 0.6 g (0.02 oz); therefore, the total weight of the receptacles on each reel was about 565 g (20 oz). Each reel weighed about 0.9 kg (2 lb), and one furnace load consisted of eight reels.

Specified hardness for these parts was 75 to 79 HR15N. Figure 14 shows the variation in hardness for 50 batches.

Copper-Chromium Alloys

Copper-chromium alloys of 0.5 to 1.0% Cr are solution treated, in molten salt or in controlled-atmosphere furnaces to avoid scaling, at 980 to 1010 °C (1800 to 1850 °F) and rapidly quenched. Solution-treated chromium copper is soft and ductile; therefore, it can be cold worked in a manner similar to that used for unalloyed copper.

After being solution treated, the material may be aged for several hours at 400 to 500 °C (750 to 930 °F) to produce special mechanical and physical properties. A typical aging cycle is 4 h or more at 455 °C (850 °F).

Typical effects of heat treatment and cold work on the properties of chromium-copper are shown in Table 13. The hard drawn specimens were obtained by reducing the cross-sectional area of solution-annealed specimens by approximately 40%.

Table 13 Typical effects of heat treatment and cold work on properties of Cu-1% Cr alloys

Condition	**Ultimate tensile strength**		**Yield strength**[(a)]		**Elongation**[(b)]**, %**	**Hardness**	Electrical conductivity, % IACS
	MPa	**ksi**	**MPa**	**ksi**			
Alloy C18200							
Solution treated	240	35	105	15	42	50 HRF	**35-42**
Solution treated and aged	350	51	275	40	15	90 HB[(c)]	**75-82**
Solution treated and drawn 40%	415	60	310	45	15	65 HRB	**40**
Solution treated, hard drawn, and aged	435	63	385	56	18	68-75 HRB	**80**
Solution treated, aged, and drawn 30%	480	70	425	62	18	75-80 HRB	**80**
Alloy C81500							

(a) At 0.5% extension under load.

(b) In 50 mm (2 in.).

(c) 500 kg load

Copper-Zirconium Alloys

The solution treatment of zirconium-copper of the composition 99.7% Cu (min), 0.13 to 0.30% Zr consists of heating to 900 to 980 °C (1650 to 1795 °F) and quenching in water. The material may then be precipitation hardened for 1 to 4 h at 500 to 550 °C (930 to 1020 °F). If cold working is done prior to aging, the aging temperature is reduced to 370 to 480 °C (700 to 900 °F) for 1 to 4 h.

Time at the solution-treating temperature should be minimized in order to limit grain growth and possible internal oxidation by a reaction of the zirconium with the furnace atmosphere. Because the solution and diffusion of the zirconium occur rapidly at the solution-treating temperature, holding at temperature is not required.

Optimum mechanical properties and resistance to softening are developed with a maximum solution of zirconium. If material containing 0.15% Zr or more is heated above 980 °C (1795 °F), the Cu_3Zr phase will begin to melt. A slight amount of melting will not affect mechanical properties, but if excessive melting occurs, the ductility of the alloy will decrease.

Normally, as the solution temperature is increased from 900 to 980 °C (1650 to 1795 °F), the aging temperature should also be increased to maintain high electrical conductivity. Aging treatments that produce the best combination of mechanical properties and electrical conductivity are:

Condition	**Temperature**		Time ,h
	°C	**°F**	
Solution treated			
At 900 °C (1650 °F)	500	930	**3**
At 900 °C (1650 °F) and cold worked	400	750	**3**
At 980 °C (1795 °F)	550	1020	**3**

The increase in the strength of zirconium-copper depends primarily on cold working. Although aging results in some increase in strength, its chief effect is to increase electrical conductivity. The properties developed by various combinations of heat treatment and cold working are given in Table 14.

Table 14 Effect of heat treatment and cold work on properties of copper-zirconium alloy C15000

Solution-treating temperature[a]		**Amount of cold work, %**	**Aging**			**Tensile strength**		**Yield strength**		**Elongation**[b]**, %**	**Hardness, HRB**	Electrical conductivity, % IACS
			Temperature		**Time, h**							
°C	**°F**		**°C**	**°F**		**MPa**	**ksi**	**MPa**	**ksi**			

900	1650	20	475	885	1	310	45	260	38	25	48	**85 min**
900	1650	80	425	795	1	425	62	380	55	12	64	**85 min**
980	1795	None	. . .	. . .	. . .	200	29	41[(c)]	6[(c)]	54	. . .	**64**
980	1795	20	. . .	. . .	. . .	270	39	250[(c)]	36[(c)]	26	37	**64**
980	1795	80	. . .	. . .	. . .	440	64	420[(c)]	61[(c)]	19	73	**64**
980	1795	None	500	930	3	205	30	90	13	51	. . .	**87**
980	1795	None	550	1025	3	205	30	90	13	49	. . .	**95**
980	1795	20	400	750	3	330	48	260	38	31	50	**80**
980	1795	20	450	840	3	330	48	275	40	28	57	**92**
980	1795	85	400	750	3	495	72	440	64	24	79	**85**
980	**1795**	**85**	**450**	**840**	**3**	**470**	**68**	**425**	**62**	**23**	**74**	**91**

(a) Hold 30 min, water quench.

(b) In 50 mm (2 in.).

(c) 0.5% extension under load

Miscellaneous Precipitation-Hardening Alloys

Other alloys that can be age hardened are the nickel-tin bronze alloys C94700 and C94800, copper-nickel-beryllium alloy C96600, and the complex, special alloys C99400 and 99500. The solution-treating and precipitation-hardening treatments for these alloys are shown in Table 15.

Table 15 Typical heat-treating schedules and resulting properties for precipitation-hardening miscellaneous alloys

Alloy	**Solution treatment**			**Tempering treatment**			**Tensile strength**		**Yield strength[(a)]**		**Elongation[(b)], %**	Hardness, HB[(c)]
	Temperature		**Time, min**	**Temperature**		**Time, min**						
	°C	**°F**		**°C**	**°F**		**MPa**	**ksi**	**MPa**	**ksi**		

C94700	775-800	1425-1475	120	305-325	580-620	300	585	85	415	60	10	**180**
C94800	. . .	. . .	. . .	305-325	580-620	360-1000	415	60	205	30	8	**120**
C96600	995	1825	60	510	950	180	760	110	485	70	7	**230**
C99400	885	1625	60	480	900	60	545	79	370	54	. . .	**170**
C99500	**885**	**1625**	**60**	**480**	**900**	**60**	**595**	**86**	**425**	**62**	**8**	**196**

(a) At 0.2% extension under load for C96600; at 0.5% extension under load for all other alloys.

(b) In 50 mm (2 in.).

(c) 3000 kg load

A protective atmosphere of exothermic gas or dissociated ammonia is recommended during the aging of these alloys to produce bright surfaces. Parts heated in gas-fired or oil-fired furnaces in which the products of combustion are used as a protective atmosphere may tarnish slightly and require cleaning. Aging in an oxidizing atmosphere results in scaling.

Alloys C19000 and C19100 (Cu-4Ni-0.25P) also respond to precipitation hardening. The alloys are solution treated at 705 to 790 °C (1300 to 1450 °F). A reducing or neutral atmosphere should be used to prevent internal oxidation, especially on thin sections. Water quenching is preferred, although rapid air cooling may be adequate for separate small parts. Precipitation hardening is accomplished by aging the alloy at 425 to 480 °C (800 to 900 °F) for 1 to 3 h. While annealing is required to facilitate cold working prior to aging, temperatures as low as 620 °C (1150 °F) followed by normal air cooling are adequate.

Spinodal-Hardening Alloys

Spinodal structures are composed of a fine, homogeneous mixture of two phases that form by the growth of composition waves in a solid solution during a suitable heat treatment. The phases of the spinodal product differ in composition from each other and from the parent phase but have the same crystal structure as the parent phase. The fineness of spinodal structures is characterized by the distance between regions of identical composition, which is of the order of 50 to 1000 Å.

The conditions for the formation of a spinodal structure are thermodynamic and diffusional; the particular alloy system must have a miscibility gap (either stable or metastable), and the atoms of the two component metals must possess sufficient mobility at the heat-treating temperature. A phase diagram of a hypothetical binary alloy system with a stable miscibility gap is shown in Fig. 15. An alloy of composition C_0 that is homogenized in the single-phase α region and then held within the spinodal region is unstable to composition variations and will transform spontaneously to the two product phases α_1 and α_2 without requiring nucleation. If an alloy decomposes within the spinodal region by a diffusional process that allows composition variations to increase in magnitude, it is said to decompose spinodally. The resulting spinodal structures refer to phase mixtures that are derived from a particular kinetic process governing the initial stages of phase separation. The chemical spinodal line shown in Fig. 15 is not a phase boundary but a demarcation indicating a difference in thermodynamic stability.

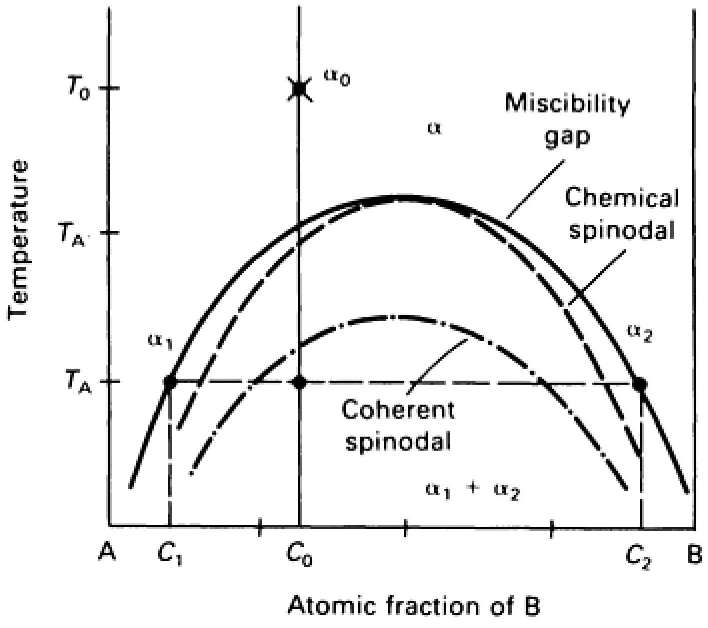


Fig. 15 Phase diagram of a binary alloy system that contains a miscibility gap in the solid state. An equilibrium structure for alloy C_0 at temperature T_A would contain two α phases of compositions C_1 and C_2. Spinodal decomposition can occur in the temperature-composition range below the chemical-spinodal line, which is the locus of points defined by the inflection points of the isothermal free energy (*G*) composition curves ($\partial^2 G/\partial C^2 = 0$).

The spinodal reaction is a spontaneous unmixing or diffusional clustering distinct from classical nucleation and growth in metastable solutions. This different kinetic behavior, which does not require a nucleation step, was first described by Gibbs in his treatment of the thermodynamic stability of undercooled or supersaturated phases. At small undercoolings or low supersaturations ($T_{A'}$), the solution is metastable; the appearance of a second phase requires relatively large localized compositional fluctuations. This is the classical nucleation process, giving rise to so-called critical nuclei, which can grow spontaneously. As the particles of the new phase grow by diffusion, the matrix composition is adjusted toward equilibrium. At large supersaturations (T_A), the solution is unstable, and the two-phase mixture gradually emerges by the continuous growth of initially small amplitude fluctuations (Fig. 16). The rate of reaction is controlled by the rate of atomic migration and the diffusion distances involved, which depend on the scale of decomposition (undercooling).

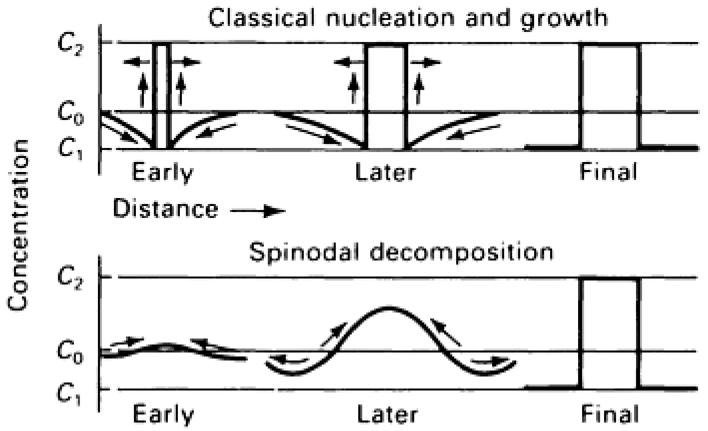


Fig. 16 Two sequences for the formation of a two-phase mixture by diffusion processes: nucleation and growth, and spinodal decomposition

The essential features of the spinodal process can be understood by considering this diffusional clustering as the inverse of the homogenization of a nonuniform solid solution exhibiting a sinusoidal variation of composition with distance. Long wavelength fluctuations grow sluggishly because of the large diffusion distances; short wavelength fluctuations are suppressed by the so-called gradient, or surface energy, of the diffuse or incipient interfaces that evolve during phase separation. Therefore, the microstructure that develops during spinodal decomposition has a characteristic periodicity that is typically 2.5 to 10 nm (25 to 100 Å) in metallic systems.

The heat treatment that causes the spinodal decomposition of a hypothetical alloy of composition C_0 (Fig. 15) is:

- Homogenize at a temperature above the miscibility gap, such as T_0, so that only statistical variations in composition exist within the specimen
- Cool rapidly to a temperature within the spinodal region, such as T_A, and hold at that temperature, or continuously cool the specimen from T_0, to room temperature

Table 16 lists the recommended solution treatment for the copper-nickel-chromium and copper-nickel-tin spinodal-hardening alloys. It is important to maintain control within the limits shown in order to obtain the proper heat-treating response in the subsequent spinodal aging treatment. Exceeding the upper limit may result in excessive grain growth in wrought materials, which could impair formability in the solution-annealed condition. Overheating cast material may cause incipient melting, resulting in brittle material that does not respond to spinodal hardening, particularly in the copper-nickel-tin alloys. Solution treating below the minimum temperature results in incomplete solution and failure of the material to harden fully during the spinodal aging treatment.

Table 16 Recommended solution-heat-treating temperatures and times for spinodal alloys

Alloy	**Alloy number**	**Solution-heat-treating temperature**		Time at temperature, h
		°C	**°F**	
Cu-30Ni-3Cr	C71900	900-950	1650-1740	$\frac{1}{2}$ **-2**
Cu-4Ni-4Sn	C72600	700-760	1300-1400	$\frac{1}{2}$ **-2**
Cu-9Ni-6Sn	C72700	730-790	1350-1450	$\frac{1}{2}$ **-2**
Cu-10Ni + 8Sn + 0.2Nb	C72800	805-845	1480-1550	$\frac{1}{2}$ **-2**

Wrought materials of some of these alloys can be extensively cold worked, with up to 90% reduction, after an effective solution treatment and quench. Solution anneals used between working schedules must be controlled toward the lower end of the temperature range and the minimum holding times to minimize grain growth because the solution temperature is above the recrystallization temperature. However, wrought alloys should be solution treated for approximately $\frac{1}{2}$ h for each inch of section thickness (or fraction thereof).

Homogenization. Cast microstructures of spinodal-hardening alloys generally require homogenization to encourage a uniform distribution of hardening elements and adequate response to the hardening treatments. The C71900 alloy may be homogenized by a prolonged solution-treating temperature. The copper-nickel-tin alloys have a tendency to develop porosity at higher temperatures, and therefore homogenization is best accomplished by first heating the alloys to 725 °C (1335 °F) and holding long enough to spheroidize the γ phase (3 to 12 h). The temperature is then increased to the regular solution temperature in preparation for the quench.

Oxidation. When spinodal copper-nickel-tin alloys are solution treated in air or oxidizing atmospheres, oxidation is encountered, which can be extremely abrasive to tools although it will not substantially affect the mechanical properties of the spinodal-hardened material. The oxide generally does not penetrate far below the surface of these alloys, and it can be removed by mechanical, chemical, or abrasive cleaning methods.

Quenching is a critical step of the solution process for copper-nickel-tin alloys. Successful heat treating requires that the material be quenched at the highest possible rate from the solution-treating temperature. It is therefore necessary to provide both rapid transfer from furnace to quench tank and an efficient quenching medium. Delays sufficient to cause the loss of temperature before the quench could allow the copper-nickel-tin intermetallic γ phase to form, reducing the effectiveness of the entire heat treatment. The quenching medium, which is generally water, must be sufficiently cold and agitated to maintain a rapid cooling rate to below the 200 °C (400 °F) level to ensure that no premature spinodal hardening occurs.

In some circumstances, particularly with the low-tin alloys (C72600 and C72700), oil, air, or cold-gaseous-medium quenching may be used for small parts or very thin sections, but a careful evaluation of these methods should be conducted to ensure the adequacy of the quench. Both mechanical testing of fully treated materials and metallographic examination of the microstructure should be employed to evaluate the quenching practice. The overall cooling rate of the quenching of spinodal-hardening C71900 (copper-nickel-chromium) alloy is somewhat less critical, but it is equally important to begin the quench at a temperature above the 900 °C (1650 °F) temperature.

Spinodal Hardening (Aging). Table 17 gives typical aging treatments and some resultant properties of various spinodal-hardening alloys. The effect of cold working between the solution quench and aging steps is also given for the copper-nickel-tin alloys. The copper-nickel-chromium (C71900) alloy can be hardened by slow cooling from the solution-treating (full annealing) range through 760 °C (1400 °F) or by a spinodal aging treatment in the 425 to 760 °C (800 to 1400 °F) range after a solution treatment. Slow cooling from solution temperature tends to produce slightly greater ductility.

Table 17 Typical strengths and recommended aging times for various spinodal alloys

Alloy	Alloy number	Solution-treated and cold-worked temper	Aging cycle, h at °C (°F)	Tensile strength		Yield strength[a]		Elongation, %
				MPa	ksi	MPa	ksi	
Cu-4Ni-4Sn	C72600	TD 02($\frac{1}{2}$ H)	1 $\frac{1}{2}$ at 350 (660)	635-690	92-100	495-570	72-83 (0.05)	**12**
Cu-4Ni-4Sn	C72600	TD 06(XH)	1 $\frac{1}{2}$ at 350 (660)	690-725	100-105	565-620	82-90 (0.05)	**9**
Cu-4Ni-4Sn	C72600	TD 08(S)	1 $\frac{1}{2}$ at 350 (660)	705-795	102-115	565-655	82-95 (0.05)	**7**

Cu-9Ni-6Sn	C72700	TD 04(H)	$1\frac{1}{2}$ at 350 (660)	860-1035	125-150	760-895	110-130 (0.05)	**8**
Cu-9Ni-6Sn	C72700	TD14(SS)	$1\frac{1}{2}$ at 350 (660)	1055-1145	153-166	930-985	135-143 (0.05)	**. . .**
Cu-10Ni-8Sn-0.2Nb	C72800	TB 00 cast and solution treated	4-6 at 350 (660)	830-965	120-140	550-690	80-100 (0.01)	**3**
Cu-10Ni-8Sn-0.2Nb	C72800	TB 00 hot worked and solution treated	3-5 at 350 (660)	965-1070	140-155	690-825	100-120 (0.01)	**6-14**
Cu-10Ni-8Sn-0.2Nb	C72800	TD 01($\frac{1}{4}$ H)	3 at 350 (660)	1140-1240	165-180	895-930	130-135 (0.01)	**7**
Cu-10Ni-8Sn-0.2Nb	C72800	TD 04(H)	3 at 350 (660)	1205-1380	175-200	930-1000	135-145 (0.01)	**7**
Cu-10Ni-8Sn-0.2Nb	C72800	TD 06(XH)	3 at 350 (660)	1205-1380	175-200	965-1035	140-150 (0.01)	**5**
Cu-10Ni-8Sn-0.2Nb	C72800	TD 08(S)	3 at 350 (660)	1240-1380	180-200	1000-1070	145-155 (0.01)	**4**
Cu-10Ni-8Sn-0.2Nb	C72800	TD 14(SS)	$1\frac{1}{2}$ at 350 (660)	1240-1380	180-200	1070-1140	155-165 (0.01)	**2.5**
Cu-15Ni-8Sn	C72900	TD 14(SS)	$1\frac{1}{2}$ at 350 (660)	1140-1380	165-200	1035-1170	150-170 (0.05)	**3**
Cu-30Ni-3Cr	**C71900**	**Hot extruded**	**$1\frac{1}{2}$ at 760 (405)**	**550**	**80**	**345**	**50 (0.20)**	**25**

(a) Offset shown in parentheses

The Cu-Ni-Sn alloys are hardened by treating in the rather narrow temperature range of 350 to 360 °C (660 to 680 °F). The development of the optimum properties requires the careful control of temperature and time at temperature. The use of hardness alone to evaluate results may not be adequate because high hardness may be maintained where excessive aging causes a decrease in elastic properties. Variations in tensile properties of 70 to 100 MPa (10 to 15 ksi) are possible without a significant hardness change.

Microduplexing. The copper-nickel-tin spinodal alloys can be treated using a combination of cold working and heat treatment called microduplexing. The alloys are cold worked to significant reductions (typically 40 to 60%) and given a partial solution treatment below the single-phase boundary, typically at 725 °C (1335 °F). The alloy is then aged at the higher spinodal-hardening temperature level of 425 °C (800 °F) for an extended time. The higher aging temperature is used to keep the aging time within reason, as microduplex age hardening takes place much more slowly than full spinodal hardening. This treatment results in moderately high tensile properties and significantly greater ductility. The curves in Fig. 17 show the effect of the microduplex treatment in comparison to conventional spinodal treatment using a 425 °C (800 °F) age.

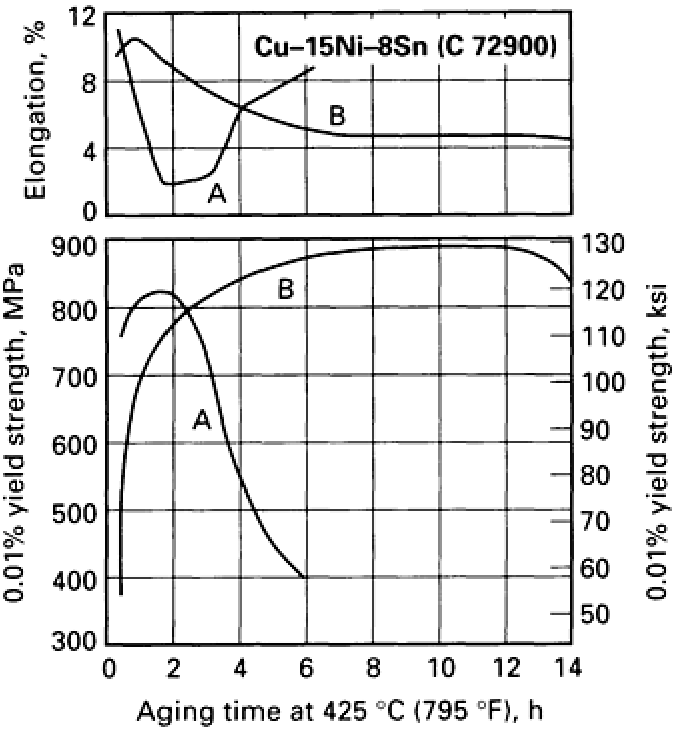


Fig. 17 Aging response of Cu-15Ni-8Sn (C72900) solution treated below the single-phase boundary (microduplexed) and above the single-phase boundary. Treatments prior to aging: A, solution treated above the single-phase boundary at 825 °C (1520 °F) for 30 min and water quenched; B (microduplexed), solution treated below the single-phase boundary at 725 °C (1340 °F) for 1 h and water quenched

Effect of Grain Size. The temperatures required for solution treatment are well into the recrystallization/growth range for spinodal-hardening alloys. The normal grain size obtained in properly treated wrought products is in the 0.010 to 0.090 mm (0.0004 to 0.0035 in.) range, but coarser grain sizes have been used without adverse results. Maintaining low solution temperatures in an attempt to minimize grain growth is good practice, but is second in importance to ensuring a complete solution treatment and adequate quench. An extremely fine grain size (2 to 4 μm) may be produced in the microduplexing treatment of copper-nickel-tin alloys because of the much lower solution-treating temperature and the nucleating effects of undissolved γ phase particles.

Fixturing in Close Tolerances. Excellent dimensional reproducibility can be achieved without fixturing during heat treatment. This is because the spinodal alloys do not undergo a crystallographic change during hardening. The chemical segregation (spinodal decomposition) is not accompanied by a second phase that can cause distortion during the aging process. Therefore, stability is greatly increased over that of precipitation-hardening alloys. Fixturing may nonetheless be necessary for extremely tight dimensional control, but this is rare.

Copper-Aluminum (Aluminum Bronze) Alloys

The microstructures and consequent heat treatabilities of aluminum bronzes vary with aluminum content much the same as these characteristics vary with carbon content in steels. Unlike steels, aluminum bronzes are tempered above the normal transformation temperature, typically in the range from 565 to 675 °C (1050 to 1250 °F). In the selection of

tempering temperatures, consideration must be given to both required properties and the hardness obtained upon quenching. Normal tempering time is 2 h at temperature. Moreover, heavy or complex sections should be heated slowly to avoid cracking. After the tempering cycle has been completed, it is important that aluminum bronzes be cooled rapidly using water quenching, spray cooling, or fan cooling. Slow cooling through the range from 565 to 275 °C (1050 to 530 °F) can cause the residual tempered martensitic β phase to decompose, forming the embrittling α-β eutectoid. The presence of appreciable amounts of this eutectoid structure can result in low tensile elongation, low energy of rupture, severely reduced impact values, and reduced corrosion resistance in some media. For adequate protection against detrimental eutectoid transformation, cooling after tempering should bring the alloy to a temperature below 370 °C (700 °F) within about 5 min, and to a temperature below 275 °C (530 °F) within 15 min. Normally, the danger of eutectoid transformation is much lower in nickel-aluminum bronzes, and these alloys can be air cooled after tempering.

The normal precautions used in the heat treating of steel have been found to be applicable to aluminum bronze, with critical cooling rates being somewhat lower than those for steel. Soaking time should be at least 45 min at temperature, and longer times may be used without fear of excess surface oxidation. Oil quenching is used on heavy, complex sections to avoid quench cracking, particularly in nickel-aluminum bronzes such as C63000.

Alpha-aluminum bronzes are those aluminum bronzes that contain less than 9% Al, or less than 8.5% Al with up to 3% Fe. They are essentially single-phase alloys, except for fine iron-rich particles in those alloys that contain iron. For α-aluminum bronzes, effective strengthening can be attained only by cold work, and annealing and/or stress relieving is the only heat treatment of practical use. The most prevalent alloys of this group are C60600, C61000, C61300, and C61400. In addition, alloys containing up to 9.6% Al, with microstructures containing small amounts of β phase at high temperatures, have such limited heat treatability that they, too, can be hardened only by cold work.

Annealing of α -aluminum bronzes is carried out at temperatures from about 540 to about 870 °C (1000 to 1600 °F), with the iron-containing alloys requiring temperatures nearer the high end of this range. Alloys of intermediate composition (containing small amounts of β phase), such as C61900, are normally annealed at 595 to 650 °C (1100 to 1200 °F). Figure 18 presents annealing curves for typical α-aluminum bronze alloys C61300 and C61400.

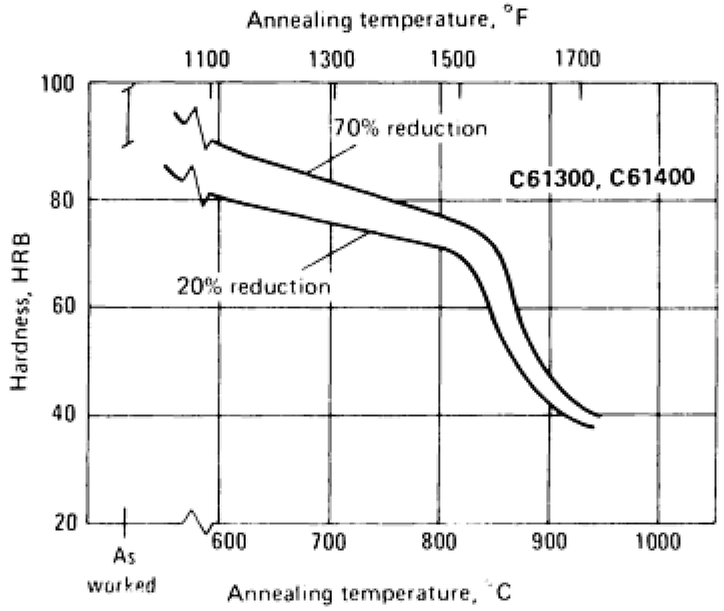


Fig. 18 Annealing curves for cold-reduced α-aluminum bronzes. Time at annealing temperature, 1 h

Complex α-β aluminum bronzes are those aluminum bronzes whose normal microstructures contain more than one phase to the extent that beneficial quench and temper treatments are possible. These copper-aluminum alloys, with and without iron, are heat treated by procedures somewhat similar to those used for the heat treatment of steel and have isothermal transformation diagrams that resemble those of carbon steels. For these alloys, the quench-hardening treatment is essentially a high-temperature soak intended to dissolve all of the a phase into the β phase. Quenching results in a hard room-temperature β martensite structure, and subsequent tempering reprecipitates fine α needles in the structure, forming

a tempered β martensite. Table 18 gives typical tensile properties and hardnesses of α-β aluminum bronzes after various stages of heat treatment.

Table 18 Typical heat treatments and resulting properties for complex (α-β) aluminum bronzes

Alloy	**Typical condition**[(a)]	**Tensile strength**		**Yield strength**[(b)]		**Elongation**[(c)]**, %**	Hardness, HB
		MPa	**ksi**	**MPa**	**ksi**		
C62400	As-forged or extruded	620-690	90-100	240-260	35-38	14-16	**163-183**
	Solution treated at 870 °C (1600 °F) and quenched, tempered 2 h at 620 °C (1150 °F)	675-725	98-105	345-385	50-56	8-14	**187-202**
C63000	As-forged or extruded	730	106	365	53	13	**187**
	Solution treated at 855 °C (1575 °F) and quenched, tempered 2 h at 650 °C (1200 °F)	760	110	425	62	13	**212**
C95300	As-cast	495-530	72-77	185-205	27-30	27-30	**137-140**
	Solution treated at 855 °C (1575 °F) and quenched, tempered 2 h at 620 °C (1150 °F)	585	85	290	42	14-16	**159-179**
C95400	As-cast	585-690	85-100	240-260	35-38	14-18	**156-179**
	Solution treated at 870 °C (1600 °F) and quenched, tempered 2 h at 620 °C (1150 °F)	655-725	95-105	330-370	48-54	8-14	**187-202**
C95500	As-cast	640-710	93-103	290-310	42-45	10-14	**183-192**
	Solution treated at 855 °C (1575 °F) and quenched,	**775-**	**112-**	**440-**	**64-**	**10-14**	**217-234**

(a) As-cast condition is typical for moderate sections shaken out at temperatures above 540 °C (1000 °F) and fan cooled or mold cooled, annealed at 620 °C (1150 °F), and fan (rapid) cooled.

(b) At 0.5% extension under load.

(c) In 50 mm (2 in.)

Heat Treating of Magnesium Alloys

Revised by Archie Stevenson, Magnesium Elektron, Inc.

Introduction

MAGNESIUM ALLOYS usually are heat treated either to improve mechanical properties or as a means of conditioning for specific fabricating operations. The type of heat treatment selected depends on alloy composition and form (cast or wrought), and on anticipated service conditions.

Solution heat treatment improves strength and results in maximum toughness and shock resistance. Artificial aging (precipitation heat treatment) after solution treatment gives maximum hardness and yield strength, but with some sacrifice of toughness. As applied to castings, artificial aging without prior solution treatment or annealing is a stress-relieving treatment that also somewhat increases tensile properties. Annealing of products lowers tensile properties considerably and increases ductility, thereby facilitating some types of fabrication. Modifications of these basic treatments have been developed for specific alloys, to obtain the most desirable combinations of properties. For example, increasing the aging time for some magnesium alloy castings considerably increases yield strength (although with some sacrifice of ductility). Also, combinations of solution treating, strain hardening, and artificial aging are applied to alloy HM21A sheet to improve mechanical properties over those attainable by solution treating and artificial aging alone.

For certain magnesium alloys, development of properties depends almost entirely on heat treatment. In magnesium-zirconium alloys, however, the extremely pronounced grain-refining effect of the zirconium also plays a very important role in improving mechanical properties.

The basic temper designations outlined in Table 1 for magnesium alloys are used throughout this article to indicate the various types of heat treatment. For a detailed explanation of these designations, which are the same as those applied to aluminum alloys, see the article "Alloy and Temper Designation Systems for Aluminum and Aluminum Alloys," in *Properties and Selection: Nonferrous Alloys and Special-Purpose Materials,* Volume 2, *ASM Handbook.*

Table 1 Basic temper designations

Designation	Expanation
F	As-fabricated
O	Annealed, recrystallized (wrought products only)
H	Strain hardened (wrought products only)
H1	Strain hardened only
H2	Strain hardened and partially annealed
H3	Strain hardened and stabilized
W	Solution heat treated; unstable temper
T	Heat treated to produce stable tempers other than F, O, or H

T2	Annealed (cast products only)
T3	Solution heat treated and cold worked
T4	Solution heat treated
T5	Artificially aged only
T6	Solution heat treated and artificially aged
T7	Solution heat treated and stabilized
T8	Solution heat treated, cold worked, and artificially aged
T9	Solution heat treated, artificially aged, and cold worked
T10	Artificially aged and cold worked

Note: For a more complete explanation of the designations outlined here, see Volume 2 of this *ASM Handbook* series.

The mechanical properties of most magnesium casting alloys can be improved by heat treatment. Casting alloys can be grouped into seven general classes of commercial importance on the basis of composition:

- Magnesium-aluminum-manganese (example: AM100A)
- Magnesium-aluminum-zinc (examples: AZ63A, AZ81A, AZ91C, AZ92A)
- Magnesium-zinc-zirconium (examples: ZK51A, ZK61A)
- Magnesium-rare earth metal-zinc-zirconium (examples: EZ33A, ZE41A)
- Magnesium-rare earth metal-silver-zirconium, with or without thorium (examples: QE22A, QH21A)
- Magnesium-thorium-zirconium, with or without zinc (examples: HK31A, ZH62A, HZ32A)
- Magnesium-zinc-copper(example: ZC63A)

In most wrought alloys, maximum mechanical properties are developed through strain hardening, and these alloys generally are either used without subsequent heat treatment or merely aged to a T5 temper. Occasionally, however, solution treatment, or a combination of solution treatment with strain hardening and artificial aging, will substantially improve mechanical properties. Wrought alloys that can be strengthened by heat treatment are grouped into five general classes according to composition:

- Magnesium-aluminum-zinc (example: AZ80A)
- Magnesium-thorium-zirconium (example: HK31A)
- Magnesium-thorium-manganese (examples: HM21A, HM31A)
- Magnesium-zinc-zirconium (example: ZK60A)
- Magnesium-zinc-copper (example: ZC71A)

Types of Heat Treatment

The heat treatments commonly used for various magnesium alloys, both cast and wrought, are indicated by temper designations in Table 2.

Table 2 Heat treatments commonly applied to magnesium alloys

Alloy	Heat treatment[(a)]
Casting alloys	
AM100A	T4, T5, T6, T61[(b)]
AZ63A	T4, T5, T6
AZ81A	T4
AZ91C	T4, T6
AZ92A	T4, T6
EZ33A	T5
EQ21A	T6
HK31A	T6
HZ32A	T5
QE22A	T6
QH21A	T6
WE43A	T6
WE54A	T6
ZC63A	T6
ZE41A	T5
ZE63A	T6[(c)]
ZH62A	T5

ZK51A	T5
ZK61A	T4, T6
Wrought alloys	
AZ80A	T5
HM21A	T5, T8, T81[(d)]
HM31A	T5
ZC71A	F, T5, T6
ZK60A	T5

(a) Indicated by temper designations (see Table 1).

(b) Same as T6 except aged for longer time to increase yield strength.

(c) Thermal treatment must include hybriding.

(d) Mill modification of T8 to improve mechanical properties

Annealing. Wrought magnesium alloys in various conditions of strain hardening or temper can be annealed by being heated at 290 to 455 °C (550 to 850 °F), depending on alloy, for one or more hours (Table 3). This procedure usually will provide a product with the maximum anneal that is practical. Because most forming operations on magnesium are done at elevated temperature, the need for fully annealed wrought material is less than with many other metals.

Table 3 Annealing temperatures for wrought magnesium alloys

Alloy	Original temper	Annealing temperature[(a)]	
		°C	°F
AZ31B	F, H10, H11, H23, H24, H26	345	650
AZ31C	F	345	650
AZ61A	F	345	650

AZ80A	F, T5, T6	385	725
HK31A	H24	400	750
HM21A	T5, T8, T81	455	850
HM31A	T5	455	850
ZK60A	F, T5, T6	290	550

(a) Time at temperature, 1 h or more

Stress Relieving of Wrought Alloys. Stress relieving is used to remove or reduce residual stresses induced in wrought magnesium products by cold and hot working, shaping and forming, straightening, and welding.

Table 4 gives the recommended stress-relieving times and temperatures for wrought magnesium alloys to obtain assemblies with maximum freedom from stress. When extrusions are welded to hard-rolled sheet, the lower stress-relieving temperature and the longer time should be used to minimize distortion; for example, use 150 °C (300 °F) for 60 min rather than 260 °C (500 °F) for 15 min.

Table 4 Recommended stress-relieving treatments for wrought magnesium alloys

Alloy	Sheet						Extrusions and forgings		
	Annealed			Hard rolled					
	Temperature		Time, min	Temperature		Time, min	Temperature		Time, min
	°C	°F		°C	°F		°C	°F	
AZ31B	345	650	120	150	300	60	. . .	. . .	. . .
AZ31B-F	. . .	. . .	. . .	. . .	. . .	. . .	260	500	15
AZ61A	345	650	120	205	400	60	. . .	. . .	. . .
AZ61A-F	. . .	. . .	. . .	. . .	. . .	. . .	260	500	15
AZ80A-F	. . .	. . .	. . .	. . .	. . .	. . .	260	500	15
AZ80A-T5	. . .	. . .	. . .	. . .	. . .	. . .	205	400	60

HK31A	345	650	60	290	550	30	. . .	. . .	. . .
HM21A-T5	. . .	. . .	. . .	. . .	. . .	. . .	370	700	30
HM21A-T8	. . .	. . .	. . .	370	700	30	. . .	. . .	. . .
HM21A-T81	. . .	. . .	. . .	400	750	30	. . .	. . .	. . .
HM31A-T5	. . .	. . .	. . .	. . .	. . .	. . .	425	800	60
ZC71A-T5	. . .	. . .	. . .	. . .	. . .	. . .	330	625	60
ZK60A-F	230	450	180	. . .	. . .	. . .	260	500	15
ZK60A-T5	. . .	. . .	. . .	. . .	. . .	. . .	150	300	60

Note: Stress relieving after welding, to prevent stress-corrosion cracking, is necessary only for alloys that contain more than 1.5% aluminum.

Stress Relieving of Castings. The precision machining of castings to close dimensional limits, the necessity of avoiding warpage and distortion, and the desirability of preventing stress-corrosion cracking in welded magnesium-aluminum casting alloys make it mandatory that cast components be substantially free from residual stresses. Although magnesium castings do not normally contain high residual stresses, the low modulus of elasticity of magnesium alloys means that comparatively low stresses can produce appreciable elastic strains.

Residual stresses may arise from contraction due to mold restraint during solidification, from nonuniform cooling after heat treatment, or from quenching. Machining operations also can result in residual stress and require intermediate stress relieving prior to final machining.

Weld repairs may introduce severe stresses and should be followed by some type of heat treatment to prevent subsequent movement and cracking, as discussed in the section of this article concerning heat treatment of repair-welded castings.

The following heat treatments for castings will provide stress relief without significantly affecting mechanical properties:

Alloy	**Temper**	**Heat treatment**
Mg-Al-Mn	All	1 h at 260 °C (500 °F)
Mg-Al-Zn	All	1 h at 260 °C (500 °F)
ZK61A	T5	2 h at 330 °C (625 °F) and then 48 h at 130 °C (265 °F)

ZE41A	All	2 h at 330 °C (625 °F)

Solution Treating and Aging. Schedules for solution treating and aging of magnesium alloys are summarized in Table 5. In solution treating of magnesium-aluminum-zinc alloys, parts should be loaded into the furnace at approximately 260 °C (500 °F) and then raised to the appropriate solution-treating temperature slowly, to avoid fusion of eutectic compounds and resultant formation of voids. The time required to bring the load from 260 °C (500 °F) to the solution-treating temperature is determined by the size of the load and by the composition, size, weight, and section thickness of the parts, but 2 h is a typical time. All other heat-treatable magnesium alloys can be loaded into the furnace at the solution-treating temperature. For alloy HK31A, it is important to bring the load to temperature as rapidly as possible to avoid grain coarsening.

Table 5 Recommended solution-treating and aging schedules for magnesium alloy castings and wrought alloy ZC71A

For castings up to 50 mm (2 in.) in section thickness; heavier sections may require longer times at temperature.

Alloy	Final temper	Aging[a]			Solution treating[c]					Aging after solution treating		
		Temperature		Time, h	Temperature		Time, h	Maximum temperature		Temperature		Time, h
		°C, ±6[b]	°F, ±10[b]		°C, ±6[b]	°F, ±10[b]		°C	°F	°C, ±6[b]	°F, ±10[b]	
Magnesium-aluminum-zinc castings[d]												
AM100A	T5	232	450	5	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
	T4	. . .	. . .	. . .	424[e]	795[e]	16-24[e]	432	810	. . .	. . .	. . .
	T6	. . .	. . .	. . .	424[e]	795[e]	16-24[e]	432	810	232	450	5
	T61	. . .	. . .	. . .	424[e]	795[e]	16-24[e]	432	810	218	425	25
AZ63A	T5	260[f]	500[f]	4[f]	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
	T4	. . .	. . .	. . .	385	725	10-14	391	735	. . .	. . .	. . .
	T6	. . .	. . .	. . .	385	725	10-14	391	735	218[f]	425[f]	5[f]
AZ81A	T4	. . .	. . .	. . .	413[e]	775[e]	16-24[e]	418	785	. . .	. . .	. . .
AZ91C	T5	168[g]	335[g]	16[g]	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
	T4	. . .	. . .	. . .	413[e]	775[e]	16-24[e]	418	785	. . .	. . .	. . .

	T6	. . .	. . .	. . .	413(e)	775(e)	16-24(e)	418	785	168(h)	335(h)	16(h)
AZ92A	T5	260	500	4	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
	T4	. . .	. . .	. . .	407(i)	765(i)	16-24(i)	413	775	. . .	. . .	. . .
	T6	. . .	. . .	. . .	407(i)	765(i)	16-24(i)	413	775	218	425	5
Magnesium-zinc-copper castings												
ZC63A(j)	T6	. . .	. . .	. . .	440	825	4-8	445	835	200	390	16
Magnesium-zirconium castings												
EQ21A(j)	T6	. . .	. . .	. . .	520	970	4-8	530	985	200	390	16
EZ33A	T5	175	350	16	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
HK31A(k)	T6	. . .	. . .	. . .	566	1050	2	571	1060	204	400	16
HZ32A	T5	316	600	16	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
QE22A(j)	T6	. . .	. . .	. . .	525	980	4-8	538	1000	204	400	8
QH21A(j)	T6	. . .	. . .	. . .	525	980	4-8	538	1000	204	400	8
WE43A(j)	T6	. . .	. . .	. . .	525	980	4-8	535	995	250	480	16
WE54A(j)	T6	. . .	. . .	. . .	527	980	4-8	535	995	250	480	16
ZE41A	T5	329(l)	625(l)	2(l)	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
ZE63A(m)	T6	. . .	. . .	. . .	480	895	10-72	491	915	141	285	48
ZH62A	T5	329	625	2	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
		plus: 177	350	16	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
ZK51A	T5	177(n)	350(n)	12(n)	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .

ZK61A	T5	149	300	48	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
	T6	. . .	. . .	. . .	499[o]	930[o]	2[o]	502	935	129	265	48
Wrought products												
ZC71A[j]	T5	180	355	16	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
ZC71A[j]	T6	. . .	. . .	. . .	430	805	4-8	435	815	180	355	16

(a) Aging to the T5 temper is done from the as-fabricated (f) condition.

(b) Except where quoted differently.

(c) After solution treatment and before subsequent aging, castings are cooled to room temperature by fast fan cooling, except where otherwise indicated. Use carbon dioxide, sulfur dioxide, or 0.5 to 1.5% sulfur hexafluoride in carbon dioxide as a protective atmosphere above 400 °C (750 °F).

(d) For solution treating, Mg-Al-Zn alloys are loaded into the furnace at 260 °C (500 °F) and brought to temperature over a 2-h period at a uniform rate of temperature increase.

(e) Alternative treatment, to prevent germination (excessive grain growth): 6 h at 413 ± 6 °C (775 ± 10 °F), 2 h at 352 ± 6 °C (665 ± 10 °F), 10 h at 413 ± 6 °C (775 ± 10 °F).

(f) Alternative treatment: 5 h at 232 ± 6 °C (450 ± 10 °F).

(g) Alternative treatment: 4 h at 216 ± 6 °C (420 ± 10 °F).

(h) Alternative treatment: 5 to 6 h at 216 ± 6 °C (420 ± 10 °F).

(i) Alternative treatment, to prevent germination (excessive grain growth): 6 h at 407 ± 6 °C (765 ± 10 °F), 2 h at 352 ± 6 °C (665 ± 10 °F), 10 h at 407 ± 6 °C (765 ± 10 °F).

(j) Quench from solution-treating temperature either in water at 65 °C (150 ° F) or in other suitable medium.

(k) Alloy HK31A castings must be loaded into the furnace already at temperature and brought back to temperature as quickly as possible.

(l) This treatment is adequate for development of satisfactory properties; it may be followed by 16 h at 177 ± 6 °C (350 ± 10 °F) to provide very slight improvements in mechanical properties.

(m) Alloy ZE63A must be solution treated in a special hydrogen atmosphere because its mechanical properties are developed through hydriding of

some of its alloying elements. Hydriding time depends on section thickness; as a guide, 6.4 mm ($\frac{1}{4}$ in.) sections require approximately 10 h, and 19 mm ($\frac{3}{4}$ in.) sections require about 72 h. Following solution treatment, ZE63A should be quenched in oil, water spray, or air blast.

(n) Alternative treatment: 8 h at 218 ± 6 °C (425 ± 10 °F).

(o) Alternative treatment: 10 h at 482 ± 6 °C (900 ± 10 °F)

During aging, magnesium alloy parts should be loaded into the furnace at the treatment temperature, held for the appropriate period, and then cooled in still air. As indicated in Table 5, there is a choice of artificial aging treatments for some alloys; results are closely similar for the alternative treatments given.

Reheat Treating. Under normal circumstances, when mechanical properties are within expected ranges and the prescribed heat treatment has been carried out, reheat treating is seldom necessary. However, if the microstructures of heat-treated castings indicate too high a compound rating, or if the castings have been aged excessively by slow cooling after solution treating, reheat treating is called for. Most magnesium alloys can be reheat treated with little danger of germination (excessive grain growth). When reheat treating of alloy HK31A is necessary, however, the castings should be checked carefully for evidence of germination. To prevent germination in Mg-Al-Zn alloys, solution reheat-treating time should be limited to 30 min (assuming proper solution treatment of thick sections during prior heat treatment).

Effects of Major Variables

Casting size and section thickness, relation of casting size to volume capacity of the furnace, and arrangement of castings in the furnace are mechanical considerations that can affect heat-treating schedules for all metals.

Section Size and Heating Time. There is no general rule for estimating time of heating per unit of thickness for magnesium alloys. However, because of the high thermal conductivity of these alloys, combined with their low specific heat per unit volume, parts reach soaking temperature quite rapidly. The usual procedure is to load the furnace and to begin the soaking period when the loaded furnace reaches the desired temperature.

The heat-treating times given in Table 5 have been found to be satisfactory for normal furnace loads and for castings of moderate section thickness. In the heat treating of magnesium alloy castings with thick sections (occasionally as low as 25 mm, or 1 in. but usually over 50 mm, or 2 in.), a good rule is to double the time at the solution-treating temperature. For example, the usual solution treatment for AZ63A castings is 12 h at about 385 °C (725 °F), whereas 25 h at about 385 °C is suggested for castings with section thicknesses greater than 50 mm (2 in.). Similarly, the suggested solution-treating schedule for preventing excessive grain growth in AZ92A castings is 6 h at about 405 °C (765 °F), 2 h at about 350 °C (665 °F), and 10 h at about 405 °C; but for castings with sections more than 50 mm (2 in.) thick, it is recommended that the last soak at 405 °C be extended from 10 to 19 h. The best way to determine whether additional solution-treating time is required is to cut a section through the thickest portion of a scrap casting and examine the center of the section microscopically: if heat treatment is complete, this examination will reveal a low compound rating.

Heat-Treating Time and Temperature. As demonstrated by the data in Fig. 1, 2, 3, and 4, the mechanical properties of magnesium alloys can be varied within wide limits by varying the heat-treating times and temperatures recommended in Table 5. Although the highest mechanical properties in test bars of QE22A-T6 (Fig. 1) were obtained by solution treating for 4 h at 540 °C (1000 °F), less distortion due to sagging is experienced in production castings solution treated for 8 h at 525 °C (980 °F). The risk of incipient melting can also occur at the higher temperature.

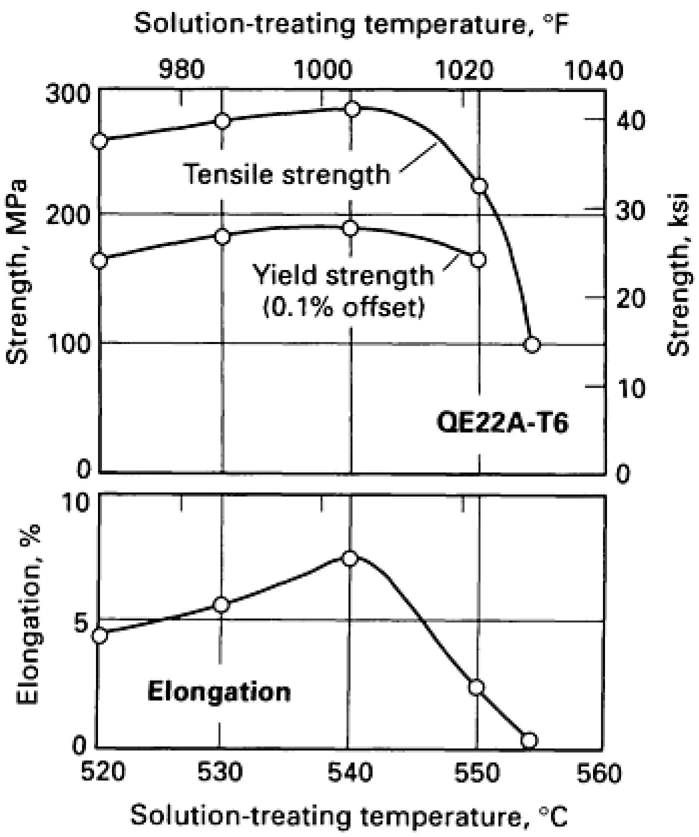


Fig. 1 Tensile properties of alloy QE22A-T6 as functions of solution-treating temperature. Data were obtained from test bars of casting alloy QE22A-T6 machined from 25 mm (1 in.) diam cast specimens. The bars were held at temperature for 4 h.

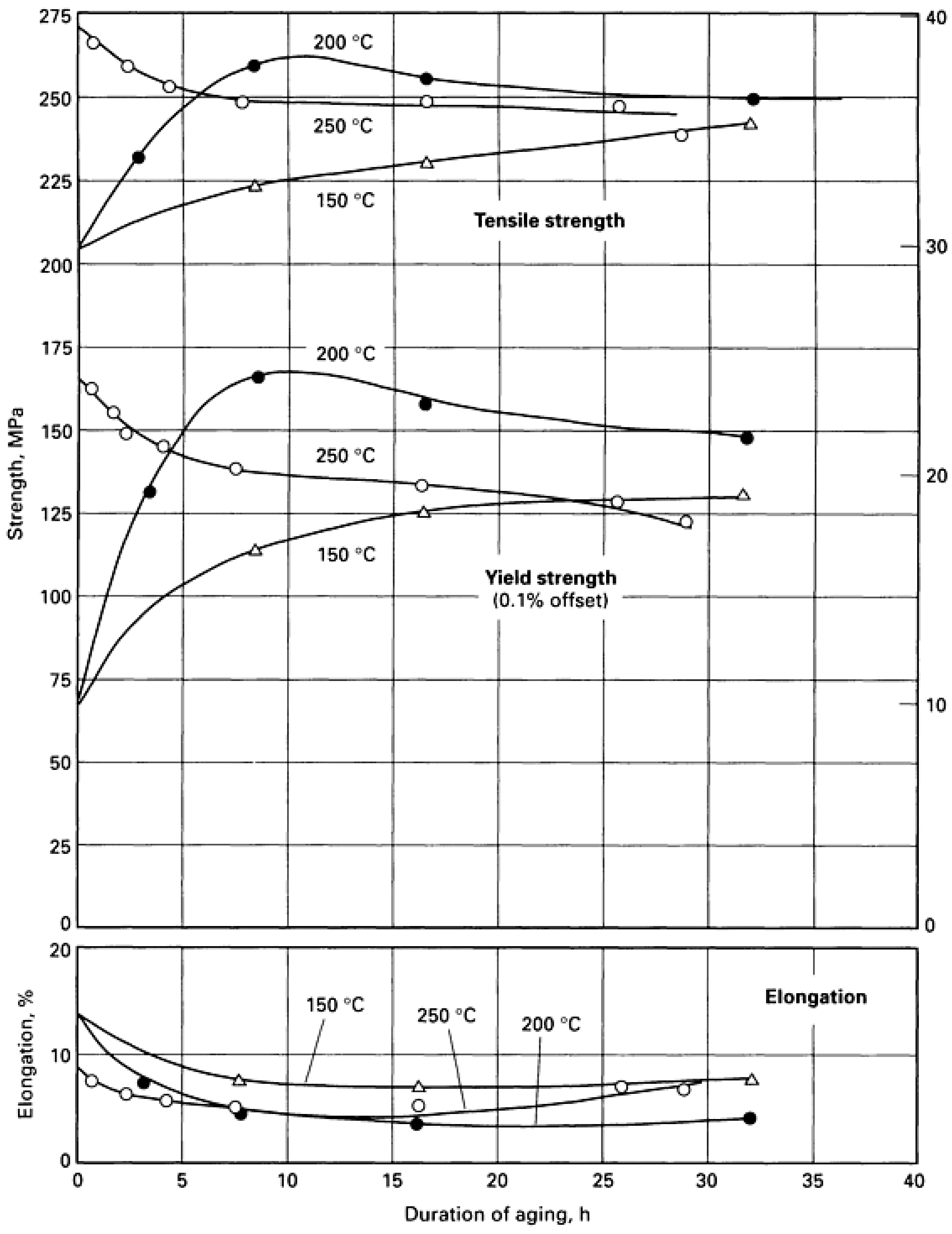


Fig. 2 Tensile properties of alloy QE22A-T6 as functions of aging time and temperature. Data were obtained from test bars of casting alloy QE22A-T6 machined from 25 mm (1 in.) diam cast specimens.

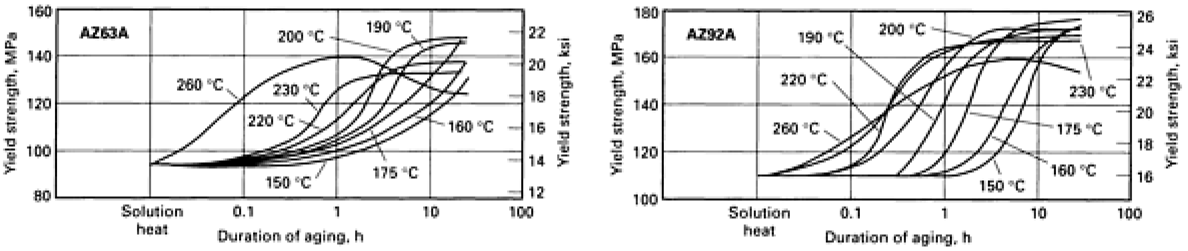


Fig. 3 Variation of yield strength with aging time and temperature for sand cast AZ63A and AZ92A

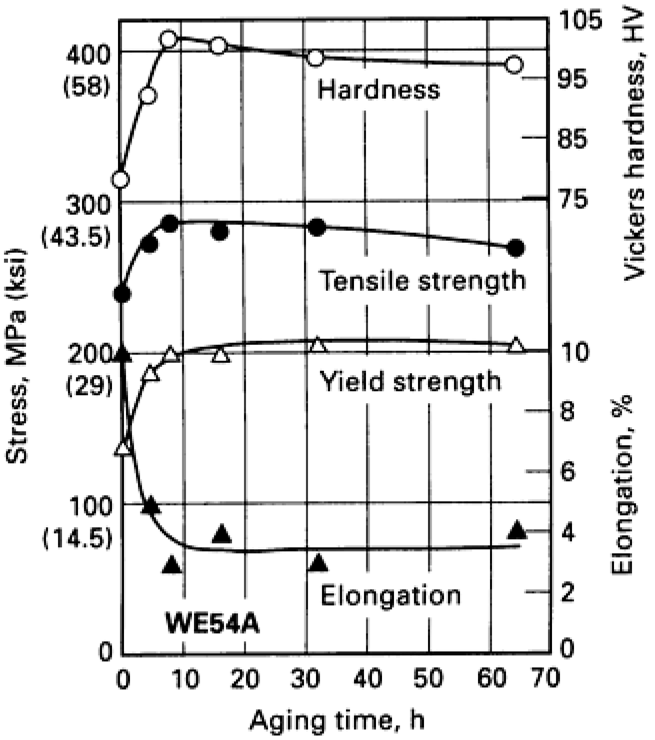


Fig. 4 Effect of aging time at 250 °C (480 °F) on the hardness and tensile properties of WE54A-T6. Data derived from test bars cut from 25 mm (1 in.) sand cast plate

Protective Atmospheres. Although magnesium alloys can be heat treated in air, protective atmospheres are almost always used for solution treating. Government specification MIL-M-6857, for heat treating of magnesium castings, requires a protective atmosphere for solution treating above 400 °C (750 °F). Protective atmospheres serve the dual purpose of preventing surface oxidation (which, if severe, can decrease strength) and of preventing active burning should the furnace exceed proper temperature.

The three gases normally used are sulfur hexafluoride, sulfur dioxide, and carbon dioxide. Inert gases also may be used; however, in most instances, these gases are not practical because of higher cost. A concentration of 0.5 to 1.5% sulfur hexafluoride in carbon dioxide will prevent active burning above 600 °C (1110 °F). Sulfur dioxide is available bottled, whereas carbon dioxide may be obtained either bottled or as the product of recirculated combustion gases from a gas-fired furnace. A concentration of 0.7% (0.5% min) sulfur dioxide will prevent active burning to a temperature of 565 °C (1050 °F), provided that melting of the alloy has not occurred. Carbon dioxide in a concentration of 3% will prevent active burning to 510 °C (950 °F), and a carbon dioxide concentration of 5% will provide protection to about 540 °C (1000 °F).

Sulfur hexafluoride is more expensive than either sulfur dioxide or carbon dioxide but has the advantage of being nontoxic and noncorrosive. Sulfur dioxide is also more expensive on a volume basis than carbon dioxide, but the volume

of sulfur dioxide required for a protective atmosphere is only $\frac{1}{6}$ the volume of carbon dioxide required. Thus, the cost of producing a protective atmosphere with bottled gases is less using sulfur dioxide. Where gas-fired furnaces are used and the atmosphere is obtained by recirculating combustion gases, a carbon dioxide atmosphere has the lower cost.

The use of sulfur dioxide requires frequent cleaning of furnace controls and fixtures and replacement of furnace parts because of the formation of corrosive sulfuric acid in the furnace system. When heat treating both magnesium and aluminum alloy castings in the same furnace is desired, a carbon dioxide atmosphere is required because sulfur dioxide is harmful to aluminum. Government regulations regarding the use of sulfur dioxide also suggest the use of carbon dioxide.

Equipment and Processing

In solution treating and artificial aging of magnesium alloys, it is standard practice to use an electrically heated or gas-fired furnace equipped with a high-velocity fan or comparable means for circulating the atmosphere and promoting uniformity of temperature. However, because the atmosphere for solution treating sometimes contains sulfur dioxide, only furnaces that are gastight and that provide an inlet for introducing protective atmosphere are suitable.

The atmosphere is circulated past the heating elements and through the load in the basket. A rapid rate of circulation is necessary for maintaining an even distribution of temperature throughout the load. The minimum rate of circulation varies with furnace design and loading practice; one manufacturer recommends a rate equivalent to about 45 changes of atmosphere per minute.

Furnace Loading. Loading of furnaces used for heat treatment of magnesium parts is an important consideration. Parts must be clean and free from grinding dust, shavings, chips, sawings, and other fines; this is particularly important at the higher temperatures used for solution treatment. A furnace load should be comprised of only one alloy composition because of the variation in nonequilibrium fusion points among various alloys. Furnaces should be loaded in an orderly manner that will not interfere with air circulation and cause uneven heating.

Temperature Control. A high degree of temperature control is required for heat treating of magnesium alloys. As indicated in Table 5, the maximum allowable temperature variation is ±6 °C (±10 °F) for the solution-treating operation.

The safest and most suitable temperature-control system for solution and precipitation treating of magnesium alloys consists of three types of furnace controls. The first control detects the temperature within the heating chamber and controls the source of heat so as to attain and hold a desired predetermined temperature. This control is composed of a temperature-sensing device (usually a thermocouple) and a recording controller.

The second control is a furnace-charge-temperature sensor and is used to determine when the load has reached temperature. It consists of a thermocouple strategically located in the charge and a temperature-indicating device; an indicator-controller may be used to actuate an alarm, signal, or timing device to indicate that the charge has reached temperature. This control is useful for preventing overshooting of the desired maximum temperature because of high heat input or because the load is small in comparison with the size of the furnace.

The third control is a safety device and is used to prevent serious overheating of the load or a possible magnesium fire. It consists of a thermocouple, usually located in the roof of the furnace, and an indicating controller that will turn off the source of heat to the furnace. This controller should require resetting before the furnace will heat again.

Quenching Media. Magnesium alloy products normally are quenched in air following solution treatment. Still air usually is sufficient; forced-air cooling is recommended for dense loads or for parts that have very thick sections. The only common exceptions to air quenching are alloys QE22A and QH21A, for which water quenching at 60 to 95 °C (140 to 200 °F) is used to develop the best mechanical properties. Glycol or oil quenchants will produce similar properties with reduced distortion. For QE22A products subject to distortion as a result of the severity of water quenching, air cooling may be used provided that the cooling rate exceeds 3 °C/s (5 °F/s). The effects of quenching in still air, in forced air, and in water at 65 °C (150 °F) on the tensile properties of separately cast test bars of QE22A-T6 are indicated by the data in Table 6.

Table 6 Effect of quenching medium on average tensile properties of QE22A-T6

Quenching medium	Tensile strength		Yield strength[(a)]		Elongation[(b)], %
	MPa	ksi	MPa	ksi	
Still air[(c)]	232	33.6	158	22.9	3.8
Air blast[(c)]	250	36.2	182	26.4	3.5
Water at 65 °C (150 °F)[(c)]	270	39.2	190	27.5	3.0
30% glycol at room temperature[(d)]	269	39.0	190	27.5	3.0

(a) At 0.2% offset.

(b) In 50 mm or 2 in.

(c) Properties determined on bars machined from 25 mm (1 in.) diam separately cast specimens.

(d) Properties determined on bars machined from castings

Control of Distortion. The strength of cast magnesium alloys decreases at elevated temperature to such an extent that it is often necessary during solution treating to prevent intricate castings from sagging from their own weight and to keep flat castings from warping as a result of the relief of casting stresses. To accomplish these ends, tie bars are made an integral part of the casting, simple fixturing is used, or complicated cast or machined fixtures are produced. The method used depends on the complexity and quantity of castings to be made, and on the degree of dimensional control required. Whatever the method, it should not interfere unnecessarily with the free circulation of heat about the castings. Although fixturing decreases warpage of castings, some castings still require straightening after solution treating. Straightening is most readily done after solution treating, prior to aging.

Prevention of Heat-Treating Problems

Six common problems that may be encountered in heat treating magnesium alloys are oxidation, fusion voids, warpage, grain coarsening, germination, and inconsistent properties. Causes and prevention are discussed in Table 7.

Table 7 Causes and prevention of problems commonly encountered in heat treatment of magnesium alloys

Oxidation
Cause: Heat treating without use of protective or inert atmosphere; can lead to local weakening of the metal part, and even to burning of the metal in the furnace.
Prevention: Heat treat in a controlled atmosphere containing about 0.5 to 1.5% SO_2 or 3 to 5% CO_2, or 0.5 to 1.5% SF_6 in CO_2, or (less practical because more costly) in an inert-gas atmosphere. Ensure that furnace is clean and completely dry.

Fusion voids
Cause: Use of improper rate of heating from 260 to 370 °C (500 to 700 °F) for Mg-AI-Zn alloys, or exceeding recommended temperature in solution heat treating of these alloys or of the alloys that contain zinc, thorium, and rare earth metals as major alloying elements. Fusion voids are not normally observed when the solidus temperature of the Mg Zr alloys is exceeded. In this instance that grain-boundary phase will run along the grain-boundary forming long, narrow regions. This is normally accompanied by grain coarsening.
Prevention: Charge furnace with Mg-Al-Zn alloys at 260 °C (500 °F) and then heat gradually to solution-treating temperature over a period of 2 h. Control solution temperature so as not to exceed designated temperature by more than 6 °C (10 °F).
Warpage
Cause: Lack of support of castings during heat treatment; uneven distribution of heat.
Prevention: Support long spans of thin cross section; use jigs for intricate shapes. Distribute load in furnace to obtain good circulation of atmosphere.
Grain coarsening
Cause: Occurs in HK31A as a result of delay in attaining solution temperature or of holding at solution temperature for an excessive period.
Prevention: Prior to solution treating of HK31A, furnace should be at temperature; castings should be loaded quickly, and the loaded furnace should be closed and brought to temperature as rapidly as possible. Time at temperature should be controlled.
Germination
Cause: Grain growth, which occurs in AM 100A, AZ81A, AZ91C, and AZ92A toward the end of the solution-treating cycle.
Prevention: Use antigermination heat-treating schedules (presented as alternative treatments in footnotes [e] and [j] in Table 5).
Inconsistent properties
Cause: Insufficient or excessive furnace temperature, inadequate circulation of heat in the furnace, faulty temperature control, very slow cooling from the solution-treating temperature, or inadequate solution-treating time for heavy sections.
Prevention: Check temperature at various positions in furnace with standardized thermocouple. Distribute castings in furnace to provide adequate circulation of heat. Check temperature controls often, and ensure that controls are located so as to provide uniformity of temperature. Increase solution-treating time to allow complete homogenization.

Dimensional Stability. In normal service up to approximately 95 °C (200 °F), all magnesium casting alloys exhibit good dimensional stability and can be considered free from additional dimensional changes.

Some cast magnesium-aluminum-manganese and magnesium-aluminum-zinc alloys in certain tempers exhibit slight permanent growth after relatively long exposure to temperatures exceeding 95 °C (Fig. 5 and 6). This growth, although slight, can give rise to problems as in the following example.

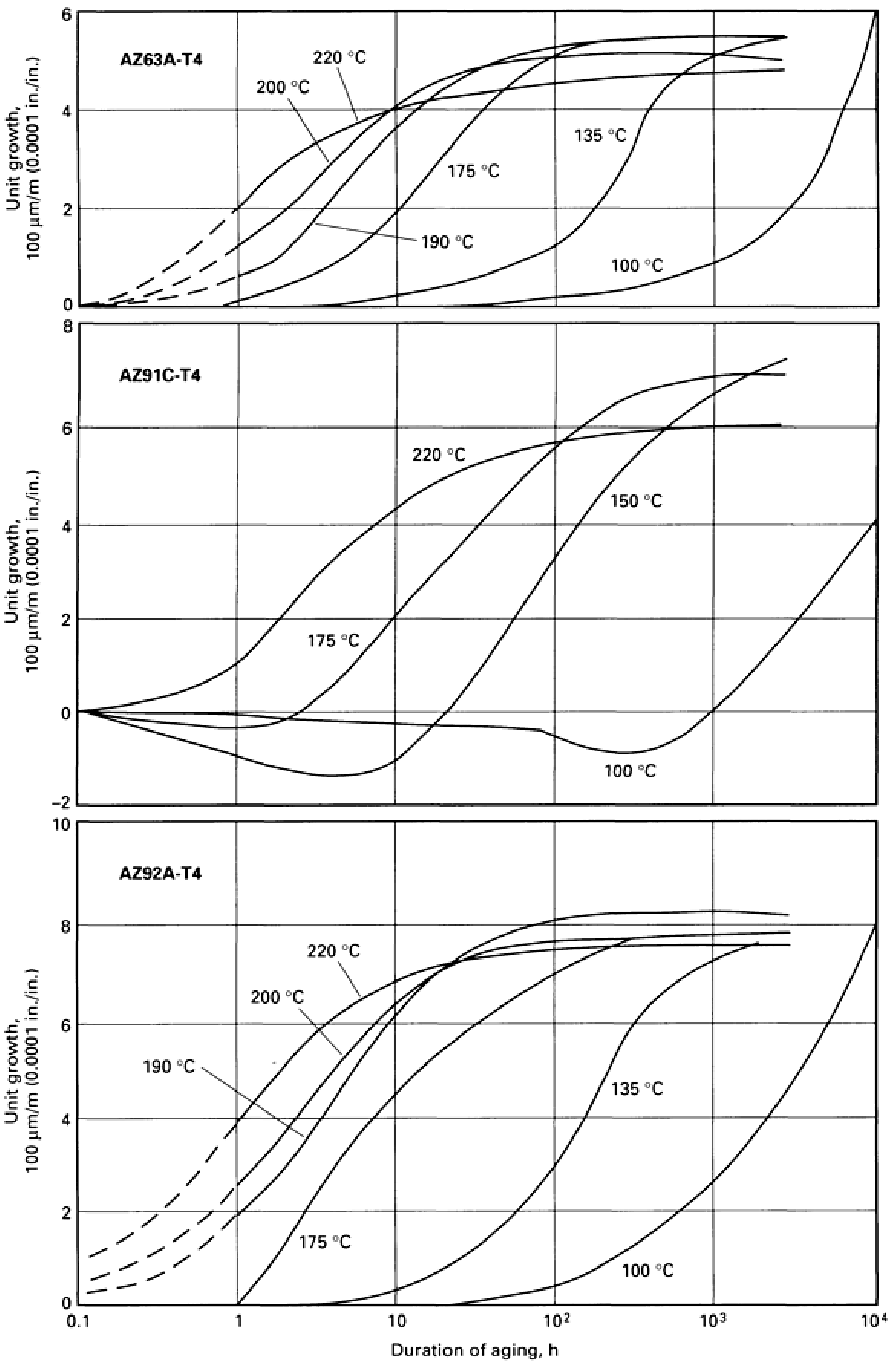


Fig. 5 Variation of growth with aging time and temperature for solution-treated AZ63A, AZ92A, and AZ91C

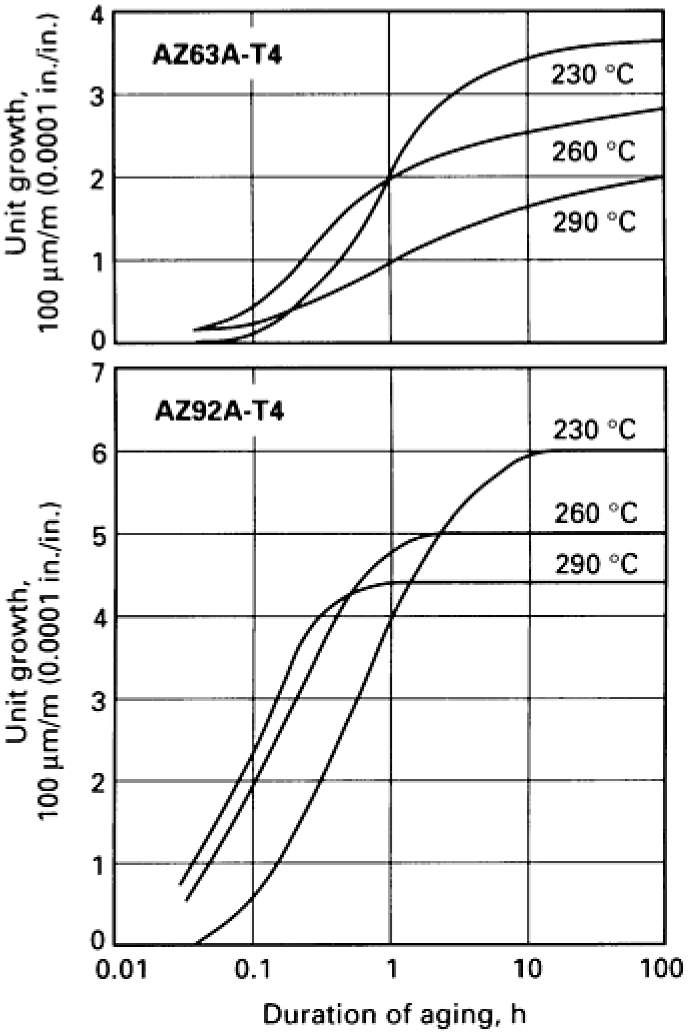


Fig. 6 Variation of growth with aging time and temperature for solution-treated AZ63A and AZ92A

Example: Dimensional Change of Engine Cover Plate.

An aircraft-engine cover plate, sand cast of alloy AZ63A, was used in the as-cast condition (F temper), and the operating temperature of the engine was high enough to cause growth. As a result of this growth, it was necessary to pry off the cover plate when the engine was taken down for overhauling, and the plate could not be replaced because the holes did not line up properly with mating studs. This problem could have been eliminated by proper choice of temper (T5 or T6) prior to placing the cover in service.

In contrast to the growth characteristics of the magnesium-aluminum-zinc alloys are those of the magnesium alloys containing thorium, rare earth metals, and zirconium as major alloying elements. These alloys normally are used in the T5 or T6 temper, and they shrink, rather than grow, on exposure to elevated temperature (Table 8).

Table 8 Contraction of magnesium casting alloys at elevated temperatures

Alloy	Temperature		Unit contraction, 100 μin/m (0.0001 in./in.), after exposure time, h, of			
	°C	°F	10	100	1000	5000

EZ33A-T5	205	400	1.1	1.3	1.3	1.3
	260	500	1.3	1.6	1.8	1.9
	315	600	1.2	1.5	1.7	1.8
	370	700	1.0	1.2	1.3	1.4
HK31A-T6	205	400	0.3	0.3	0.3	0.3
	260	500	0.3	0.5	0.7	0.7
	315	600	0.2	0.5	1.3	1.3
	370	700	0.6	1.1	1.1	1.1
HZ32A-T5	205	400	1.1	1.3	1.4	1.4
	260	500	0.8	1.0	1.1	1.2
	315	600	0.8	1.0	1.1	1.2
	370	700	0.6	0.8	0.9	1.0

Heat Treatment of Weld-Repaired Castings

Magnesium sand castings that have been reclaimed or repaired by welding may be subsequently heat treated to relieve residual stresses. Heat treatment also may be necessary for restoring the mechanical properties of the casting when these have been impaired or modified by preheating prior to welding, or for heat treating the weld zone as such.

Table 9 shows the heat-treating schedules recommended for magnesium castings after welding. The heat-treating procedures shown are based on both the temper of the casting before the welding operation and the temper desired after welding. These postwelding heat treatments are normally all that is required for adequate stress relief of castings and for optimum mechanical properties in weld areas. The solution treatments here require the use of a protective atmosphere to prevent oxidation or burning. Only the minimum time for complete solution ($\frac{1}{2}$ h) is used for the welded casting alloys AZ81A, AZ91C, and AZ92A if the castings were in the T4 or the T6 condition prior to welding.

Table 9 Postweld heat treatments for magnesium alloy castings

Alloy	Welding rod	Temper before welding	Desired temper after welding	Postweld heat treatment
AZ63A	AZ63A or AZ92A[(a)]	F	T4	12 h at 385 ± 6 °C (725 ± 10 °F)[(b)]

	AZ92A[a]	F	T6	12 h at 385 ± 6 °C (725 ± 10 °F)[b], plus 5 h at 220 °C (425 °F)
		T4	T4	$\frac{1}{2}$ h at 385 ± 6 °C (725 ± 10 °F)
		T4 or T6	T6	$\frac{1}{2}$ h at 385 ± 6 °C (725 ± 10 °F), plus 5 h at 220 °C (425 °F)
AZ81A	AZ92A or AZ101	T4	T4	$\frac{1}{2}$ h at 413 ± 6 °C (775 ± 10 °F)[c]
AZ91C	AZ92A or AZ101	T4	T4	$\frac{1}{2}$ h at 413 ± 6 °C (775 ± 10 °F)[c]
		T4 or T6	T6	$\frac{1}{2}$ h at 413 ± 6 °C (775 ± 10 °F)[c], plus 4 h at 215 °C (420 °F) or 16 h at 170 °C (335 °F)
AZ92A	AZ92A	T4	T4	$\frac{1}{2}$ h at 407 ± 6 °C (765 ± 10 °F)[c]
		T4 or T6	T6	$\frac{1}{2}$ h at 407 ± 6 °C (765 ± 10 °F)[c], plus 4 h at 260 °C (500 °F) or 5 h at 220 °C (425 °F)
EQ21A	EQ21A	T4 or T6	T6	1 h at 505 ± 6 °C (940 ± 10 °F), quench, 16 h at 205 °C (400 °F)
EZ33A	EZ33A	F or T5	T5	2 h at 345 °C (650 °F)[d], and/or 5 h at 215 °C (420 °F), or 24 h at 220 °C (425 °F)
HK31A	HK31A[g]	T4 or T6	T6	16 h at 205 °C (400 °F)[e]
HZ32A	HZ32A[g]	F or T5	T5	16 h at 315 °C (600 °F)
QE22A	QE22A	T4 or T6	T6	1 h at 510 ± 6 °C (950 ± 10 °F), quench, 16 h at 205 °C (400 °F)
QH21A	QH21A	T4 or T6	T6	1 h at 510 ± 6 °C (950 ± 10 °F), quench, 16 h at 205 °C (400 °F)
WE43A	WE43A	T4 or T6	T6	1 h at 510 ± 6 °C (950 ± 10 °F), quench, 16 h at 205 °C (400 °F)

WE54A	WE54A	T4 or T6	T6	1 h at 510 ± 6 °C (950 ± 10 °F), quench, 16 h at 205 °C (400 °F)
ZC63A	ZC63A	T4 or T6	T6	1 h at 425 ± 6 °C (797 ± 10 °F), quench, 16 h at 205 °C (400 °F)
ZE41A	ZE41A[(g)]	F or T5	T5	2 h at 330 °C (625 °F)[(f)]
ZH62A	ZH62A[(g)]	F or T5	T5	12 h at 250 °C (480 °F)[(f)]
ZK51A	ZK51A[(g)]	F or T5	T5	2 h at 330 °C (625 °F), plus 16 h at 175 °C (350 °F)

(a) AZ63A rod must be used for welding AZ63A in the F temper because 12 h at 385 °C (725 °F) causes germination in welds made with AZ92A rod; AZ92A rod normally is used for welding AZ63A in the T4 or T6 condition unless AZ63A rod is required by specifications.

(b) Preheat to 260 °C (500 °F); heat to specified temperature at no more than 83 °C/h (150 °F/h).

(c) Use carbon dioxide or sulfur dioxide atmosphere.

(d) Heating for 2 h at 345 °C (650 °F) results in slight loss of creep strength.

(e) Alternative treatment: 1 h at 315 °C (600 °F), plus 16 h at 205 °C (400 °F).

(f) Alternative treatment: 2 h at 330 °C (625 °F), plus 16 h at 175 °C (350 °F).

(g) Or EZ33A

Welded Mg-Al-Zn alloy castings that do not require solution treatment after welding should be stress relieved 1 h at 260 °C (500 °F), to eliminate the possibility of stress-corrosion cracking.

Evaluation of Heat-Treated Parts

The effectiveness of heat-treating procedures can be determined by hardness and tensile tests and by microscopic examination.

Indentation hardness tests are rapid and usually can be performed on the parts heat treated, without the necessity for a special test specimen. Brinell and Rockwell E hardness tests are normally used, but the Rockwell 15T superficial test may be required for thin sections. Soft material with large grains should be tested by the Brinell method for best results. The strength of magnesium alloys usually increases as hardness increases, but a graph of strength values determined from hardness plotted against actual strength values from the same specimens shows so much scatter that hardness cannot be used as an index for strength. Furthermore, hardness cannot indicate how an alloy will machine, or how easily it can be fabricated by other methods; it is primarily a measure of the temper of the material, and normally it suffices for this purpose.

Tensile tests more accurately indicate the temper of magnesium alloys. For casting alloys, test specimens can be separately cast unmachined, although specimens machined from castings are more representative of actual casting

properties. Test bars must be machined from extrusions, forgings, and sheet. Test bars from extrusions and forgings are machined round for convenience. Standard ASTM specimens and procedures are usually employed to help ensure uniform results and avoid errors from variable testing speed, presence of scratches, and other causes.

Microscopic examination of heat-treated magnesium alloys can be used to evaluate the alloy for the following conditions:

- Massive compound in cast alloys
- Percentage of pearlitic type of precipitate in cast alloys
- Porosity and "burning" voids in improperly solution heat-treated cast alloys
- Grain size in cast and wrought alloys
- Massive compound in extruded, forged, or rolled alloys

These conditions can be easily detected by comparing polished specimens with standard micrographs.

Determination of Temper. For alloys AZ91C and AZ92A, the following solution can be applied to heat-treated parts to identify the T6 conditions: 60 parts ethylene glycol; 20 parts glacial acetic acid; 19 parts distilled water; 1 part nitric acid, 42° Be. For ZE41A, the following solution can be applied to heat-treated parts to identify the T5 condition: 5 parts glacial acetic acid; 95 parts distilled water. For either of these tests, the test surface should be prepared by sanding first with 180-grit paper and then with 220- to 400-grit paper to produce a smooth area about 25 mm (2 in.) square. After the test section has been wiped clean, one drop of the solution is applied with an eyedropper. After 30 s, the test section is rinsed with water and blotted dry with a piece of soft cloth.

For AZ91C and AZ92A, the surface of a part in a T6 condition will appear darker where etched. For ZE41A, the surface will appear lighter where etched if the part is in the T5 condition. This alloy will show a bluish tint in the as-cast condition, whereas alloy ZE41A in the T5 temper--either 2 h at 330 °C (625 °F) or 2 h at 330 °C plus 16 h at 175 °C (350 °F)--tends to show a brown-to-beige tint.

The inspected area should be wiped clean, and a fresh type I chrome pickle should be applied to prevent corrosion.

Prevention and Control of Magnesium Fires

Improper heat treating of magnesium alloy castings not only will result in damaged castings but also may cause fire. Only clean, dry castings should be introduced into the furnace. Castings contaminated with filings, chips, oil, or other foreign matter should first be cleaned. The furnace itself should be protected from these same contaminants and should be completely dry. The charge should consist of castings of only one alloy, and the recommended heat-treating cycle for that alloy should be closely followed.

Occasionally, because of equipment malfunction, carelessness, or operator error, fires do occur. They are usually detectable either by an increase in furnace temperature without an increase in input of heat or by seepage of light-colored smoke from the furnace.

Caution: Under no circumstance should water be used to extinguish a magnesium fire.

All power, fuel, and protective-atmosphere lines should be shut off immediately. This in itself may extinguish small fires, which will die from lack of oxygen in a tight furnace. Should the fire continue to burn, several methods of extinguishing it are possible, depending on the nature of the fire. If the fire is small and the burning castings are readily accessible and can be *safely* removed from the furnace, they should be removed to a steel container and covered with commercially available fire-extinguishing powder intended for use with magnesium. If the burning castings are not both safely and readily accessible, a pump can be used to throw a stream of powder onto the burning castings in the furnace.

When the fire is such that neither of the above methods can safely be used for extinguishing it, another method is the use of boron trifluoride (BF_3) or boron trichloride (BCl_3), both of which are available as bottled gases. As with the other methods, all power, fuel, and protective-atmosphere lines should be shut off.

Boron trifluoride gas is introduced into the furnace through a pipe in the furnace door or wall so that a minimum concentration of 0.04% is produced. The gas flow is continued until the fire is extinguished and the temperature of the furnace drops to 370 °C (700 °F). Teflon hose is suitable for transferring the pressurized boron trifluoride gas from bottle to furnace.

Boron trichloride gas also is introduced into the furnace through a pipe in the furnace door or wall, in a concentration of about 0.4%. To ensure a sufficient volume of gas, a bank of infrared lamps or some other suitable device is required for heating the bottled gas. Boron trichloride gas reacts with hot magnesium to form a protective film over the castings. A supply of gas is maintained until the fire is extinguished and the temperature of the furnace drops to 370 °C (700 °F). In a totally enclosed furnace, it is feasible to employ the furnace fan to circulate the boron trifluoride or boron trichloride extinguishing gas around the castings. (Teflon hose can be used for transferring the boron trichloride gas from the bottle to the furnace.)

Boron trichloride predates boron trifluoride as a fire extinguisher for magnesium. Boron trifluoride is preferred because it is effective in lower concentration, it does not require a heat source to ensure an adequate supply of gas, and its reaction products are less hazardous than those of boron trichloride. The fumes of boron trichloride are irritating and are ranked with hydrochloric acid fumes as a health hazard.

If the heat-treating furnace fire includes more than several hundred pounds of magnesium parts, is well advanced prior to discovery, involves a large pool of metal on the floor of the furnace, or is in a furnace with excessive air leaks, these gases cannot be expected to extinguish the fire completely. However, both boron trifluoride and boron trichloride are effective in slowing or suppressing the fire until it can be extinguished with other solid materials.

Dry cast iron chips, graphite powder combined with heavy hydrocarbons, and (occasionally) foundry melting flux have been used for extinguishing large magnesium fires; the effectiveness of these materials is based on smothering the fire from the oxygen of the atmosphere in the furnace.

Besides the normal safety equipment used by personnel in fire fighting, colored glasses should be used when fighting a magnesium fire, for protection of the eyes against the characteristic intense white light.

Heat Treating of Nickel and Nickel Alloys

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Introduction

NICKEL AND THE NICKEL ALLOYS are, in some ways, easier to heat treat than many of the iron-base alloys that depend on carbon-related microstructural changes to achieve desired properties. Nickel is an austenite former, and in the nickel and high-nickel family of alloys, no allotropic phase transformations occur--the alloys are austenitic from the melting temperature down to absolute zero. While some precipitates may form such as carbides and the γ' hardening phase, these do not change the basic austenitic-type structure of the matrix. (See the article "Heat Treating of Superalloys" in this Volume for discussions on the formation of carbides and γ' precipitates.)

Because nickel is found in nature as nickel sulfide and nickel oxide ores, it has a natural tendency to combine with sulfur and/or oxygen. One of the most important factors to consider when heat-treating nickel or the nickel alloys is to minimize exposure to sulfur, whether in solid form (such as lubricants, grease, or temperature-indicating sticks) or in gaseous form (such as SO_2 or H_2S). When embrittlement by sulfur occurs, there are no techniques that can be used to reclaim the affected material; the contaminated area must be either removed, such as by grinding, or scrapped.

Because nickel has a very low solubility for carbon in the solid state, it does not readily carburize. For this reason the nickel-chromium alloys, most notably Inconel 600, are used as fixtures in carburizing furnaces. Almost all heat treatment methods used with nickel and the nickel alloys are employed either to soften them, such as annealing, or to increase their strength, such as age hardening.

Types of Heat Treatment

Nickel and the nickel alloys may be subjected to one or more of six principal types of heat treatment, depending on chemical composition, fabrication requirements, and intended service. These methods include:

- *Annealing.* A heat treatment designed to produce a recrystallized grain structure and softening in work-hardened alloys. Annealing usually requires temperatures between 705 and 1205 °C (1300 and 2200 °F), depending on alloy composition and degree of work hardening
- *Solution annealing.* A high-temperature anneal (1150 to 1315 °C, or 2100 to 2400 °F) of certain nickel alloys to put carbides in solid solution and produce a coarse grain size for enhanced stress-rupture properties
- *Stress relieving.* A heat treatment used to remove or reduce stresses in work-hardened non-age-hardenable alloys without producing a recrystallized grain structure. Stress-relieving temperatures for nickel and nickel alloys range from 425 to 870 °C (800 to 1600 °F), depending on alloy composition and degree of work hardening
- *Stress equalizing.* A low-temperature heat treatment used to balance stresses in cold-worked material without an appreciable decrease in the mechanical strength produced by cold working
- *Solution treating.* A high-temperature heat treatment designed to put age-hardening constituents into solid solution. Normally applied to age-hardenable materials before the aging treatment
- *Age hardening* (precipitation hardening). A treatment performed at intermediate temperatures (425 to 870 °C, or 800 to 1600 °F) on certain alloys to develop maximum strength by precipitation of a dispersed phase throughout the matrix

Figure 1 shows the effect on room-temperature mechanical properties of colddrawn Monel 400 rod when the rod is held for 3 h at various temperatures. Heating at 700 °C (1300 °F) or above produces the soft annealed condition; heating in the range of 400 to 595 °C (750 to 1100 °F) results in stress relieving; and heating in the range of 260 to 480 °C (500 to 900 °F) results in stress equalization, which produces an increase in the proportional limit, a slight increase in tensile strength and no significant change in elongation.

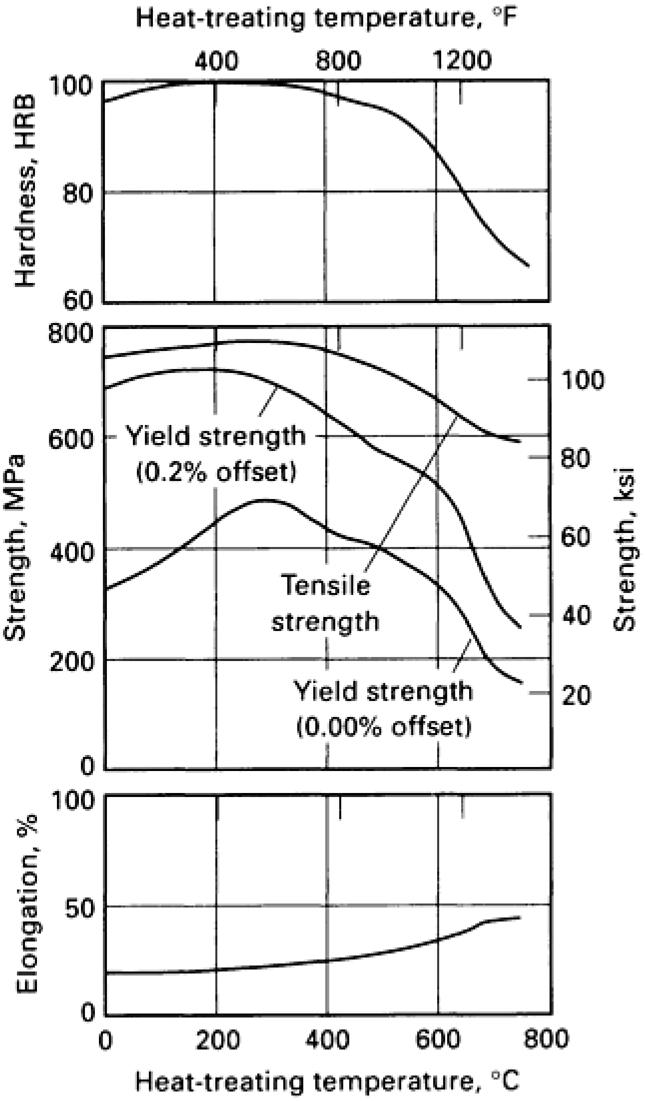

Fig. 1 Effects on room-temperature properties of cold-drawn Monel 400 rod held for 3 h at various temperatures

Annealing

The annealing of nickel and nickel alloys consists of heating the metal at a predetermined temperature for a definite time and then slowly or rapidly cooling it to produce a change in mechanical properties, usually a complete softening, as the result of recrystallization. Nickel and nickel alloys that have been hardened by cold-working operations, such as rolling, deep drawing, spinning, or severe bending, require softening before cold working can be continued. The thermal treatment that does this is known as annealing, or soft annealing.

The differences in chemical composition among nickel and nickel alloys (Table 1) necessitate modifications in annealing temperatures (Table 2) and furnace atmospheres. The precipitation-hardening alloys must be cooled rapidly after annealing if maximum softness is desired. Annealing methods may be divided into three categories: batch, continuous, and specialty. These are described below.

Table 1 Nominal compositions of nickels and nickel alloys

Material	Composition, wt%

	Ni	C	Mn	Fe	Si	Cu	Cr	Ti	Al	Mo	Co	Other
Nickel 200	99.5	0.06	0.25	0.15	0.05	0.05	. . .	. . .	. . .	. . .	. . .	. . .
Nickel 201	99.5	0.01	0.20	0.15	0.05	0.05	. . .	. . .	. . .	. . .	. . .	. . .
Monel 400	66.0	0.12	0.90	1.35	0.15	31.5	. . .	. . .	. . .	. . .	. . .	. . .
Monel R-405	66.0	0.18	0.90	1.35	0.15	31.5	. . .	. . .	. . .	. . .	. . .	0.04 S
Monel K-500	65.0	0.15	0.60	1.00	0.15	29.5	. . .	0.50	2.80	. . .	. . .	. . .
Inconel 600	76.0	0.04	0.20	7.20	0.20	0.10	15.8	. . .	. . .	. . .	. . .	. . .
Inconel 601	60.5	0.05	0.50	14.1	0.25	. . .	23.0	. . .	1.35	. . .	. . .	. . .
Inconel 617	54.0	0.07	. . .	. . .	. . .	. . .	22.0	. . .	1.00	9.0	12.5	. . .
Inconel 625	61.0	0.05	0.25	2.5	. . .	. . .	21.5	. . .	. . .	9.0	. . .	3.65 Nb
Inconel 718	52.5	0.04	0.20	18.0	0.20	0.10	19.0	0.80	0.60	3.00	. . .	5.20 Nb
Inconel X-750	73.0	0.04	0.70	6.75	0.30	0.05	15.0	2.50	0.80	. . .	. . .	0.85 Nb
Hastelloy B-2	69.0	0.01	. . .	1.0	. . .	. . .	. . .	. . .	. . .	28.0	. . .	. . .
Hastelloy C-276	57.0	0.01	. . .	5.5	. . .	. . .	15.5	. . .	. . .	16.0	. . .	4.0 W, 0.30 V
Hastelloy X	48.0	0.10	. . .	18.5	. . .	. . .	22.0	. . .	. . .	9.0	1.0	0.6 W

Table 2 Annealing, stress-relieving, and stress-equalizing schedules for nickels and nickel alloys

Material	Soft annealing							
	Continuous				Batch			
	Temperature		Time[(a)], min	Cooling method[(b)]	Temperature		Time, h	Cooling method
	°C	°F			°C	°F		
Nickel 200	815-925	1500-1700	$\frac{1}{2}$-5	AC or WQ	705-760	1300-1400	2-6	AC

Material	Stress relieving				Stress equalizing			
	Temperature		Time, min	Cooling method	Temperature		Time, h	Cooling method
	°C	°F			°C	°F		
Nickel 201	760-870	1400-1600	$\frac{1}{2}$-5	AC or WQ	705-760	1300-1400	2-6	AC
Monel 400	870-980	1600-1800	$\frac{1}{2}$-15	AC or WQ	760-815	1400-1500	1-3	AC
Monel R-405	870-980	1600-1800	$\frac{1}{2}$-15	AC or WQ	760-815	1400-1500	1-3	AC
Monel K-500	870-1040	1600-1900	$\frac{1}{2}$-20	WQ	870-1040	1600-1900	1-3	WQ
Inconel 600	925-1040	1700-1900	$\frac{1}{2}$-60	AC or WQ	925-980	1700-1800	1-3	AC
Inconel 601	1095-1175	2000-2150	$\frac{1}{2}$-60	AC or WQ	1095-1175	2000-2150	1-3	AC
Inconel 617	1120-1175	2050-2150	$\frac{1}{2}$-60	AC or WQ	1120-1175	2050-2150	1-3	AC
Inconel 625	980-1150	1800-2100	$\frac{1}{2}$-60	AC or WQ	980-1150	1800-2100	1-3	AC
Inconel 718	955-1065	1750-1950	$\frac{1}{2}$-60	AC	955-1065	1750-1950	1-3	AC
Inconel X-750	955-1150	1750-2100	$\frac{1}{2}$-60	AC	955-1150	1750-2100	1-3	AC
Hastelloy B-2	1095-1185	2000-2165	5-10	AC or WQ	1095-1175	2000-2150	1	AC or WQ
Hastelloy C-276	1215	2220	5-10	WQ	1215	2220	1	WQ
Hastelloy X	1175	2150	$\frac{1}{2}$-15	AC or WQ	1175	2150	1	AC or WQ

Nickel 200	480-705	900-1300	$\frac{1}{2}$-120	AC	260-480	500-900	1-2	AC
Nickel 201	480-705	900-1300	$\frac{1}{2}$-120	AC	260-480	500-900	1-2	AC
Monel 400	540-650	1000-1200	$\frac{1}{2}$-120	AC	230-315	450-600	1-3	AC
Monel R-405	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Monel K-500	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Inconel 600	760-870	1400-1600	5-60	AC	760-870	1400-1600	1-2	AC
Inconel 601	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Inconel 617	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Inconel 625	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Inconel 718	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Inconel X-750	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Hastelloy B-2	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Hastelloy C-276	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .
Hastelloy X	. . .	. . .	. . .	. . .	. . .	. . .	. . .	. . .

(a) Times given represent actual ranges that thin sheet/strip products and heavy cross sections would receive in continuous furnaces.

(b) AC, air cool: WQ, water quench

Batch annealing is a frequently used method of annealing because of its simplicity. It is the method of choice if the material requires a period of soak at temperature. The furnaces can be open (material exposed to products of combustion or direct radiant heat from electrical elements) or closed (material indirectly heated, that is, a muffle is used). Open annealing is used most often. The material to be annealed is heated at the selected temperature and protected from oxidation, in a fuel-heated furnace by the products of combustion and in an electric furnace by a reducing gas. During preliminary heating of the furnace, the burners may be adjusted for optimum combustion, but, before charging, the air supply should be reduced to provide the excess of reducing gases required. Also the top vents or dampers should be partly or fully closed to provide a positive gas pressure over the hearth, thereby preventing air leakage. Closed-annealing

temperature control is just as critical as in open annealing. What dictates closed as opposed to open annealing is usually the undesirability of oxide on the work. Closed annealing invariably has a protective atmosphere within the enclosure to minimize oxidation during heat treatment. In most instances, the weight of the protective cover exceeds that of the work; consequently, the amount of fuel required, heat times, and cost are greater than in open annealing. Parts are usually carried into the furnace in alloy trays, and a protective atmosphere is introduced. The atmosphere flows continuously during annealing, pressurizing the furnace and preventing the infiltration of outside air. If the protective atmosphere is CO or H_2, the gas should be flared off as it escapes the enclosure.

Continuous Annealing. A continuous-annealing facility is used when large volumes of product are involved and high throughput desired. Continuous furnaces are complex, requiring more frequent inspections and maintenance than a batch-type furnace, and the initial capital outlay is usually higher than for a comparable batch unit. Most continuous furnaces are of the open variety in which the nickel parts are exposed directly to the products of combustion. Temperature control is critical because the annealing period is short (Table 2). Continuous furnaces are not used for extended soaks; the hot-zone dwell time is quite short compared to a batch furnace. Also, temperature uniformity within the hot zone is more difficult to achieve because of the constant introduction of cold metal into the furnace. Closed annealing in a continuous furnace has the same characteristics as batch furnace annealing. The necessity to minimize oxidation is critical; the reducing atmosphere is continually introduced into the furnace, creating a positive furnace pressure. Most heat treatments of this nature take place in an alloy muffle or supertight furnace lined with high-quality alumina brick for better control of atmosphere and quality.

Specialty Annealing. These processes are so specialized and/or difficult that a separate category has been established to fully recognize their uniqueness. Specialty annealing methods include the use of vacuum furnaces, salt baths, and fluidized-bed furnaces. The percentage of nickel alloys heat treated in these types of facilities is small but growing. Brief descriptions are given below.

Vacuum Furnace. This type of furnace is used extensively for small parts. The furnace is usually heated electrically, and the hot zone evacuated to about 5 to 6 μm. A small amount of hydrogen is then added to maintain the low oxygen pressures needed to prevent oxidation. The hot zone is sometimes back-flushed with an inert or reducing gas for cooling purposes. Material must be very clean prior to annealing.

Salt Bath Furnace. Salt bath annealing is used for special work with small parts. Inorganic salts, such as chlorides and carbonates of sodium, potassium, and barium, which are relatively stable at temperatures considerably above their respective melting points, are fused in large metallic or refractory containers at temperatures up to about 700 °C (1300 °F); at higher temperatures, heat-resisting iron-nickel-chromium alloy pots or refractory containers should be used. Excessive fuming of the bath is an indication that its maximum usable temperature has been exceeded.

Particular care must be exercised to remove all traces of sulfur from the fused salts in order to prevent embrittlement of the work. This may be accomplished in 2 to 3 h by adding to the fused chlorides and carbonates a small amount ($\geq$0.5 kg, or $\geq$1 lb) of a mixture consisting (by volume) of three parts powdered borax and one part powdered charcoal. If testpieces of nickel strip or wire do not embrittle after 3 or 4 h in the purified salt bath, the desulfurizing treatment has been sufficient.

The material to be annealed is placed in the molten salts and absorbs heat rapidly. After being annealed, the work metal is quenched in water to free it from particles of the salt mixture. The annealed material will not be bright and may be flash pickled to achieve a bright surface.

Fluidized-bed furnace is a relatively new development. It has the excellent temperature uniformity and rapid heat-up features of the salt bath furnace, without the safety hazards associated with molten salt. Typically, a bed of 80 mesh alumina powder is fluidized by flowing a gas up through the material at 140 MPa (20 psig) pressure. The fluidizing gas is usually either air or metallurgical-grade nitrogen.

Dead-Soft Annealing. When the nickel alloys are annealed at higher temperatures and for longer periods, a condition commonly described as dead-soft is obtained, and the hardness numbers that result are 10 to 20% lower than those of the so-called soft condition. Because this treatment is accompanied by an increase in the grain size of the metal, it should be used only for those few applications in which grain size is of little importance.

Torch Annealing. Some large equipment is hardened locally by fabricating operations. If the available annealing furnace is too small to hold the workpiece, the hardened sections can be annealed with the flames of oil or acetylene

torches adjusted so that they are highly reducing. The work should first be warmed gently with sweeping motions of the torch and should not be brought to the annealing temperature until sufficient preheating has been done to prevent cracking as a result of the sudden release of stress. (It should be noted that torch annealing is a poor method for general use because it provides irregular and insufficient annealing and produces heavily oxidized surfaces.)

Process Control Factors in Annealing

Among the more important process control factors in annealing nickel and nickel alloys are the selection of suitably sulfur-free fuels for heating, control of furnace temperature, effects of prior cold working and of cooling rates, control of grain size, control of protective atmospheres, and protection from contamination by foreign material.

Fuels for Heating. Nickel and nickel alloys are subject to intergranular attack when heated in the presence of sulfur or sulfur compounds. Fuels for heating must be low in sulfur content.

Gas is the best fuel for heating nickel alloys and should be used if available. Good heating is achieved readily with gas because of the ease with which gas can be mixed with air and its supply controlled. Gaseous fuels require little combustion space, and the automatic control of temperature and furnace atmosphere is easily accomplished.

Natural gas, consisting chiefly of methane (CH_4) and smaller amounts of ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}), and essentially free of sulfur compounds, is available in many areas.

Bright Annealing. The temperatures required for the soft annealing of nickel and nickel alloys are sufficiently high to cause slight surface oxidation unless the materials are heated in vacuum or in a furnace provided with a reducing atmosphere. Nickel 200, Monel 400, and similar alloys remain bright and free from discoloration when heated and cooled in a reducing atmosphere. However, nickel alloys containing chromium, titanium, and aluminum form a thin oxide film. Even if oxidation is not important, the furnace atmosphere must be suitably sulfur-free and not strongly oxidizing.

The protective atmosphere most commonly used in heating nickel and nickel alloys is that provided by controlling the ratio between the fuel and air supplied to burners firing directly into the furnace. A desirable reducing condition may be obtained by using a slight excess of fuel so that the products of combustion contain at least 4% carbon monoxide plus 4% hydrogen with no more than 0.05% uncombined oxygen. This is considered an 8% reducing atmosphere and can be obtained by burning an air/gas ratio of 9.25/1 of 1160 kJ (1100 Btu) natural gas.

Another method of maintaining desired conditions of furnace atmosphere is to introduce a prepared atmosphere into the heating and cooling chambers. This can be added to the products of combustion in a directly-fired furnace, although the introduction of prepared atmospheres is more commonly practiced with indirectly heated equipment.

Prepared atmospheres suitable for use with nickel and nickel alloys include dried hydrogen, dried nitrogen, dissociated ammonia, and cracked or partially reacted natural gas. Properties of various protective atmospheres are shown in Table 3. Nickels, modified nickels, and nickel-copper alloys can be bright annealed in all of these atmospheres (except for the first one listed in Table 3, that is, completely burned fuel, lean atmosphere) provided the dew point is 4.4 °C (40 °F) or lower. Inconel 600 and other alloys containing chromium, molybdenum, or both, require completely dissociated ammonia or dried hydrogen for bright annealing. A dew point of -51 °C (-60 °F) or lower is necessary with a positive furnace pressure.

Table 3 Prepared atmospheres suitable for annealing of nickels and nickel alloys

Atmospheres 2 through 7 can be used for bright annealing of nickel, modified nickels, and nickel-copper alloys; atmosphere 4 or atmosphere 7 must be used for bright annealing of nickel alloys that contain chromium, molybdenum, or both.

Atmosphere	Air-to-gas ratio[(a)]	Composition, vol %						Dew point (approximate)	
		H_2	CO	CO_2	CH_4	O_2	N_2	°C	°F
1 Completely burned fuel, lean atmosphere	10:1	0.5	0.5	10.0	0.0	0.0	89.0	Saturated[(b)]	Saturated[(b)]

2 Partially burned fuel, medium-rich atmosphere	6:1	15.0	10.0	5.0	1.0	0.0	69.0	Saturated[(b)]	Saturated[(b)]
3 Reacted fuel, rich atmosphere	3:1	38.0	19.0	1.0	2.0	0.0	40.0	20	70
4 Dissociated ammonia (complete dissociation)	No air	75.0	0.0	0.0	0.0	0.0	25.0	-55 to -75	-70 to -100
5 Dissociated ammonia, partially burned	1.25:1[(c)]	15.0	0.0	0.0	0.0	0.0	85.0	Saturated[(b)]	Saturated[(b)]
6 Dissociated ammonia, completely burned	1.8:1[(c)]	1.0	0.0	0.0	0.0	0.0	99.0	Saturated[(b)]	Saturated[(b)]
7 Electrolytic hydrogen, dried[(d)]	No air	100.0	0.0	0.0	0.0	0.0	0.0	-55 to -75	-70 to -100

(a) Based on use of natural gas containing nearly 100% methane and rated at 37 MJ/m^3 (1000 Btu/ft^3). For high-hydrogen manufactured gas (20 MJ/m^3, or 550 Btu/ft^3), ratios are about 50% of values listed. For manufactured gas with lower hydrogen and high carbon monoxide contents (17 MJ/m^3, or 450 Btu/ft^3), ratios are about 40% of values listed. For propane, ratios are about twice those listed. For butane, multiply listed values by three.

(b) When atmosphere is cooled by tap water heat exchangers, dew point will be about 6 to 8 °C (10 to 15 °F) above the temperature of the tap water. Dew point may be reduced to about 5 °C (40 °F) by refrigeration equipment and to -55 °C (-70 °F) or lower by activated-absorption equipment.

(c) Ratio of air to dissociated ammonia.

(d) Dried to a dew point of -55 to -75 °C (-70 to -100 °F) by alumina plus molecular sieve

The conditions for bright annealing should be maintained during heating, regardless of the method used for cooling. If facilities for cooling under protective atmosphere are not available, nickel and nickel alloys may be quenched in a 2% (by volume) solution of denatured alcohol. This will reduce the oxide flash formed by the oxygen of the air during transfer from the furnace to the quenching tank.

Manufactured gases are produced from coal or oil, both of which may contain substantial amounts of sulfur. These gases should not be used unless the sulfur compounds are effectively removed during gas manufacture. Sulfur occurs in these manufactured gases as hydrogen sulfide (H_2S) and organic sulfides.

Suppliers of manufactured gas try to keep the total sulfur content of their product to a value below the maximum set by state regulatory agencies. Thus, manufactured gas supplied to consumers usually contains less than 6.9 g of total sulfur per 10 m^3 of gas (less than 30 gr per 100 ft^3). This sulfur content may vary considerably from day to day, but, where adequate maintenance of sulfur removal is observed by the gas supplier, total sulfur content will average 2.3 to 3.4 g per 10 m^3 (10 to 15 gr per 100 ft^3) or lower. This sulfur content is acceptable for heating nickel alloys; however, the generally accepted statutory limit (6.9 g per 10 m^3, or 30 gr per 100 ft^3) is marginal.

Two other satisfactory gaseous fuels are butane and propane, which are components of natural gas that liquefy and separate out when the gas if compressed. Both fuels are stored and shipped in tank cars that range in capacity from 30 to 57 m^3 (8000 to 15,000 gal); the fuels may be distributed throughout a plant in pipelines as liquids under their own vapor pressures. Butane can be considered in a sense an oil fuel of high volatility, and proper means must be provided for gasifying it by heating, before it is mixed with air for combustion. Propane is more volatile and does not require the application of heat to convert it from liquid to gas. It is obtainable in cylinders equipped with pressure regulators to control the flow of gas. These cylinders are useful for occasional work in heating small objects.

Control of Furnace Temperature. The importance of the accurate control of annealing temperature cannot be overemphasized. Satisfactory indicating, controlling, recording, and controlling-recording pyrometers are available. Iron-Constantan and Chromel-Alumel thermocouples should be changed every three months (or more often, if required). Noble metal thermocouples such as platinum, are the preferred method of measuring and monitoring temperature because of their inherent ability to resist diseasing at elevated temperatures. Their accuracy and sensitivity are equal to or better than those of the nonplatinum thermocouples. All thermocouples should be checked daily for accuracy.

Effect of Prior Cold Work. The greater the amount of cold work to which the material has been subjected before annealing, the lower the temperature required to produce the same degree of softness without increasing grain size and the shorter the time required at any one temperature.

The amount of any type of previous cold work also has a critical influence on the ductility of nickel and nickel alloys after annealing. If only a small amount of cold work is done (for example, ~10% reduction), full ductility for deep drawing and spinning cannot be restored by annealing because of excessive grain growth due to critical strain, even though the hardness is reduced to that of soft material. A minimum of approximately 20% cold working is required between anneals to ensure maximum ductility and softness following annealing.

Effect of Cooling Rate. Neither slow cooling, whether in or out of the furnace, nor rapid cooling by quenching has any specific effect on the softness of the annealed, solid-solution nickel materials. Therefore, rapid cooling is preferable (except for heavy sections, in which it may set up excessive thermal stresses), both as a time-saver and to minimize the amount of oxidation. Some of the age-hardenable alloys, such as Monel K-500, must be cooled rapidly by quenching from the annealing temperature to ensure the maximum response to subsequent age-hardening treatment.

Control of Grain Size. Coarse-grained material is unsuitable for most cold-working operations. A coarse grain in the high-nickel materials cannot be refined by thermal treatment. It can be removed only by cold working sufficiently to effect recrystallization to a smaller grain size during a subsequent annealing treatment. Maximum workability is obtained with material that has been annealed without allowing appreciable grain growth to occur. The average grain diameter should not exceed 0.064 mm (0.0025 in.) (ASTM No. 5). This gives the best combination of ductility to permit extensive deformation, strength to withstand the action of tools, and surface quality to facilitate polishing.

Effect of Fluctuating Atmospheres. If nickel and nickel alloys are annealed in atmospheres that fluctuate between oxidizing (excess of air) and reducing (excess of carbon monoxide or hydrogen), severe inter-crystalline attack will occur, with resulting embrittlement, even though the atmosphere is sulfur-free. This type of embrittlement can be prevented by maintaining a constant and sufficient excess of reducing atmosphere during heating and cooling. Alloys containing chromium or molybdenum are affected less than are nickel and nickel-copper alloys.

Protection from Contamination by Foreign Material. Many of the new lubricants used for deep drawing and spinning contain sulfur or lead and are removable with alkaline cleaner solutions at 82 °C (180 °F). Unless these elements are removed before annealing, they will cause embrittlement. The chlorohydrocarbons used in the past will no longer be permitted due to safety and ecological considerations. Alternate methods, such as water-soluble lubricants, will be required as more restrictive laws are enacted. Lubricants of any type should be removed entirely from the material before annealing. Paints and other adherent substances that may contain sulfur, as well as lead or similarly harmful ingredients, should be removed by appropriate methods before annealing.

Stress Relieving

In stress relieving, careful regulation of time and temperature is required. These variables are usually determined experimentally for each application; some typical ranges are given in Table 2. Figure 1 shows the effect of stress relief, at temperatures from about 400 to about 600 °C (750 to 1100 °F), on the room-temperature properties of Monel 400.

Stress Equalizing

Stress equalizing is a low-temperature heat treatment (Table 2) that results in what is known as partial recovery. This recovery, which precedes any detectable microscopic structural change, consists of a considerable increase in the proportional limit, slight increases in hardness and tensile strength, no significant change in elongation or reduction of area, a balancing of stresses, and the return of electrical conductivity toward its characteristic value for the alloy in the annealed condition.

The temperature required for stress equalizing depends on the composition of the alloy. Figure 1 shows an optimum temperature range of about 230 to 315 °C (450 to 600 °F) for cold-drawn Monel 400 rod. A temperature range of about 275 °C (525 °F) is recommended for commercial use. Long treatment time at this temperature has no detrimental effect.

Stress equalizing is usually applied to coil springs, wire forms, and flat spring stampings. If coil springs are to be given a cold "set," or cold pressing, after coiling, the stress equalization should be carried out *before* the setting operation, which involves stressing the material beyond the elastic limit. Any cold-working stresses set up by this operation are in a direction such that the stresses will benefit, rather than harm, the material. If stress is equalized *after* cold pressing, part of the beneficial cold-working stress is removed.

Age Hardening

The addition of niobium, aluminum, silicon, titanium, and certain other alloying elements to nickel and nickel alloys, separately or in combinations, produces an appreciable response to age hardening. The effect is dependent on both chemical composition and aging temperature; it is caused by the precipitation of submicroscopic particles throughout the grains, which results in a marked increase in hardness and strength.

Prior Solution Treating. Unlike precipitation-hardening stainless steels and aluminum-base alloys, the nickel alloys normally do not require solution treating in the upper annealing temperature range prior to age hardening. However, solution treating may be used to enhance special properties (Table 4). For example, Inconel X-750 may be solution treated for 2 to 4 h at 1150 °C (2100 °F) and air cooled prior to a double (high and low temperature) aging cycle to develop maximum creep, relaxation, and rupture strength at temperatures above about 600 °C (1100 °F). This combination of heat treatments is considered essential for high-temperature springs and turbine blades made of Inconel X-750.

Table 4 Solution-treating and age-hardening schedules for nickel alloys

Alloy	Solution treating				Age hardening
	Temperature		Time, h	Cooling method[a]	
	°C	°F			
Monel K-500	980	1800	$\frac{1}{2}$-1	WQ	Heat to 595 °C (1100 °F), hold 16 h; furnace cool to 540 °C (1000 °F), hold 6 h; furnace cool to 480 °C (900 °F), hold 8 h; air cool.
Inconel 718 (AMS 5662)	980	1800	1	AC	Heat to 720 °C (1325 °F), hold 8 h; furnace cool to 620 °C (1150 °F), hold until furnace time for entire age-hardening cycle equals 18 h; air cool.
Inconel 718 (AMS 5664)	1065	1950	1	AC	Heat to 760 °C (1400 °F), hold 10 h; furnace cool to 650 °C (1200 °F), hold until furnace time for entire age-hardening cycle equals 20 h; air cool.
Inconel X-750 (AMS 5668)	1150	2100	2-4	AC	Heat to 845 °C (1550 °F), hold 24 h; air cool; reheat to 705 °C (1300 °F), hold 20 h; air cool.
Inconel X-750 (AMS 5671)	980	1800	1	AC	Heat to 730 °C (1350 °F), hold 8 h; furnace cool to 620 °C (1150 °F), hold until furnace time for entire age-hardening cycle equals 18 h; air cool.
Hastelloy X	1175	2150	1	AC	Heat to 760 °C (1400 °F), hold 3 h; air cool; reheat to 595 °C (1100 °F), hold

(a) WQ, water quench; AC, air cool

Age-hardening practices for several nickel alloys are summarized in Table 4 and in the article "Heat Treating of Superalloys" in this Volume. In general, nickel alloys are soft when quenched from temperatures ranging from 790 to 1220 °C (1450 to 2225 °F); however, they may be hardened by holding at 480 to 870 °C (900 to 1600 °F) or above and then furnace or air cooling. Quenching is not a prerequisite to aging; the alloys can be hardened from the hot-worked and cold-worked conditions, as well as from the soft condition.

Hardening Techniques. Nickel alloy parts are sometimes hardened in sealed boxes placed inside a furnace, although small horizontal or vertical furnaces without boxes may be used also. The box or furnace should hold the parts loosely packed, yet afford a minimum of excess space. Electric furnaces with hot fans provide the optimum temperature uniformity of ±6 °C (±10 °F) and the freedom from contamination required for this work. Gas-heated furnaces, particularly those of the radiant-tube type, can be made so that they give satisfactory results. It is difficult to obtain good results from oil heating, even with muffle furnaces. All lubricants should be removed from the work before hardening.

Because of the long aging time and the difficulty of excluding air from the box or furnace, truly bright hardening cannot be accomplished commercially. For semibright hardening, dry hydrogen (see atmosphere 7 in Table 3) or cracked and dried ammonia (see atmosphere 4 in Table 3) should be used. Care should be exercised in the use and handling of these gases in the age-hardening temperature range that happens to span the minimum ignition temperature of hydrogen, 575 °C (1065 °F). When bright or semibright hardening is not required, other atmospheres may be used, such as nitrogen, cracked natural gas free of sulfur, cracked city gas, cracked hydrocarbons, or a generated gas. The use of sulfur-free gases is necessary to avoid embrittlement.

Salt baths are used occasionally for small parts. The hardened material is never bright and must be flash pickled to restore the natural color. Inorganic salts are used, such as chlorides and carbonates of sodium and potassium, which are relatively stable at temperatures considerably above their respective melting points. It is extremely important that the salts be free of all trace of sulfur so that the work does not become embrittled. Fluidized beds can also be used for this process and are viable substitutes for salt baths without the hazards of molten salts.

Heat-Resisting Alloys

Procedures for heat treating the nickel-base alloys used in turbine engines and for other high-temperature applications are described in the article "Heat Treating of Superalloys" in this Volume. Properties and applications of high-temperature nickel-base alloys can be found in Volumes 1 and 2 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.*

Heat Treating of Titanium and Titanium Alloys

Revised by Roger Gilbert, IMI Titanium; and C. Richard Shannon, Teledyne Allvac

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Introduction

TITANIUM AND TITANIUM ALLOYS are heat treated in order to:

- Reduce residual stresses developed during fabrication (stress relieving)
- Produce an optimum combination of ductility, machinability, and dimensional and structural stability (annealing)
- Increase strength (solution treating and aging)
- Optimize special properties such as fracture toughness, fatigue strength, and high-temperature creep strength

Various types of annealing treatments (single, duplex, β, and recrystallization annealing, for example), and solution treating and aging treatments, are imposed to achieve selected mechanical properties. Stress relieving and annealing may

be employed to prevent preferential chemical attack in some corrosive environments, to prevent distortion (a stabilization treatment), and to condition the metal for subsequent forming and fabricating operations.

Alloy Types and Response to Heat Treatment

The response of titanium and titanium alloys to heat treatment depends on the composition of the metal and the effects of alloying elements on the α-β crystal transformation of titanium. In addition, not all heat treating cycles are applicable to all titanium alloys, because the various alloys are designed for different purposes. Alloys Ti-5Al-2Sn-2Zr-4Mo-4Cr (commonly called Ti-17) and Ti-6Al-2Sn-4Zr-6Mo are designed for strength in heavy sections; Ti-6Al-2Sn-4Zr-2Mo and Ti-6Al-5Zr-0.5Mo-0.2Si, for creep resistance; Ti-6Al-2Nb-1Ta-1Mo and Ti-6Al-4V-ELI, for resistance to stress corrosion in aqueous salt solutions and for high fracture toughness; Ti-5Al-2.5Sn and Ti-2.5Cu, for weldability; and Ti-6Al-6V-2Sn, Ti-6Al-4V, and Ti-10V-2Fe-3Al, for high strength at low-to-moderate temperatures.

Effects of Alloying Elements on α-β Transformation. Unalloyed titanium is allotropic. Its close-packed hexagonal structure (α phase) changes to a body-centered cubic structure (β phase) at 885 °C (1625 °F), and this structure persists at temperatures up to the melting point.

With respect to their effects on the allotropic transformation, alloying elements in titanium are classified as α stabilizers or βstabilizers. Alpha stabilizers, such as oxygen and aluminum, raise the α-to-β transformation temperature. Nitrogen and carbon are also α stabilizers, but these elements usually are not added intentionally in alloy formulation. Beta stabilizers, such as manganese, chromium, iron, molybdenum, vanadium, and niobium, lower the α-to-β transformation temperature and, depending on the amount added, may result in the retention of some βphase at room temperature. Alloying elements such as zirconium and tin have essentially no effect on the α-to-β transformation temperature.

Alloy Types. Based on the types and amounts of alloying elements they contain, titanium alloys are classified as α, near-α, α-β, or βalloys (see, for example, the titanium alloy compositions listed in Volume 2 of *ASM Handbook*, formerly 10th Edition *Metals Handbook*). The response of these alloy types to heat treatment is briefly described below.

Alpha and near-alpha titanium alloys can be stress relieved and annealed, but high strength cannot be developed in these alloys by any type of heat treatment (such as aging after a solution beta treatment and quenching). Near-α alloys are alloys with predominantly a stabilizer, plus limited βstabilizers (normally, 2% or less).

The commercial βalloys are, in reality, metastable βalloys. When these alloys are exposed to selected elevated temperatures, the retained β phase decomposes and strengthening occurs. For β alloys, stress-relieving and aging treatments can be combined, and annealing and solution treating may be identical operations.

Alpha-beta alloys are two-phase alloys and, as the name suggests, comprise both αand β phases at room temperature. These are the most common and the most versatile of the three types of titanium alloys. Phase compositions, sizes, and distributions can be manipulated by heat treatment within certain limits to enhance a specific property or to attain a range of strength levels. A summary of typical heat treatments for α-β titanium alloys is given in Table 1.

Table 1 Summary of heat treatments for α-β Ti alloys

Heat treatment designation	Heat treatment cycle	Microstructure
Duplex anneal	Solution treat at 50-75 °C (90-135 °F) below Tβ[(a)], air cool and age for 2-8 h at 540-675 °C (1000-1250 °F)	Primary α, plus Widmanstätten α- βregions
Solution treat and age	Solution treat at ~40 °C (70 °F) below Tβ, water quench[(b)] and age for 2-8 h at 535-675 °C (995-1250 °F)	Primary α, plus tempered α' or a β- αmixture
Beta anneal	Solution treat at ~15 °C (30 °F) above Tβ, air cool and stabilize at 650-760 °C (1200-1400 °F) for 2 h	Widmanstätten α- βcolony microstructure

Beta quench	Solution treat at ~15 °C (30 °F) above T β, water quench and temper at 650-760 °C (1200-1400 °F) for 2 h	Tempered α'
Recrystallization anneal	925 °C (1700 °F) for 4 h, cool at 50 °C/h (90 °F/h) to 760 °C (1400 °F), air cool	Equiaxed α with β at grain-boundary triple points
Mill anneal	α - β hot work plus anneal at 705 °C (1300 °F) for 30 min to several hours and air cool	Incompletely recrystallized α with a small volume fraction of small β particles

Source: Ref 1

(a) T β is the β transus temperature for the particular alloy in question.

(b) In more heavily β -stabilized alloys such as Ti-6Al-2Sn-4Zr-6Mo or Ti-6Al-6V-2Sn, solution treatment is followed by air cooling. Subsequent aging causes precipitation of α phase to form an α- β mixture.

Beta transus temperatures for various commercial titanium alloys are listed in Table 2. When the heat treatment involves heating near the β transus, the transus temperature of each heat in a lot must be accurately determined.

Table 2 Beta transformation temperatures of titanium alloys

Alloy	**Beta transus**	
	°C, ± 15	**°F, ± 25**
Commercially pure Ti, 0.25 O_2 max	910	1675
Commercially pure Ti, 0.40 O_2 max	945	1735
α and near-α alloys		
Ti-5Al-2.5Sn	1050	1925
Ti-8Al-1Mo-1V	1040	1900
Ti-2.5Cu (IMI 230)	895	1645
Ti-6Al-2Sn-4Zr-2Mo	995	1820
Ti-6Al-5Zr-0.5Mo-0.2Si (IMI685)	1020	1870
Ti-5.5Al-3.5Sn-3Zr-1Nb-0.3Mo-0.3Si (IMI 829)	1015	1860

Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.3Si (IMI 834)	1045	1915
Ti-6Al-2Cb-1Ta-0.8Mo	1015	1860
Ti-0.3Mo-0.8Ni (Ti code 12)	880	1615
α-β alloys		
Ti-6Al-4V	1000[a]	1830[b]
Ti-6Al-7Nb (IMI 367)	1010	1850
Ti-6Al-6V-2Sn (Cu + Fe)	945	1735
Ti-3Al-2.5V	935	1715
Ti-6Al-2Sn-4Zr-6Mo	940	1720
Ti-4Al-4Mo-2Sn-0.5Si (IMI 550)	975	1785
Ti-4Al-4Mo-4Sn-0.5Si (IMI 551)	1050	1920
Ti-5Al-2Sn-2Zr-4Mo-4Cr (Ti-17)	900	1650
Ti-7Al-4Mo	1000	1840
Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si	970	1780
Ti-8Mn	800[c]	1475[d]
β or near-β alloys		
Ti-13V-11Cr-3Al	720	1330
Ti-11.5Mo-6Zr-4.5Sn (Beta III)	760	1400
Ti-3Al-8V-6Cr-4Zr-4Mo (Beta C)	795	1460
Ti-10V-2Fe-3Al	805	1480
Ti-15V-3Al-3Cr-3Sn	760	1400

(a) ±20.

(b) ±30.

(c) ±35.

(d) ±50

Titanium mill producers generally certify the βtransus temperature for each heat supplied. The β transus of a given alloy will vary from heat to heat due to small differences in chemistry, particularly oxygen content. Methods used for β transus determination are differential thermal analysis (DTA) and metallographic examination samples heated in 5 °C (10 °F) increments through the range of expected β transus. The DTA method has become the method of preference.

Oxygen and iron levels have significant effects on mechanical properties after heat treatment. It should be realized that:

- Oxygen and iron must be near specified maximums to meet strength levels in certain commercially pure grades
- Oxygen must be near a specified maximum to meet strength levels in solution-treated and aged Ti-6Al-4V
- Oxygen levels must be kept as low as possible to optimize fracture toughness. However, the oxygen level must be high enough to meet tensile strength requirements
- Iron content must be kept as low as possible to optimize creep and stress-rupture properties. Most creep-resistant alloys require iron levels at or below 0.05 wt%

Reference cited in this section

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Stress Relieving

Titanium and titanium alloys can be stress relieved without adversely affecting strength or ductility.

Stress-relieving treatments decrease the undesirable residual stresses that result from, first, nonuniform hot forging or deformation from cold forming and straightening, second, asymmetric machining of plate (hog-outs) or forgings, and, third, welding and cooling of castings. The removal of such stresses helps maintain shape stability and eliminates unfavorable conditions, such as the loss of compressive yield strength commonly known as the Bauschinger effect.

When symmetrical shapes are machined in the annealed condition using moderate cuts and uniform stock removal, stress relieving may not be required. Compressor disks made of Ti-6Al-4V have been machined satisfactorily in this manner, conforming with dimensional requirements. In contrast, thin rings made of the same alloy could be machined at a higher production rate to more stringent dimensions by stress relieving 2 h at 540 °C (1000 °F) between rough and final machining.

Separate stress relieving may be omitted when the manufacturing sequence can be adjusted to use annealing or hardening as the stress-relieving process. For example, forging stresses may be relieved by annealing prior to machining. Large, thin rings have been processed effectively with minimum distortion by rough machining in the annealed state, followed by solution treating, quenching, partial aging, finish machining, and final aging. Partial aging relieves quenching stresses, and final aging relieves stresses developed during finish machining.

Table 3 presents combinations of time and temperature that are used for stress relieving titanium and titanium alloys. The ranges in both time and temperature indicate that more than one combination may yield satisfactory results. The higher temperatures are usually used with shorter times, and the lower temperatures are used with longer times, for effective stress relief. During the stress relief of solution-treated and aged titanium alloys, care should be taken to prevent overaging to lower strength. This usually involves the selection of a time-temperature combination that provides partial stress relief. The parts, in bulk or in fixtures, may be charged directly into a furnace operating at the stress-relief temperature. If a part is mounted in a massive fixture, a thermocouple should be attached to the largest part of the fixture.

Table 3 Recommended stress-relief treatments for titanium and titanium alloys

Parts can be cooled from stress relief by either air cooling or slow cooling.

Alloy	**Temperature**		**Time, h**
	°C	**°F**	
Commercially pure Ti (all grades)	480-595	900-1100	$\frac{1}{4}$-4
α or near-α titanium alloys			
Ti-5Al-2.5Sn	540-650	1000-1200	$\frac{1}{4}$-4
Ti-8Al-1Mo-1V	595-705	1100-1300	$\frac{1}{4}$-4
Ti-2.5Cu (IMI 230)	400-600	750-1110	0.5-24
Ti-6Al-2Sn-4Zr-2Mo	595-705	1100-1300	$\frac{1}{4}$-4
Ti-6Al-5Zr-0.5Mo-0.2Si (IMI 685)	530-570	980-1050	24-48
Ti-5.5Al-3.5Sn-3Zr-1Nb-0.3Mo-0.3Si (IMI 829)	610-640	1130-1190	1-3
Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.3Si (IMI 834)	625-750	1160-1380	1-3
Ti-6Al-2Cb-1Ta-0.8Mo	595-650	1100-1200	$\frac{1}{4}$-2
Ti-0.3Mo-0.8Ni (Ti Code 12)	480-595	900-1100	$\frac{1}{4}$-4
α-β titanium alloys			

Ti-6Al-4V	480-650	900-1200	1-4
Ti-6Al-7Nb (IMI 367)	500-600	930-1110	1-4
Ti-6Al-6V-2Sn (Cu + Fe)	480-650	900-1200	1-4
Ti-3Al-2.5V	540-650	1000-1200	$\frac{1}{2}$-2
Ti-6Al-2Sn-4Zr-6Mo	595-705	1100-1300	$\frac{1}{4}$-4
Ti-4Al-4Mo-2Sn-0.5Si (IMI 550)	600-700	1110-1290	2-4
Ti-4Al-4Mo-4Sn-0.5Si (IMI 551)	600-700	1110-1290	2-4
Ti-5Al-2Sn-4Mo-2Zr-4Cr (Ti-17)	480-650	900-1200	1-4
Ti-7Al-4Mo	480-705	900-1300	1-8
Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si	480-650	900-1200	1-4
Ti-8Mn	480-595	900-1100	$\frac{1}{4}$-2
β or near-β titanium alloys			
Ti-13V-11Cr-3Al	705-730	1300-1350	$\frac{1}{12}$-$\frac{1}{4}$
Ti-11.5Mo-6Zr-4.5Sn (Beta 111)	720-730	1325-1350	$\frac{1}{12}$-$\frac{1}{4}$
Ti-3Al-8V-6Cr-4Zr-4Mo (Beta C)	705-760	1300-1400	$\frac{1}{6}$-$\frac{1}{2}$
Ti-10V-2Fe-3A	675-705	1250-1300	$\frac{1}{2}$-2
Ti-15V-3Al-3Cr-3Sn	790-815	1450-1500	$\frac{1}{12}$-$\frac{1}{4}$

Figure 1 illustrates the effects of stress relieving Ti-6Al-4V at five temperatures ranging from 260 to 620 °C (500 to 1150 °F) for periods of time ranging from 5 min to 50 h.

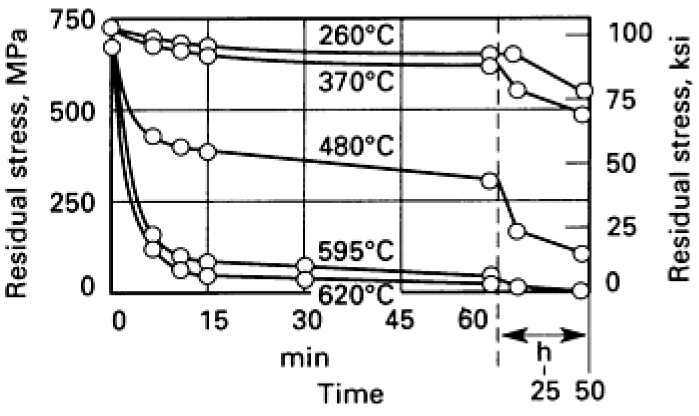

Fig. 1 Relationship between time and relief of residual stress at various temperatures for Ti-6Al-4V. Source: Ref 2

The rate of cooling from the stress-relieving temperature is not critical. Uniformity of cooling is critical, however, particularly in the temperature range from 480 to 315 °C (900 to 600 °F). Oil or water quenching should not be used to accelerate cooling because this can induce residual stresses by unequal cooling. Furnace or air cooling is acceptable.

Stress-relieving treatments must be based on the metallurgical response of the alloy involved. Generally, this requires holding at a temperature sufficiently high to relieve stresses without causing an undesirable amount of precipitation or strain aging in α-β and β alloys, or without producing undesirable recrystallization in single-phase alloys that rely on cold working for strength.

Stress relieving β alloys and the more highly alloyed α -β compositions should be done using a thermal exposure that is compatible with annealing, solution-treating, stabilization, or aging processes.

There are no nondestructive testing methods that can measure the efficiency of a stress-relief cycle other than the direct measurement of residual stresses by x-ray diffraction. No significant changes in microstructure due to stress-relieving heat treatments can be detected by optical microscopy.

Weldments. The temperatures used for stress relieving complex weldments of α or α-β alloys should be near the high ends of the ranges given in Table 3. Complex weldments may be defined as those having multiple welds in complex configurations, possibly involving combinations of machine and manual welding. In complex weldments made with commercially pure titanium, Ti-5Al-2.5Sn alloy or Ti-6Al-4V alloy, more than 70% of the residual stress is relieved during the first hour at temperature. Simple weldments of commercially pure titanium are often used without stress relief.

Reference cited in this section

2. R.A. Wood and R.J. Favor, "Titanium Alloy Handbook," Report MCIC-HB-02, Battelle Memorial Institute, Columbus, Dec 1972

Annealing

The annealing of titanium and titanium alloys serves primarily to increase fracture toughness, ductility at room temperature, dimensional and thermal stability, and creep resistance. Many titanium alloys are placed in service in the annealed state. Because improvement in one or more properties is generally obtained at the expense of some other property, the annealing cycle should be selected according to the objective of the treatment.

Common annealing treatments are:

- Mill annealing
- Duplex annealing
- Recrystallization annealing
- Beta annealing

Recommended annealing treatments for several alloys are given in Table 4. Either air or furnace cooling may be used, but the two methods may result in different levels of tensile properties. If distortion is a problem, the cooling rate should be uniform down to 315 °C (600 °F). It may be difficult to prevent distortion of close-tolerance thin sections during annealing.

Table 4 Recommended annealing treatments for titanium and titanium alloys

Alloy	Temperature		Time, h	Cooling method
	°C	°F		
Commercially pure Ti (all grades)	650-760	1200-1400	$\frac{1}{10}$-2	Air
α or near-α titanium alloys				
Ti-SAl-2.5Sn	720-845	1325-1550	$\frac{1}{6}$-4	Air
Ti-8Al-1 Mo-1V	790[(a)]	1450[(a)]	1-8	Air or furnace
Ti-2.5Cu (IMI 230)	780-800	1450-1470	0.5-1	Air
Ti-6Al-2Sn-4Zr-2Mo	900[(b)]	1650[(b)]	$\frac{1}{2}$-1	Air
Ti-6Al-5Zr-0.5Mo-0.2Si (IMI 685)	[(c)]	[(c)]	. . .	. . .
Ti-5.5Al-3.5Sn-3Zr-1Nb-0.3Mo-0.3Si (IMI 829)	[(c)]	[(c)]	. . .	. . .
Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.3Si (IMI 834)	[(c)]	[(c)]	. . .	. . .
Ti-6Al-2Cb-1Ta-0.8Mo	790-900	1450-1650	1-4	Air
α-β titanium alloys				
Ti-6Al-4V	705-790	1300-1450	1-4	Air or furnace

Ti-6Al-7Nb (IMI 367)	700	1300	1-2	Air
Ti-6Al-6V-2Sn (Cu + Fe)	705-815	1300-1500	$\frac{3}{4}$-4	Air or furnace
Ti-3Al-2.5V	650-760	1200-1400	$\frac{1}{2}$-2	Air
Ti-6Al-2Sn-4Zr-6Mo	(c)	(c)	. . .	. . .
Ti-4Al-4Mo-2Sn-0.5Si (IMI 550)	(c)	(c)	. . .	. . .
Ti-4Al-4Mo-4Sn-0.5Si (IMI 551)	(c)	(c)	. . .	. . .
Ti-5Al-2Sn-4Mo-2Zr-4Cr (Ti-17)	(c)	(c)	. . .	. . .
Ti-7Al-4Mo	705-790	1300-1450	1-8	Air
Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si	705-815	1300-1500	1-2	Air
Ti-8Mn	650-760	1200-1400	$\frac{1}{2}$-1	(d)
β or near-β titanium alloys				
Ti-13V-11Cr-3Al	705-790	1300-1450	$\frac{1}{6}$-1	Air or water
Ti-11.5Mo-6Zr-4.5Sn (Beta III)	690-760	1275-1400	$\frac{1}{6}$-1	Air or water
Ti-3Al-8V-6Cr-4Zr-4Mo (Beta C)	790-815	1450-1500	$\frac{1}{4}$-1	Air or water
Ti-10V-2Fe-3Al	(c)	(c)	. . .	. . .
Ti-15V-3Al-3Cr-3Sn	790-815	1450-1500	$\frac{1}{12}$-$\frac{1}{4}$	Air

(a) For sheet and plate, follow by $\frac{1}{4}$ h at 790 °C (1450 °F), then air cool.

(b) For sheet, follow by $\frac{1}{4}$ h at 790 °C (1450 °F), then air cool (plus 2 h at 595 °C, or 1100 °F, then air cool, in certain applications). For plate, follow by 8 h at 595 °C (1100 °F) then air cool.

(c) Not normally supplied or used in annealed condition (see Table 3).

(d) Furnace or slow cool to 540 °C (1000 °F), then air cool.

Mill annealing is a general-purpose treatment given to all mill products. It is not a full anneal and may leave traces of cold or warm working in the microstructures of heavily worked products, particularly sheet.

Duplex annealing alters the shapes, sizes, and distributions of phases to those required for improved creep resistance or fracture toughness. In the duplex anneal of the Corona 5 alloy (Ref 3), for example, the first anneal is near the β transus to globularize the deformed α and to minimize its volume fraction. This is followed by a second, lower-temperature anneal to precipitate new lenticular (acicular) α between the globular α particles. This formation of acicular α is associated with improvements in creep strength and fracture toughness.

Recrystallization annealing and β annealing are used to improve fracture toughness. In recrystallization annealing, the alloy is heated into the upper end of the α-β range, held for a time, and then cooled very slowly. In recent years, recrystallization annealing has replaced β annealing for fracture-critical airframe components.

Beta Annealing. Like recrystallization annealing, β annealing improves fracture toughness. Beta annealing is done at temperatures above the β transus of the alloy being annealed. To prevent excessive grain growth, the temperature for β annealing should be only slightly higher than the β transus. Annealing times are dependent on section thickness and should be sufficient for complete transformation. Time at temperature after transformation should be held to a minimum to control β grain growth. Larger sections should be fan cooled or water quenched to prevent the formation of a phase at the β grain boundaries.

Straightening, sizing, and flattening of titanium alloys are often necessary in order to meet dimensional requirements. The straightening of bar to close tolerances and the flattening of sheet present major problems for titanium producers and fabricators.

Unlike aluminum alloys, titanium alloys are not easily straightened when cold because the high yield strength and modulus of elasticity of these alloys result in significant springback. Therefore, titanium alloys are straightened primarily by creep straightening and/or hot straightening (hand or die), with the former being considerably more prevalent than the latter.

Straightening, sizing, and flattening may be combined with annealing by the use of appropriate fixtures. The parts, in bulk or in fixtures, may be charged directly into a furnace operating at the annealing temperature. At annealing temperatures, many titanium alloys have a creep resistance low enough to permit straightening during annealing. With proper fixturing, and in some instances judicious weighting, sheet metal fabrication and thin, complex forgings have been straightened with satisfactory results. Again, uniform cooling to below 315 °C (600 °F) can improve results.

Straightening. Creep straightening may be readily accomplished during the annealing and/or aging processes of most titanium alloys. However, if the annealing/aging temperature is below about 540 to 650 °C (1000 to 1200 °F), depending on the alloy, the times required to accomplish the desired creep straightening can be extended. Creep straightening is accomplished with rudimentary or sophisticated fixtures and loading systems, depending on part complexity and the degree of straightening required. In hot hand or die straightening, which are used most frequently on small-to-intermediate-size parts, the parts are heated to the annealing or aging temperature, hot straightened, and then stress relieved at a temperature below that used during hot straightening.

Flattening. Various jigs and processing techniques have been proposed for annealing titanium in a manner that will yield a flat product. "Creep flattening" and "vacuum creep flattening" are two such techniques. Creep flattening consists of heating titanium sheet between two clean, flat sheets of steel in a furnace containing an oxidizing or inert atmosphere.

Vacuum creep flattening is used to produce stress-free flat plate for subsequent machining. The plate is placed on a large, flat ceramic bed that has integral electric heating elements. Insulation is placed on top of the plate, and a plastic sheet is sealed to the frame. The bed is slowly heated to the annealing temperature while a vacuum is pulled under the plastic. Atmospheric pressure is used to creep flatten the plate.

Stability. In α-β titanium alloys, thermal stability is a function of β-phase transformations. During cooling from the annealing temperature, β may transform and, under certain conditions and in β alloys, may form a brittle intermediate phase known as ω. A stabilization annealing treatment is designed to produce a stable β phase capable of resisting further transformation when exposed to elevated temperatures in service. Alpha-beta alloys that are lean in β, such as Ti-6Al-4V, can be air cooled from the annealing temperature without impairing their stability. Furnace (slow) cooling may promote the formation of Ti_3Al, an ordering reaction that can degrade resistance to stress corrosion. Slight increases in strength (up to 35 MPa, or 5 ksi) can be gained in Ti-6Al-4V and in Ti-6Al-6V-2Sn by cooling from the annealing temperature to 540 °C (1000 °F) at a rate of 55 °C/h (100 °F/h).

To obtain maximum creep resistance and stability in the near-α alloys Ti-8Al-1Mo-1V and Ti-6Al-2Sn-4Zr-2Mo, a duplex annealing treatment is employed. This treatment begins with solution annealing at a temperature high in the α-β range, usually 25 to 55 °C (50 to 100 °F) below the β transus for Ti-8Al-1Mo-1V and 15 to 25 °C (25 to 50 °F) below the β transus for Ti-6Al-2Sn-4Zr-2Mo. Forgings are held for 1 h (nominal) and then air or fan cooled, depending on section size. This treatment is followed by stabilization annealing for 8 h at 595 °C (1100 °F). Final annealing temperature should be at least 56 °C (100 °F) above the maximum anticipated service temperature. Maximum creep resistance can be developed in Ti-6Al-2Sn-4Zr-2Mo by β annealing or β processing.

Reference cited in this section

3. F.H. Froes and W.T. Highberger, Synthesis of Corona 5 (Ti-4.5Al-5Mo-1.5Cr), in *Titanium Technology: Present Status and Future Trends,* Titanium Development Association, 1985, p 95-102

Solution Treating and Aging

A wide range of strength levels can be obtained in α-β or β alloys by solution treating and aging. With the exception of the unique Ti-2.5Cu alloy (which relies on strengthening from the classic age-hardening reaction of Ti_2Cu precipitation similar to the formation of Guinier-Preston zones in aluminum alloys), the origin of heat-treating responses of titanium alloys lies in the instability of the high-temperature β phase at lower temperatures. Heating an α-β alloy to the solution-treating temperature produces a higher ratio of β phase. This partitioning of phases is maintained by quenching; on subsequent aging, decomposition of the unstable β phase occurs, providing high strength. Commercial β alloys, generally supplied in the solution-treated condition, need only be aged.

After being cleaned, titanium components should be loaded into fixtures or racks that will permit free access to the heating and quenching media. Thick and thin components of the same alloy may be solution treated together, but the time at temperature (soaking time) is determined by the thickest section. For most alloys, the rule is 20 to 30 min per inch (25 mm) of thickness to reach the required temperature, followed by the required soak time.

Time/temperature combinations for solution treating are given in Table 5. A load may be charged directly into a furnace operating at the solution-treating temperature. Although preheating is not essential, it may be used to minimize the distortion of complex parts.

Table 5 Recommended solution-treating and aging (stabilizing) treatments for titanium alloys

Alloy	Solution temperature		Solution time, h	Cooling rate	Aging temperature		Aging time, h
	°C	°F			°C	°F	
α or near-α alloys							

Ti-8Al-1Mo-1V	980-1010[a]	1800-1850[a]	1	Oil or water	565-595	1050-1100	. . .
Ti-2.5Cu (IMI 230)	795-815	1465-1495	0.5-1	Air or water	390-410	735-770	8-24 (step 1)
					465-485	870-905	8 (step 2)
Ti-6Al-2Sn-4Zr-2Mo	955-980	1750-1800	1	Air	595	1100	8
Ti-6Al-5Zr-0.5Mo-0.2Si (IMI 685)	1040-1060	1905-1940	0.5-1	Oil	540-560	1005-1040	24
Ti-5.5Al-3.5Sn-3Zr-1Nb-0.3Mo-0.3Si (IMI 829)	1040-1060	1905-1940	0.5-1	Air or oil	615-635	1140-1175	2
Ti-5.8Al-4Sn-3.5Zr-0.7Nb-0.5Mo-0.3Si (IMI 834)	1020[b]	1870[b]	2	Oil	625	1155	2
α-β alloys							
Ti-6Al-4V	955-970[c][d]	1750-1775[c][d]	1	Water	480-595	900-1100	4-8
	955-970	1750-1775	1	Water	705-760	1300-1400	2-4
Ti-6Al-6V-2Sn (Cu + Fe)	885-910	1625-1675	1	Water	480-595	900-1100	4-8
Ti-6Al-2Sn-4Zr-6Mo	845-890	1550-1650	1	Air	580-605	1075-1125	4-8
Ti-4Al-4Mo-2Sn-0.5Si (IMI 550)	890-910	1635-1670	0.5-1	Air	490-510	915-950	24
Ti-4Al-4Mo-4Sn-0.5Si (IMI 551)	890-910	1635-1670	0.5-1	Air	490-510	915-950	24
Ti-5Al-2Sn-2Zr-4Mo-4Cr	845-870	1550-1600	1	Air	580-605	1075-1125	4-8
Ti-6Al-2Sn-2Zr-2Mo-2Cr-0.25Si	870-925	1600-1700	1	Water	480-595	900-1100	4-8

β or near-β alloys							
Ti-13V-11Cr-3Al	775-800	1425-1475	$\frac{1}{4}$-1	Air or water	425-480	800-900	4-100
Ti-11.5Mo-6Zr-4.5Sn (Beta III)	690-790	1275-1450	$\frac{1}{8}$-1	Air or water	480-595	900-1100	8-32
Ti-3Al-8V-6Cr-4Mo-4Zr (Beta C)	815-925	1500-1700	1	Water	455-540	850-1000	8-24
Ti-10V-2Fe-3Al	760-780	1400-1435	1	Water	495-525	925-975	8
Ti-15V-3Al-3Cr-3Sn	790-815	1450-1500	$\frac{1}{4}$	Air	510-595	950-1100	8-24

(a) For certain products, use solution temperature of 890 °C (1650 °F) for 1 h. then air cool or faster.

(b) Temperature should be selected from transus approach curve to give desired α content.

(c) For thin plate or sheet, solution temperature can be used down to 890 °C (1650 °F) for 6 to 30 min; then water quench.

(d) This treatment is used to develop maximum tensile properties in this alloy.

Solution treating of titanium alloys generally involves heating to temperatures either slightly above or slightly below the β transus temperature. The solution-treating temperature selected depends on the alloy type and practical considerations briefly described below.

Beta alloys are normally obtained from producers in the solution-treated condition. If reheating is required, soak times should be only as long as necessary to obtain complete solutioning. Solution-treating temperatures for β alloys are above the β transus; because no second phase is present, grain growth can proceed rapidly.

Alpha-Beta Alloys. Selection of a solution-treatment temperature for α-β alloys is based on the combination of mechanical properties desired after aging. A change in the solution-treating temperature of α-β alloys alters the amounts of β phase and consequently changes the response to aging (see Table 6).

Table 6 Variation of tensile properties of Ti-6Al-4V bar stock with solution-treating temperature

Solution-treating temperature	**Room.temperature tensile properties[(a)]**		**Elongation in 4*D*, %**
	Tensile strength	**Yield strength[(b)]**	

°C	°F	MPa	ksi	MPa	ksi	
845	1550	1025	149	980	142	18
870	1600	1060	154	985	143	17
900	1650	1095	159	995	144	16
925	1700	1110	161	1000	145	16
940	1725	1140	165	1055	153	16

(a) Properties determined on 13 mm ($\frac{1}{2}$ in.) bar after solution treating, quenching, and aging. Aging treatment: 8 h at 480 °C (900 °F), air cool.

(b) At 0.2% offset

To obtain high strength with adequate ductility, it is necessary to solution treat at a temperature high in the α-β field, normally 25 to 85 °C (50 to 150 °F) below the β transus of the alloy. If high fracture toughness or improved resistance to stress corrosion is required, β annealing or β solution treating may be desirable. However, heat treating α-β alloys in the β range causes a significant loss in ductility. These alloys are usually solution heat treated below the β transus to obtain an optimum balance of ductility, fracture toughness, creep, and stress-rupture properties. If the β transus is exceeded, tensile properties of α-β alloys (especially ductility) are reduced and cannot be fully restored by subsequent thermal treatment.

Near-Alpha Alloys. Like the α-β alloys, solution treatment above the β transus provides optimum creep resistance at the expense of reduced ductility and fatigue strength. To obtain the best combination of creep strength and fatigue strength, the solution temperature must be very close to but below the transus, so that only 10 to 15% of primary (untransformed) α remains. To be practical on the shop floor, a flattened β-approach curve is required so that temperature control is not as critical. In alloy IMI 834 this is achieved by the use of carbon additions (see the article "Wrought Titanium and Titanium Alloys" in Volume 2 of *ASM Handbook*, formerly 10th Edition *Metals Handbook*).

Quenching. The rate of cooling from the solution-treating temperature has an important effect on strength. If the rate is too low, appreciable diffusion may occur during cooling, and decomposition of the altered β phase during aging may not provide effective strengthening.

For alloys relatively high in β-stabilizer content and for products of small section size, air or fan cooling may be adequate; such slow cooling, where allowed by specified mechanical properties, is preferred because it minimizes distortion. Beta alloys are generally air quenched from the solution-treating temperature.

Water, a 5% brine, or caustic soda solution is preferred for quenching α-β alloys because these quenchants provide the cooling rates necessary to prevent the decomposition of the βphase obtained by solution treating, in order to provide maximum response to aging. The need for rapid quenching is further emphasized by short quench-delay requirements. Depending on the mass of the sections being heat treated, some α-β alloys can tolerate a maximum delay of 7 s, whereas more highly β-stabilized alloys can tolerate quench delay times of up to 20 s. The effect of quench delays on Ti-6Al-4V bar is shown in Fig. 2. When a Ti-6Al-4V section thickness exceeds 75 mm (3 in.), it is difficult to cool the center fast enough to maintain an unstable β phase. For this reason, the solution-treated and aged properties of Ti-6Al-4V large sections are similar to annealed properties. Less sensitive to delayed quenching are alloys such as Ti-6Al-2Sn-4Zr-6Mo, Ti-4Al-4Mo-2Sn-0.5Si, and Ti-5Al-2Sn-2Zr-4Mo-4Cr, in which fan air cooling develops good strength through 100 mm (4 in.) sections.

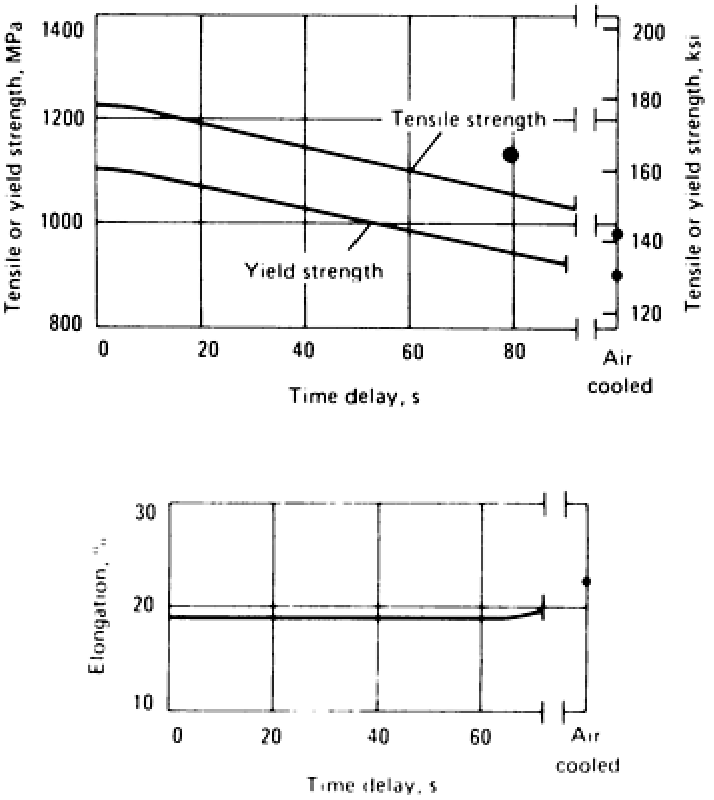

Fig. 2 Effects of quench delay on tensile properties of Ti-6Al-4V bar. Bar, 13 mm ($\frac{1}{2}$ in.) in diameter, was solution treated 1 h at 955 °C (1750 °F), water quenched, aged 6 h at 480 °C (900 °F), and air cooled. Source: Ref 4

Section size influences the effectiveness of quenching and, in turn, the response to aging. The amount and type of β stabilizer in the alloy determine the depth of hardening or strengthening. Thick sections exhibit lower tensile properties unless the alloy is highly alloyed with βstabilizers. The practical significance of section size for some alloys is given in Table 7. The effects of quenched section size on the tensile properties of Ti-6Al-4V alloy are shown in Fig. 3. The strength capabilities of solution-treated α-β alloys not highly β stabilized are greatly dependent on the oxygen content. The property levels for Ti-6Al-4V shown in Table 7 and Fig. 3 would be typical for an oxygen content between 0.17 and 0.20%. A lower oxygen content will tend to result in strength levels lower than those shown, particularly for the smaller section sizes.

Table 7 Relationship of tensile strength of solution-treated and aged titanium alloys to size

Alloy	Tensile strength of square bar in section size of											
	13 mm ($\frac{1}{2}$ in.)		25 mm (1 in.)		50 mm (2 in.)		75 mm (3 in.)		100 mm (4 in.)		150 mm (6 in.)	
	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi
Ti-6Al-4V	1105	160	1070	155	1000	145	930	135	. . .	. . .	. . .	. . .

Ti-6Al-6V-2Sn (Cu + Fe)	1205	175	1205	175	1070	155	1035	150	. . .	. . .	. . .	. . .
Ti-6Al-2Sn-4Zr-6Mo	1170	170	1170	170	1170	170	1140	165	1105	160	. . .	. . .
Ti-5Al-2Sn-2Zr-4Mo-4Cr (Ti-17)	1170	170	1170	170	1170	170	1105	160	1105	160	1105	160
Ti-10V-2Fe-3Al	1240	180	1240	180	1240	180	1240	180	1170	170	1170	170
Ti-13V-11Cr-3Al	1310	190	1310	190	1310	190	1310	190	1310	190	1310	190
Ti-11.5Mo-6Zr-4.5Sn (Beta III)	1310	190	1310	190	1310	190	1310	190	1310	190	. . .	. . .
Ti-3 Al-8V-6Cr-4Zr-4Mo (Beta C)	1310	190	1310	190	1240	180	1240	180	1170	170	1170	170

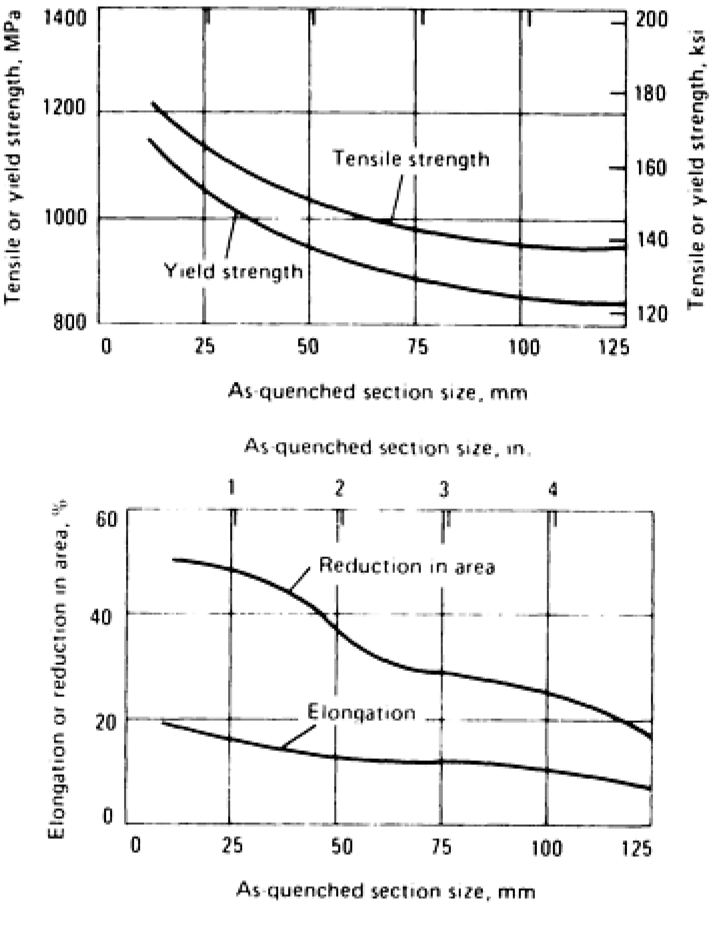

Fig. 3 Effects of quenched section size on tensile properties of Ti-6Al-4V. Source: Ref 4

Aging. The final step in heat treating titanium alloys to high strength consists of reheating to an aging temperature between 425 and 650 °C (800 and 1200 °F). Aging causes the decomposition of the supersaturated β phase retained upon quenching. A summary of aging times and temperatures is presented in Table 5. The time/temperature combination selected depends on required strength. Aging at or near the annealing temperature results in overaging. This condition,

called solution treated and overaged, or STOA, is sometimes used to obtain modest increases in strength while maintaining satisfactory toughness and dimensional stability.

Although the aged condition is not necessarily one of equilibrium, proper aging produces high strength with adequate ductility and metallurgical stability. Heat treatment of α-β alloys for high strength frequently involves a series of compromises and modifications, depending on the type of service and the special properties required, such as ductility and suitability for fabrication. This has become especially true when fracture toughness is important in design and strength is lowered to improve design life.

During the aging of some highly β-stabilized α-β alloys, β transforms first to a metastable transition phase referred to as ω phase. Retained ω phase, which produces brittleness unacceptable in alloys heat treated for service, can be avoided by severe quenching and rapid reheating to aging temperatures above 425 °C (800 °F). However, because a coarse α phase forms, this treatment might not produce optimum-strength properties. An aging practice that ensures that aging time and temperature are adequate to carry out any ω reaction to completion is usually employed. Aging above 425 °C (800 °F) is generally adequate to complete the reaction.

The metastable β alloys do not require solution treatment. Final hot working, followed by air cooling, leaves these alloys in a condition comparable to a solution-treated state. In some instances, however, solution treating at 790 °C (1450 °F) has produced better uniformity of properties after aging. Aging at 480 °C (900 °F) for 8 to 60 h produces tensile strengths of 1.10 to 1.38 GPa (160 to 200 ksi). Aging for times longer than 60 h may provide higher strengths, but will decrease ductility and fracture toughness if the alloy contains chromium and titanium-chromium compounds are formed. Short aging times can be used on cold-worked material to produce a significant increase in strength over that obtained by cold working. The use of β alloys at service temperatures above 315 °C (600 °F) for prolonged periods is not recommended because the loss of ductility caused by metallurgical instability is progressive.

Other Special Thermal Treatments. Certain physical properties, such as notch strength, fracture toughness, and fatigue resistance, can be enhanced in some alloys by special thermal treatments. Three such treatments are:

- *Solution treating and overaging of Ti-6Al-4V:* Heat 1 h at 955 °C (1750 °F), water quench, hold 2 h at 705 °C (1300 °F), air cool. Advantages: improved notch strength, fracture toughness, and creep strength at strength levels similar to those obtained by regular annealing
- *Recrystallization annealing of Ti-6Al-4V or Ti-6Al-4V-ELI:* Heat 4 h or more at 925 to 955 °C (1700 to 1750 °F), furnace cool to 760 °C (1400 °F) at a rate no higher than 56 °C/h (100 °F/h), cool to 480 °C (900 °F) at a rate no lower than 370 °C/h (670 °F/h), air cool to room temperature. Advantages: improved fracture toughness and fatigue-crack-growth characteristics at somewhat reduced levels of strength
- *Beta annealing of Ti-6Al-4V, Ti-6Al-4V-ELI, Ti-6Al-2Sn-4Zr-2Mo, Ti-6Al-4V, or Ti-6Al-4V-ELI*: Heat 5 min to 1 h at 1010 to 1040 °C (1850 to 1900 °F), air cool to 650 °C (1200 °F) at a rate of 85 °C/min (150 °F/min) or higher, then heat 2 h at 730 to 790 °C (1350 to 1450 °F), air cool. Advantages: improved fracture toughness, high cycle fatigue strength and resistance to aqueous stress corrosion. Ti-6Al-2Sn-4Zr-2Mo: Heat $\frac{1}{2}$ h at 1020 °C (1870 °F), air cool, then hold 8 h at 595 °C (1100 °F), air cool. Advantages: improved creep strength at elevated temperatures and improved fracture toughness. Disadvantages: Beta annealing of α-β alloys produces relatively low tensile ductility. In recent years, recrystallization annealing has replaced β annealing for fracture-critical airframe components
- *High α-β solution treatment of Ti-5.8Al-4Sn-3.5Zr-O.7Nb-O.5Mo-0.3Si (IMI 834):* Determine β transus approach curve on small samples by quenching from temperature and plotting the percent of β phase against temperature. Choose solution treatment temperature to give 85 to 88% β. Heat 2 h at temperature, oil quench, age at 700 °C (1290 °F) for 2 h, air cool. Advantages: Excellent combination of creep and fatigue properties with good room-temperature tensile properties

Post-Heat-Treating Requirements. Titanium reacts with the oxygen, water, and carbon dioxide normally found in oxidizing heat treating atmospheres and with the hydrogen formed by the decomposition of water vapor. Unless the heat treatment is performed in a vacuum furnace or in an inert atmosphere, the oxygen will react with the titanium at the metal surface and produce an oxygen-enriched layer commonly called α case. This brittle layer must be removed before the

component is put into service. It can be removed by machining, but certain machining operations may result in excessive tool wear. Standard practice is to remove α case by other mechanical methods or by chemical methods, or both.

Oxidation rates of commercial titanium alloys vary, and Table 8 can be used as a guide to determine how much metal should be removed. Temperature and total time at temperature must be known. One method used to check for the complete removal of α case is to etch the component with a solution composed of 18 g of ammonium bifluoride per liter of water (2.4 oz/gal). The presence or absence of α case is detected by the difference in etching characteristics: Light gray shows the presence of α case; dark gray indicates its absence. If the component has been machined, as in the case of a forging, the ammonium bifluoride treatment must be preceded by etching in a solution consisting nominally of 5% HF, 30% min HNO_3, balance water. A more sensitive method for checking for α case is the etch-anodize, or "blue etch," technique. This method is described in SAE specification AMS 2642. For other mill products, such as plate, the microexamination of representative samples removed from the plate is commonly used.

Table 8 Minimum metal removal after thermal exposure of titanium alloys in an oxidizing atmosphere

Heat-treating temperature		Time at temperature, h	Minimum stock removal per surface[(a)]	
°C	°F		mm	in.
480-593	900-1100	≤ 12	0.005	0.0002
594-648	1101-1200	≤ 4	0.008	0.0003
		4-12	0.015	0.0006
649-704	1201-1300	≤ 1	0.013	0.0005
		1-8	0.020	0.0008
		8-12	0.025	0.0010
705-760	1301-1400	≤ 1	0.025	0.0010
		1-4	0.036	0.0014
		4-8	0.038	0.0015
		8-12	0.043	0.0017
761-787	1401-1450	≤ 1	0.030	0.0012
		1-2	0.038	0.0015
		2-4	0.046	0.0018

		4-8	0.051	0.0020
		8-12	0.056	0.0022
788-815	1451-1500	$\leq \frac{1}{2}$	0.036	0.0014
		$\frac{1}{2}$-1	0.041	0.0016
		1-2	0.051	0.0020
816-871	1501-1600	$\leq \frac{1}{2}$	0.058	0.0023
		$\frac{1}{2}$-1	0.066	0.0026
		1-2	0.076	0.0030
872-898	1601-1650	$\leq \frac{1}{2}$	0.066	0.0026
		$\frac{1}{2}$-1	0.081	0.0032
		1-2	0.089	0.0035
899-926	1651-1700	$\leq \frac{1}{2}$	0.086	0.0034
		$\frac{1}{2}$-1	0.091	0.0036
		1-2	0.107	0.0042
927-954	1701-1750	$\leq \frac{1}{2}$	0.097	0.0038
		$\frac{1}{2}$-1	0.107	0.0042

		1-2	0.122	0.0048
872-898	1601-1650	≤0.5	0.066	0.0026
		0.5-1	0.081	0.0032
		1-2	0.089	0.0035
899-926	1651-1700	≤0.5	0.076	0.0030
		0.5-1	0.091	0.0036
		1-2	0.107	0.0042
927-954	1701-1750	≤0.5	0.097	0.0038
		0.5-1	0.107	0.0042
		1-2	0.122	0.0048
955-982	1751-1800	≤0.5	0.114	0.0045
		0.5-1	0.137	0.0054
		1-2	0.160	0.0063
983-1010	1801-1850	≤0.5	0.145	0.0057
		0.5-1	0.178	0.0070
		1-2	0.216	0.0085
1011-1038	1851-1900	≤0.5	0.178	0.0070
		0.5-1	0.229	0.0090
		1-2	0.292	0.0115
1039-1066	1901-1950	≤0.5	0.229	0.0090
		0.5-1	0.305	0.0120

		1-2	0.406	0.0160

(a) Values shown are typical; actual values may vary with alloy type.

Small amounts of hydrogen (100 to 200 ppm) can be tolerated in titanium alloys with the specific limiting amounts determined by the type of alloy. High hydrogen content can lead to premature failure of a component. Hydrogen pickup occurs not only during heat treatment but also during pickling or chemical cleaning operations used to remove α case. The amount of hydrogen pickup can be determined only by chemical analysis. If high hydrogen content is found, vacuum annealing is required. A typical vacuum annealing cycle consists of heating at or close to the annealing temperature for 2 to 4 h in a vacuum of ~10 μm.

Hardness testing is not recommended as a nondestructive method of checking the efficiency of heat treatment. The correlation between strength and hardness is poor. Whenever the verification of a property is required, the appropriate mechanical test should be used.

Reference cited in this section

4. Properties and Processing Ti-6Al-4V, *Timet,* April 1980

Contamination during Heat Treatment

Before being subjected to any thermal treatment, titanium components should be cleaned and dried. *Caution: Do not use ordinary tap water in cleaning titanium components. Oil, fingerprints, grease, paint, and other foreign matter should be removed from all surfaces. Cleaning is required because the chemical reactivity of titanium at elevated temperatures can lead to its contamination or embrittlement and can increase its susceptibility to stress corrosion. After cleaning, parts should be handled with clean gloves to prevent recontamination. If a component is to be sized, straightened, or heat treated in a fixture, the fixture should be free of any foreign matter and loosely adhering scale.*

Titanium is chemically active at elevated temperatures and readily oxidizes in air. However, oxidation is not of primary concern in the heat treating of titanium, although it may be a problem in sheet-forming operations. Oxygen pickup during heat treatment results in both a surface structure composed predominantly of α phase and the formation of scale. This condition is detrimental because of the brittle nature of the oxygen-enriched α structure, which is also very abrasive to either carbide or high-speed-steel machine tools. For heat treatment in oxidizing atmospheres at 955 °C (1750 °F), the α structure can extend 0.2 to 0.3 mm (0.008 to 0.012 in.) below the surface and must be removed.

An antioxidant spray coating (see Example 2 in this article) may be applied to clean sheet metal parts in order to minimize oxygen pickup. Such coatings work effectively at temperatures up to about 760 °C (1400 °F), but their use does not fully eliminate the need for removing the surface structure after heat treating.

Hydrogen Pickup. Current specifications limit hydrogen content to a maximum of 125 to 200 ppm, depending on alloy and mill form. Above these limits, hydrogen embrittles some titanium alloys, thereby reducing impact strength and notch tensile strength and causing delayed cracking.

With the exceptions of high vacuum, salt baths, and chemically inert gases such as argon, all heat-treating atmospheres contain some hydrogen at temperatures used for annealing titanium. Hydrocarbon fuels produce hydrogen as a by-product of incomplete combustion, and electric furnaces with air atmospheres contain hydrogen from the breakdown of water vapor. However, because small amounts of hydrogen can be tolerated in titanium and because inert media are expensive, most titanium heat-treating operations are performed in conventional furnaces employing oxidizing atmospheres with at least 5% excess oxygen in the flue gas. The hydrogen absorption rate increases with temperature. Stress relieving, mill annealing, and aging all result in minimal hydrogen pickup. However, substantial hydrogen absorption can occur during solution treating or β annealing. Without a protective atmosphere, electric furnaces are recommended to minimize hydrogen pickup.

An oxidizing atmosphere serves to reduce hydrogen pickup in two ways: It reduces the partial pressure of hydrogen in the surrounding atmosphere, and it provides the titanium with a protective surface oxide that retards hydrogen pickup.

Oxidation rates of titanium alloys vary considerably. A comparison of the scaling rates of commercially pure titanium and titanium alloys in air at temperatures from 650 to 980 °C (1200 to 1800 °F) is given in Fig. 4. Table 9 indicates the measurable thickness of oxide formed on commercially pure titanium after $\frac{1}{2}$ h at various temperatures in air.

Table 9 Thickness of oxide on commercially pure titanium heated for $\frac{1}{2}$ h in air

Temperature		Measurable thickness	
°C	°F	mm	in.
315	600	None	None
425	800	None	None
540	1000	None	None
650	1200	<0.005	<0.0002
705	1300	0.005	0.0002
760	1400	0.008	0.0003
815	1500	<0.025	<0.001
870	1600	<0.025	<0.001
925	1700	<0.05	<0.002
980	1800	0.05	0.002
1040	1900	0.10	0.004
1095	2000	0.36	0.014

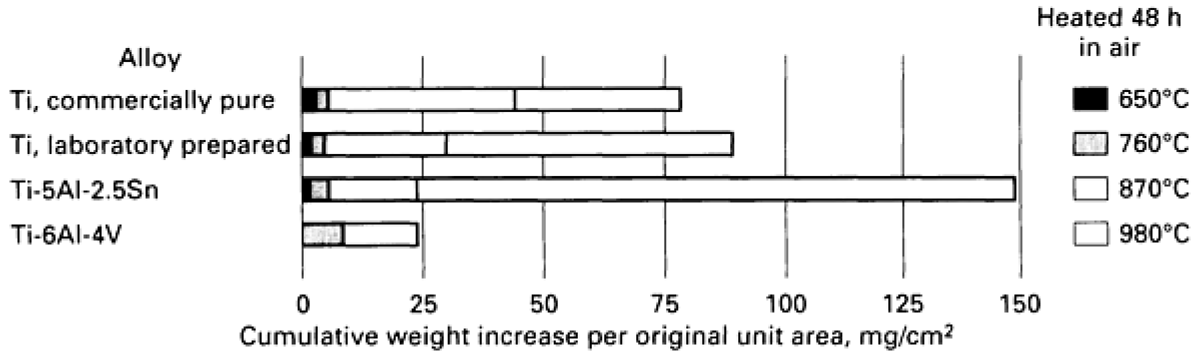

Fig. 4 Scaling rates of titanium and titanium alloys in air at various temperatures

Nitrogen is absorbed by titanium during heat treatment at a much slower rate than is oxygen and thus does not present a serious contamination problem. Dry nitrogen has been used successfully as a lower-cost protective atmosphere for heat treating titanium forgings that are to be fully machined after treatment. If absorbed in sufficient quantities, however, nitrogen forms a hard, brittle compound.

Carbon monoxide and carbon dioxide decompose in the presence of hot titanium and produce surface oxidation.

Chlorides. Titanium alloys are subject to stress corrosion when parts with high residual stress are exposed to chlorides at temperatures above 290 °C (550 °F). Salt from fingerprints, as well as the chlorides contained in some degreasing solutions, may cause stress-corrosion cracking at temperatures above 315 °C (600 °F). Although this phenomenon is readily produced in laboratory testing and is known to occur during heat treatment, hot-salt cracking has not been a significant problem in service. Care is required during thermal processing to ensure freedom from chloride contamination.

Growth during Heat Treatment

Solution treating of large parts requires allowances for growth during heat treatment. The growth due to heating may be retained after cooling, and this growth may be increased either by longer holding times at solution temperature or by lower heating rates. Table 10 gives examples of net growth of Ti-6Al-4V specimens heated to 955 °C (1750 °F).

Table 10 Effect of heating rate and time at 955 °C (1750 °F) on growth of Ti-6Al-4V

Mill heat[a]	Heating rate		Holding time[b], h	Net growth[c], %
	°C/min	°F/min		
A	3.3	6	0	0.27
B	3.3	6	0	0.22
A	3.3	6	1	0.60
B	3.3	6	1	0.49
A	3.3	6	2	1.00

B	3.3	6	2	0.90[(d)]
B	10	18	1	0.32
B[(e)]	10	18	1	0.35

Note: 50 mm (2 in.) specimens were taken in the longitudinal direction (except where otherwise indicated) from material annealed 2 h at 705 °C (1300 °F) and air cooled. No growth was observed in specimens tested during annealing.

(a) Beta transus temperatures (determined metallographically) were 990 °C (1810 °F) for heat A and 1015 °C (1860 °F) for heat B.

(b) All specimens water quenched after holding for time indicated.

(c) As determined by Leitz-Wetzler dilatometer.

(d) Calculated from curve.

(e) Specimen taken in transverse direction

Furnace Equipment and Accessories

Atmospheres. An oxidizing atmosphere should be maintained during any thermal treatment of titanium. Furnaces normally operated with exothermic atmospheres, endothermic cracked-ammonia atmospheres, or hydrogen atmospheres, because of the danger of hydrogen pickup, should be thoroughly "burned out" before being used for processing titanium. If dimensions, shape, or size do not permit the removal of scale by subsequent pickling or machining, antioxidant coatings suitable for use to 760 °C (1400 °F) can be employed to minimize contamination. A vacuum or an inert gas such as argon can also be used.

Furnaces. Titanium is usually annealed or stress relieved in conventional furnaces constructed for annealing steel. These furnaces are electric, gas fired, or oil fired, in order of decreasing popularity. The temperature-control equipment for these operations should have an accuracy of ±5 °C (±10 °F) and should be capable of controlling and recording the desired temperature within ±15 °C (±25 °F), except when control with ±10 °C (±15 °F) is required by MIL-H-81200.

Vacuum annealing furnaces are either of the cold-wall or the hot-wall type and may be heated by gas or electricity.

Cold-wall electric vacuum furnaces are used most commonly with titanium. Maximum furnace operating temperature depends on the heating elements and radiation shields, but usually these furnaces are designed for a maximum temperature of 980 °C (1800 °F) and are adequate for all titanium alloys. Hot-wall electric furnaces and gas-fired vacuum furnaces have been used in production. When the furnace employs a metallic retort, operating temperatures are held below 980 °C (1800 °F); higher temperatures can be achieved with ceramic retort tubes.

Laboratory vacuum annealing furnaces are usually operated at pressures of 0.1 μm or less, whereas production furnaces are designed to operate at pressures of 0.5 to 3.0 μm.

Vacuum annealing is expensive and is generally used only when a reduction in hydrogen content is required, further hydrogen contamination is prohibited, or allowances that can be made for stock removal are insufficient to permit surface contamination resulting from annealing in air. Hydrogen outgassing at 705 °C (1300 °F) and below is so slow that its cost may be prohibitive. A temperature of 730 °C (1350 °F) is recommended as a minimum, and temperatures from 760 to 790 °C (1400 to 1450 °F) are preferred. At a temperature of 760 °C, the removal of 100 ppm of hydrogen from 13 to 25 mm

($\frac{1}{2}$ to 1 in.) sections of Ti-6Al-4V alloy required approximately 2 h at a pressure of <10 μm. Actual time at temperature may vary widely depending on the capability of the furnace to maintain a vacuum.

Solution-treating equipment can vary from a simple furnace with accurate temperature control and a water quench tank to specialized installations for treating complex parts. Electrically heated furnaces are preferred because they minimize hydrogen pickup, although fuel-fired furnaces with slightly oxidizing conditions or with muffles that protect the metal from combustion products have been used successfully. Also, resistance and induction heating have been used to reduce heating times and to minimize contamination during solution treatment. Accuracy of temperature control equipment should be within ±3 °C (±5 °F), and the desired temperature should be controlled within ±15 °C (±25 °F).

To reduce distortion in long, thin products such as sheet or extrusions; in hollow cylinders; and in long forgings during immersion quenching, parts are often suspended vertically in an electrically heated drop-bottom furnace. In addition, weights are usually attached to the bottom ends of sheet to improve flatness during heating and to facilitate lowering of the sheet into the quench tank.

Quenching Media. Because rapid cooling is required after the solution treatment of most titanium alloys, either water or a 5% brine or caustic soda solution is most widely used as the quenching medium. Low-viscosity oil with a high flash point has been used effectively in vertical immersion quenching of sheet to reduce distortion. Quenching oils used with steel provide rapid cooling to 370 to 425 °C (700 to 800 °F), and these oils are satisfactory. Their use, however, should be limited to thin sections to avoid the degradation of strength compared to that obtained by water quenching from the same solution temperature. Various concentrations of glycol in water will produce quench rates between those of water and those of oil. During quenching, the quench media should be thoroughly agitated. Recirculating systems are preferred, with the quench media maintained at temperatures below 40 °C (100 °F).

Aging Furnaces. Because they do not involve combustion by-products, furnaces of the electrical-resistance type are preferable for aging titanium and its alloys. Retorts, however, may be used with oil-fired or gas-fired furnaces to avoid contamination. Aging furnaces are normally equipped with internal fans to promote the circulation of air or other atmosphere throughout the work zone. Temperature control equipment should be accurate to ±1 °C (±2 °F) and should be capable of controlling temperature within ±10 °C (±15 °F).

At normal aging temperatures of 480 to 595 °C (900 to 1100 °F), a protective atmosphere is not required. Aging in air produces a superficial scale that can be removed easily by mechanical or chemical means (this scale also may be left in place because it does not affect properties).

Fixtures. In fixturing titanium components or assemblies to prevent distortion, the thermal-expansion characteristics of both the titanium alloy and the fixture itself must be considered. Ideally, both the alloy and the fixture will have equivalent thermal expansion characteristics within the intended aging-temperature range. Mild steel is commonly used because it is low in cost and can be made reasonably resistant to oxidation at aging temperatures through the use of coatings such as electroless nickel. When mild steel fixtures are used, allowance must be made for the slight difference between the thermal expansion of the mild steel and that of titanium to avoid undesirable growth or distortion of the treated part.

In some applications, it is necessary to reduce or eliminate existing distortion in a part or assembly. This distortion may have resulted from water quenching, from relief of residual stresses during machining, from stresses induced by welding, or from uncontrollable springback after forming. Proper fixturing during aging can be used to minimize such distortion. Fixtures also must guard against sagging. For example, Ti-6Al-4V has a tendency to sag at 955 °C (1750 °F) during solution heat treating. Because titanium alloys exhibit creep behavior within the normal range of aging temperatures, it is possible to fixture and "creep form" components or assemblies to desired shape. Parts may also be sized by fixturing during aging.

Summary of Practice. Key considerations in the heat treating of titanium and its alloys--practices that are to be followed and those that should be avoided--are:

- Provide sufficient stock for post-treatment metal-removal requirements (contaminated metal removal)
- Clean components, fixtures, and furnaces prior to heat treatment. *Caution: (Do not use ordinary tap water to clean titanium components)*
- Do not allow temperature to exceed β transus (unless it is specified as a β anneal process). Use

temperature controls with an upper cutoff at least 15 °C (25 °F) below β transus

- Charge cold components into furnaces operating at the required temperature
- Stack and support components to allow free access of heating and quenching media. Do not nest components
- Observe quench-delay requirements to ensure a hardening response during aging
- Review property requirements and select optimum heat-treating procedure
- Review strength requirements and select proper aging cycle
- Remove α case after all heat treating is completed
- Check for the presence of hydrogen after all processing is completed
- Do not rely on inert atmosphere or vacuum for the prevention of oxygen contamination
- Ensure that a reliable β transus temperature is known and reviewed for each heat of product before treating at temperatures high in the α-β range
- Realize the significant effect of oxygen and iron on the mechanical property response after heat treatment. (See the section "Oxygen and Iron Levels" in this article)
- Do not rely on hardness tests for a measurement of the effects of heat treatment
- Do not pickle assemblies with faying surfaces

Production Examples of Heat-Treating Processes

The examples that follow describe applications of heat-treating processes to specific titanium parts and assemblies and indicate typical relationships among heat treating and other production operations.

Example 1: Heat Treatment of Welded α-Alloy Compressor Cases.

Because α alloys are not hardenable, the heat treatment of welded compressor cases made of α alloy Ti-5Al-2.5Sn was limited to annealing and stress relieving. After the subassemblies had been formed, machined, and stress relieved, the cases were assembled using manual and mechanized inert-gas-shielded tungsten arc welding and resistance welding. The completed assemblies were stress relieved for 1 h at 620 °C (1150 °F) in an electric muffle furnace with air atmosphere. Neither fixturing nor protective coating was used. After being stress relieved, the cases were descaled by grit blasting and light pickling in a nitric-hydrofluoric acid solution.

Example 2: Heat Treatment of Welded Ti-6Al-4V Wing Ribs.

After being inert-gas-shielded tungsten arc welded with Ti-6Al-4V filler rod, a wing rib made of annealed Ti-6Al-4V sheet was solution treated for 1 h at 900 °C (1650 °F) in an air muffle furnace and water quenched. The part was protected by a glass coating during heating. (The coating, which consisted of hydrous borax, boric acid, and aluminum hydrate in a volatile carrier, was sprayed on the sheet at a dry weight of 269 to 323 g/m^2, or 0.88 to 1.06 oz/ft^2.) After being quenched, the part was inserted in an aging fixture and forced into the desired shape. It was aged in the fixture for 4 h at 540 °C (1000 °F) in an air muffle furnace. Sufficient relaxation and relief of stresses occurred during aging to bring the part into conformity with dimensional requirements. After aging, the welds had an ultimate tensile strength of 1090 MPa (158 ksi), a yield strength of 985 MPa (143 ksi), and 6% elongation in 13 mm ($\frac{1}{2}$ in.).

It should be noted that in this example, the development of maximum properties in α-β alloy weldments required solution treating, followed by rapid quenching and then aging. However, if reduced strength were acceptable or higher ductility were required, workpieces could have been simply annealed after welding.

Example 3: Ti-6Al-4V Pressure Vessel.

A spherical pressure vessel 610 mm (24 in.) in diameter and 6.4 mm ($\frac{1}{4}$ in.) in wall thickness was fabricated from 19 mm ($\frac{3}{4}$ in.) thick hemispherical forgings of Ti-6Al-4V. The hemispheres were rough machined and tack welded to a special frame mounted on the lid of a cylindrical electric furnace. The rough-machined hemispheres were then solution treated for 1 h in argon at 900 °C (1650 °F), water quenched, and finish machined. Furnace loading and unloading were accomplished by the use of an overhead crane, and the parts were quenched within 6 s after being removed from the

furnace. The two hemispheres were joined by mechanical inert-gas-shielded tungsten arc welding using Ti-6Al-4V titanium filler metal and reinforced weld area. Following welding, the vessel was aged for 6 h in a circulating-air furnace at 540 °C (1000 °F). Neither fixturing nor protective coating was used. Cleaning after aging consisted of pickling in nitric-hydrofluoric acid solution.

Example 4: Ti-5Al-2.5Sn Turbojet Compressor Case.

Figure 5 shows a 760 mm (30 in.) diam jet engine compressor case that was fabricated from Ti-5Al-2.5Sn. The shell of the case was roll formed into two half-round segments after the ports had been punched. After rolling, the ports were drawn in resistance-heated dies at 595 °C (1100 °F). After being loaded in stainless steel fixtures, the half-round segments were stress relieved in an air muffle furnace for 1 h at 620 °C (1150 °F). The ports were then sized to final dimensions while the curvature of the segments was maintained with a fixture. After the ports had been drawn and the segments stress relieved, all components were cleaned by grit blasting and pickling. The half-round segments were then welded by the inert-gas-shielded tungsten arc method, and the resulting weldments were stress relieved for 1 h at 620 °C (1150 °F) without fixturing.

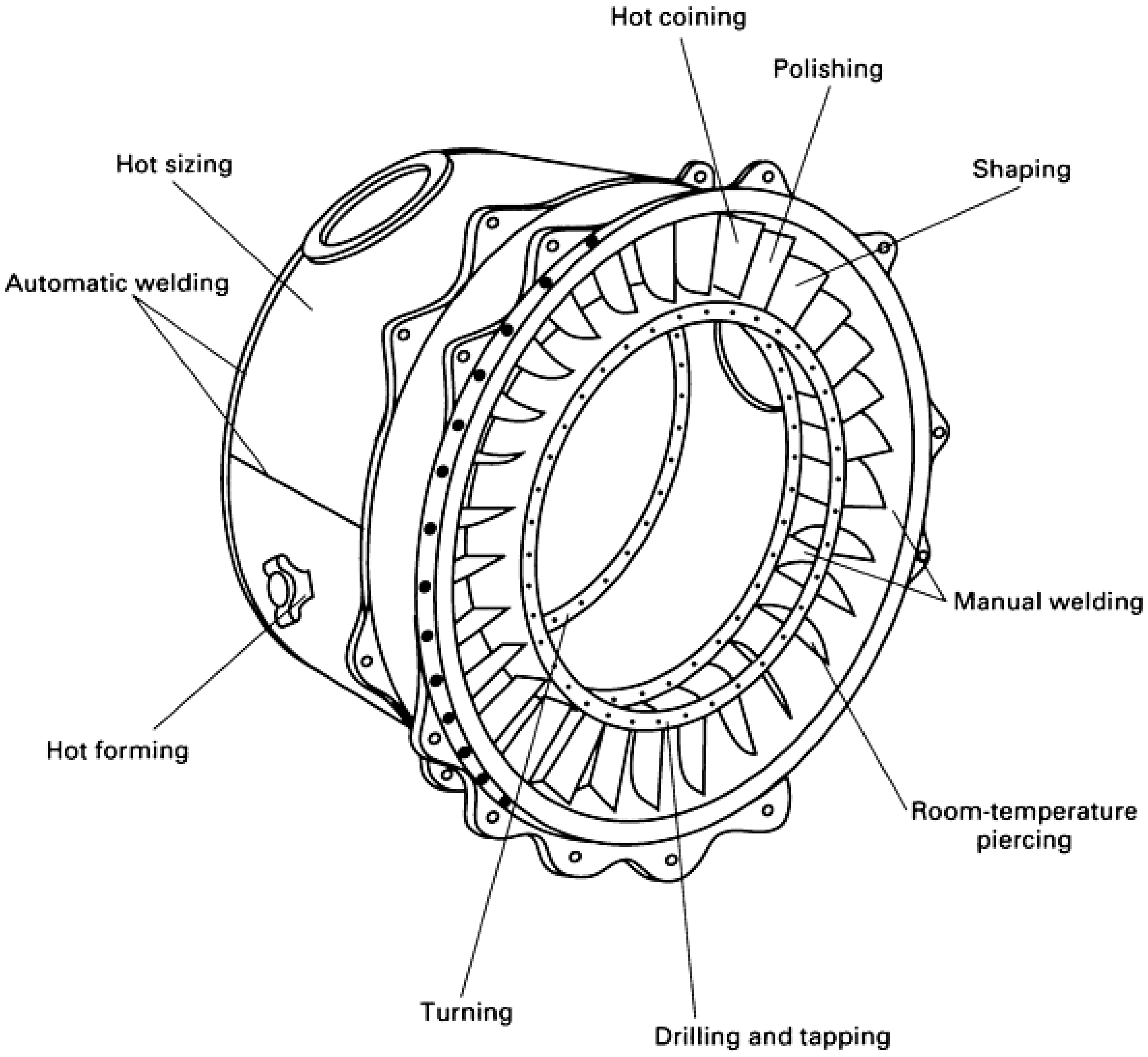

Fig. 5 Turbojet compressor case, showing fabrication processes employed in its manufacture

The shrouds were brake formed to a radius of 2.5 *t* at room temperature. Between brake-forming operations, the shrouds were resistance heated in air at 595 °C (1100 °F) for 5 min. Following brake forming, the shrouds were wrap formed to their final diameters at 120 °C (250 °F) in heated dies to reduce springback. They were then stress relieved 1 h at 620 °C (1150 °F) in air, and air cooled. No fixturing was necessary for maintaining tolerances.

The vanes were fabricated from machined bar stock and sheet. The annealed material was welded to form hollow vanes and then hot coined at 650 °C (1200 °F) in dies to flatten the parts and relieve welding stresses. Following coining, the vanes were cleaned and machined to an airfoil contour.

The final assembly was made by joining the various stress-relieved components by fusion welding. After assembly, the entire compressor case was stress relieved (without fixturing) in an air furnace for 1 h at 620 °C (1150 °F) and air cooled. Then the assembly was cleaned by grit blasting and pickling.

Example 5: Ti-6Al-4V Wing Section.

Skins of Ti-6Al-4V were stretched formed at room temperature in the fully annealed condition and solution treated in air for 30 min at 900 °C (1650 °F). After being water quenched, the distorted parts were placed in a steel aging frame and clamped to make them conform to the desired configuration. The skins and fixtures were aged 4 h at 540 °C (1000 °F) in a muffle furnace. Relaxation during aging was sufficient to bring the skins within drawing tolerances.

Example 6: Extruded Ti-6Al-4V T-Section Wing Section.

Ti-6Al-4V wing sections (1.22 m, or 48 in., long) for spars were hung vertically on a rack for solution treatment in an air muffle furnace at 900 °C (1650 °F). The rack and the parts were then rapidly quenched in water. Straightening the distorted (primarily, bowed) extrusions was accomplished by the use of fixtures during aging. The parts were subjected to a 50% overbend by insert spacers and aged 4 h at 540 °C (1000 °F) before being machined. This aging cycle was repeated after each of the three required machining operations. Heat treating was performed without protective atmosphere. After the solution treatment and the first aging treatment, the parts were pickled in nitric-hydrofluoric acid solution. Pickling removed the contaminated surface layer and increased tool life in machining.

Example 7: Ti-6Al-4V Rocket Motor Cases.

In the fabrication of rocket motor cases made of Ti-6Al-4V, the individual components were machined to a maximum wall thickness of 12.7 mm (0.500 in.), or to 7.62 mm (0.300 in.) wherever possible, allowing at least 1.3 mm (0.050 in.) of stock for cleanup after solution treating. Only cylindrical components were placed in fixtures for the solution-treating operation. Solution treating was performed by holding the parts for 2 h at a temperature 19 to 33 °C (35 to 60 °F) below the β transus (aim: 28 °C, or 50 °F, below β transus) in a bottom-loading gantry furnace and then quenching them rapidly in a violently agitated 3% solution of sodium hydroxide.

Tensile test coupons, representative of all parts in the load, were heated and quenched with the work. Before the parts themselves were aged, the test coupons were aged for 8 h at each of four temperatures--480, 510, 540, and 565 °C (900, 950, 1000, and 1050 °F)--to determine the optimum aging temperature in terms of desired mechanical properties. Then the parts were fixtured (a predetermined load was applied to promote creep forming), aged 8 h at optimum temperature, and air cooled. The use of a protective atmosphere was not required.

After being aged, the components were machined to final dimensions before welding in order to remove surface material that had been oxidized and contaminated during solution treating. Components were then welded into the final assemblies without preheating or postheating. The completed assemblies were stress relieved for 2 h at 480 °C (900 °F) and air cooled.

Heat Treating of Tin-Rich Alloys

Revised by William B. Hampshire, Tin Information Center

Introduction

IN HEAT TREATING of tin-rich alloys, it is difficult to secure an effective and permanent degree of hardening. Tin melts at 232 °C (505 K), and therefore room temperature (about 295 K) is well over one-half the absolute melting point. It follows that high-temperature behavior such as recrystallization and recovery can occur in fairly short times, even at room temperature. Tin is also an unusual metal because it can work soften under certain conditions, and so heat treating can be used in these cases to restore some of the original hardness and strength.

Heat treating of tin-rich alloys has been practiced for bearing alloys, pewterware, and organ pipe alloys. Some of the principles underlying these applications will be reviewed first.

Binary Alloys

Tin-antimony, tin-bismuth, tin-lead, and tin-silver alloys can all be temper hardened by solution treatment and aging. However, only the tin-antimony alloys can be permanently strengthened by heat treatment; all other tin-rich binary alloys will gradually soften at room temperature. The greatest improvement obtainable in binary tin-antimony alloys occurs in the alloy that contains 9% Sb; a hardness of 21 HB and a tensile strength of 51 MPa (7.4 ksi) can be increased to 26 HB and 65 MPa (9.4 ksi). This alloy is tempered for 48 h at 100 °C (212 °F) after being quenched from 225 °C (435 °F). During this tempering treatment, ductility decreases from 20 to 10% elongation (in 50 mm, or 2 in.).

Ternary Alloys

Permanent effects produced by heat treatment also carry over into ternary alloys of tin, antimony, and cadmium. This was discovered during an early investigation of the strength and hardness of ternary alloys containing up to 43% Cd and 14% Sb using chill-cast specimens. It was found that the strengthening effect of cadmium in the terminal solution tin phase (alpha) is much greater than that of antimony. In this study, the maximum stable values obtained in alloys containing 7 to 9% Sb and 5 to 7% Cd were as follows: tensile strength, 108 MPa (15.7 ksi); elongation, 15% (in 50 ram, or 2 in.); and hardness, 35 HB. The presence of the sigma phase (principally SbSn) as primary cuboids had no effect on strength or hardness, but the presence of primary epsilon (CdSb) destroyed the useful mechanical properties. Therefore, alloys containing cadmium generally use compositions that restrict the formation of the primary (CdSb) epsilon phase. The maximum combination of strength, ductility, and hardness is obtained in alloys that have finely dispersed precipitates of the sigma and epsilon phases in an alpha matrix, or finely dispersed epsilon in a matrix of alpha with a eutectoid of alpha plus gamma (cadmium-rich solid solution). These structures are typically achieved by quenching or rapid cooling from elevated temperatures to avoid precipitation of primary sigma and epsilon.

Additional heat-treatment studies have been directed to a group of cold-workable tin-rich alloys containing 3 to 8% Cd and 1 to 9% Sb. Two forms of hardening were observed on quenching of these alloys from 185 to 200 °C (365 to 390 °F). One form results from the change in solubility of antimony in tin or in the beta phase. The other, which produces more intensive hardening, is analogous to hardening of binary cadmium-tin alloys by quenching and depends on suppression of eutectoid decomposition of the beta phase. Permanent improvement results in the first instance. Therefore, a maximum tensile strength of 101 MPa (14.6 ksi) was achieved in a Sn-3Cd-7Sb alloy that was quenched from 190 °C (375 °F) and then aged for either 24 h at 100 °C (212 °F) or 18 months at room temperature.

Further studies have been carded out on tin-base alloys containing 7 to 10% Sb and 0 to 3% Cd in an effort to locate a bearing alloy that would be suitable at mildly elevated temperatures. In this composition range, it was found that alloys containing 0.5 to 2% Cd (but not 3%) can be strengthened considerably by quenching and tempering.

Optimum properties (tensile strength: 92 MPa, or 13.4 ksi) were obtained in a Sn-9Sb-1.5Cd alloy quenched from 220 °C (430 °F) and then aged for 1000 h at 140 °C (285 °F). This alloy consists of finely divided sigma and epsilon phases in a matrix of alpha.

Pewter

Many pewter articles are manufactured from sheet prepared by cold reduction of cast bars or slabs. Tin-rich pewter alloys containing antimony and copper will work harden during sheet-rolling operations that involve small percentage reductions (20%). If left standing at room temperature, the alloy will recrystallize and soften until it has reverted to the hardness of the original cast bar or slab. On the other hand, if large reductions (such as 90%) are made and the crystals are heavily worked, the alloy will work soften. Then, as crystals increase in size, hardness increases slightly, but never to the level of the original cast material.

The hardness values of spun pewterware, or of other articles that have been manufactured by mechanically working the metal, can be restored by heat treatment at temperatures from 110 to 150 °C (230 to 300 °F). The time required varies from 3 h at the lower temperature to a few minutes at the higher temperature. A tin alloy containing 6% Sb and 2% Cu hardens to 90% of the hardness of the as-cast material after annealing for 1 h at 200 °C (390 °F). Longer annealing times at lower temperatures have smaller but similar effects on the recovery from work softening.

Introduction

LEAD is normally considered to be unresponsive to heat treatment. Yet, some means of strengthening lead and lead alloys may be required for certain applications. Lead alloys for battery components, for example, can benefit from improved creep resistance in order to retain dimensional tolerances for the full service life. Battery grids also require improved hardness to withstand industrial handling.

The absolute melting point of lead is 327.4 °C (621.3 °F). Therefore, in applications in which lead is used, recovery and recrystallization processes and creep properties have great significance. Attempts to strengthen the metal by reducing the grain size or by cold working (strain hardening) have proved unsuccessful. Lead-tin alloys, for example, may recrystallize immediately and completely at room temperature. Lead-silver alloys respond in the same manner within two weeks.

Transformations that are induced in steel by heat treatment do not occur in lead alloys, and strengthening by ordering phenomena, such as in the formation of lattice superstructures, has no practical significance.

Despite these obstacles, however, attempts to strengthen lead have met with some success.

Solid-Solution Hardening

In solid-solution hardening of lead alloys, the rate of increase in hardness generally improves as the difference between the atomic radius of the solute and the atomic radius of lead increases.

Specifically, in one study of possible binary lead alloys it was found that the following elements, in the order listed, provided successively greater amounts of solid-solution hardening: thallium, bismuth, tin, cadmium, antimony, lithium, arsenic, calcium, zinc, copper, and barium. Unfortunately, these elements have successively decreasing solid-solution solubilities, and therefore the most potent solutes have the most limited solid-solution hardening effects. Within the midrange of this series, however, are elements that, when alloyed with lead, produce useful strengthening.

A useful level of strengthening normally requires solute additions in excess of the room-temperature solubility limit. In most lead alloys, homogenization and rapid cooling result in a breakdown of the supersaturated solution during storage. Although this breakdown produces coarse structures in certain alloys (lead-tin alloys, for example), it produces fine structures in others (such as lead-antimony alloys). In alloys of the lead-tin system, the initial hardening produced by alloying is quickly followed by softening as the coarse structure is formed.

At suitable solute concentrations in lead-antimony alloys, the structure may remain single phase with hardening by Guinier-Preston (GP) zones formed during aging. At higher concentrations, and in certain other systems, aging may produce precipitation hardening as discrete second-phase particles are formed.

Alloys that exhibit precipitation hardening typically are less susceptible to overaging and therefore are more stable with time than alloys hardened by GP zones. Lead-calcium and lead-strontium alloys have been observed to age harden through discontinuous precipitation of a second phase--Pb_3Ca in lead-calcium alloys and Pb_3Sr in lead-strontium alloys--as grain boundaries move through the structure.

Solution Treating and Aging

Useful strengthening of lead can be attained by adding sufficient quantities of antimony to produce hypoeutectic lead-antimony alloys. Small amounts of arsenic have particularly strong effects on the age-hardening response of such alloys, and these effects are enhanced by solution treating and rapid quenching prior to aging.

An investigation (Ref 1) was conducted on the effects of additions of 0.15% arsenic on the age-hardening behavior of five hypoeutectic lead-antimony alloys. Accurately weighed quantities of commercially pure lead, antimony, and arsenic were melted under a nitrogen atmosphere to produce the alloys listed below:

Alloy	Antimony, %	Arsenic, %
200	2.0	. . .
215	2.0	0.15
400	4.0	. . .
415	4.0	0.15
600	6.0	. . .
615	6.0	0.15
800	8.0	. . .
815	8.0	0.15
1000	10.0	. . .
1015	10.0	0.15

To minimize segregation during solidification, the melts, each weighing about 100 g (3.5 oz), were chilled rapidly by casting into a shallow horizontal steel boat. Pieces weighing about 15 g (0.5 oz) were cut from the castings and were used as hardness test specimens after being subjected to one of two heat treatments. One group of specimens, designated group A, was air cooled from the liquid state and quenched in ice water as soon as solidification was complete. Another group, designated group B, was solution treated for 4 h at 250 °C (480 °F) and then quenched in ice water.

In view of the rapid age hardening of the arsenical alloys, commencing the hardness tests as soon after quenching as possible was desirable, and one minute was chosen as a reasonable period. For group B specimens, this was easily achieved by solution treating the specimens, which had previously been ground with 600-grade paper, in a stream of nitrogen in a vertical tube furnace. The specimens were then dropped into ice water and transferred after 20 s to water at room temperature. Hardness of these specimens was measured with a Vickers hardness tester using a 2.5 kg load.

Because the specimens in group A could not be prepared for hardness testing before they were quenched, a different procedure was necessary to permit testing to commence after 1 min. These specimens were remelted in small flat-based cylindrical cups punched from thin aluminum foil. After quenching, the foil was peeled from the specimen and the hardness measurement was made on the flat surface (after the top surface had been quickly smoothed on a file to ensure proper seating in the test machine).

Cooling curves were obtained for the specimens in group A by means of Chromel-Alumel thermocouples, which were thinly sheathed with mild steel. After remelting, the thermocouple was removed before the beginning of solidification. Quenching then was timed to follow complete solidification on the basis of the previous cooling curves. The group A specimens were cooled at a rate of 1 °C/s (1.8 °F/s) to solidification at 232 °C (450 °F). These specimens showed evidence of surface segregation.

Hardness tests were continued for up to two years, with the specimens being stored at ambient temperature, which for the majority of the time was between 20 and 22 °C (68 and 72 °F). To investigate variations in hardness, tests were made on some of the specimens using a Reichert microhardness tester (5.3 g load, applied for 10 s).

Test Results. Results of hardness testing showed that lead-antimony alloys of commercial purity demonstrate significant age hardening, particularly after solution treating, as shown in Fig. 1 and 2. In the quench-cast alloys of group A, the hardness at any time increased with antimony content. For the solution-treated specimens of group B, aging was more effective for alloys with lower antimony contents.

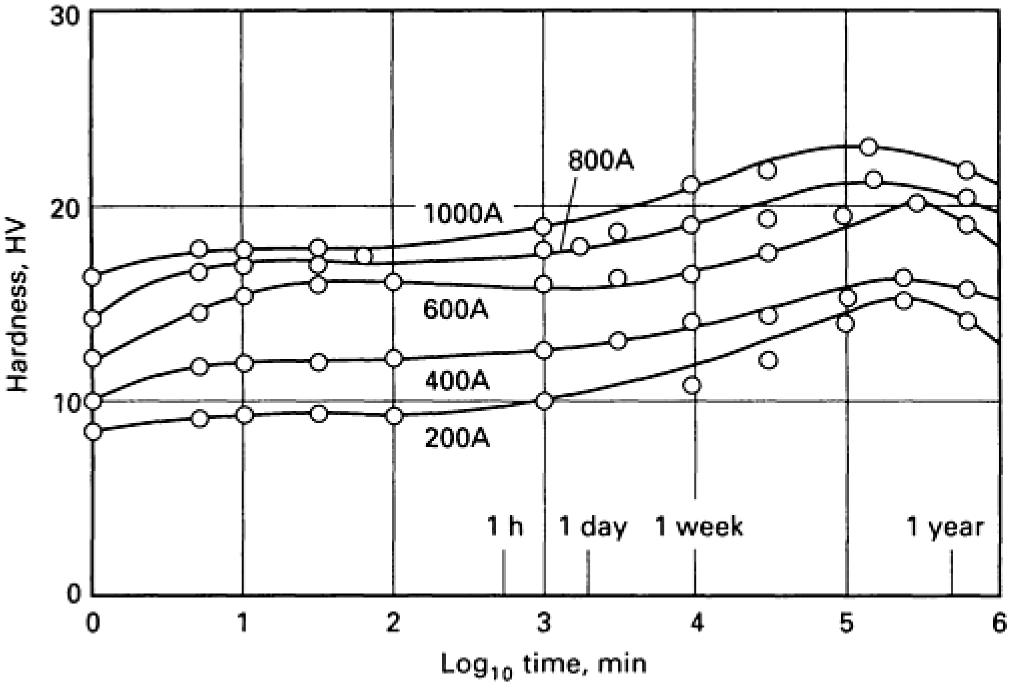

Fig. 1 Age hardening of lead-antimony alloys, solidified and water quenched

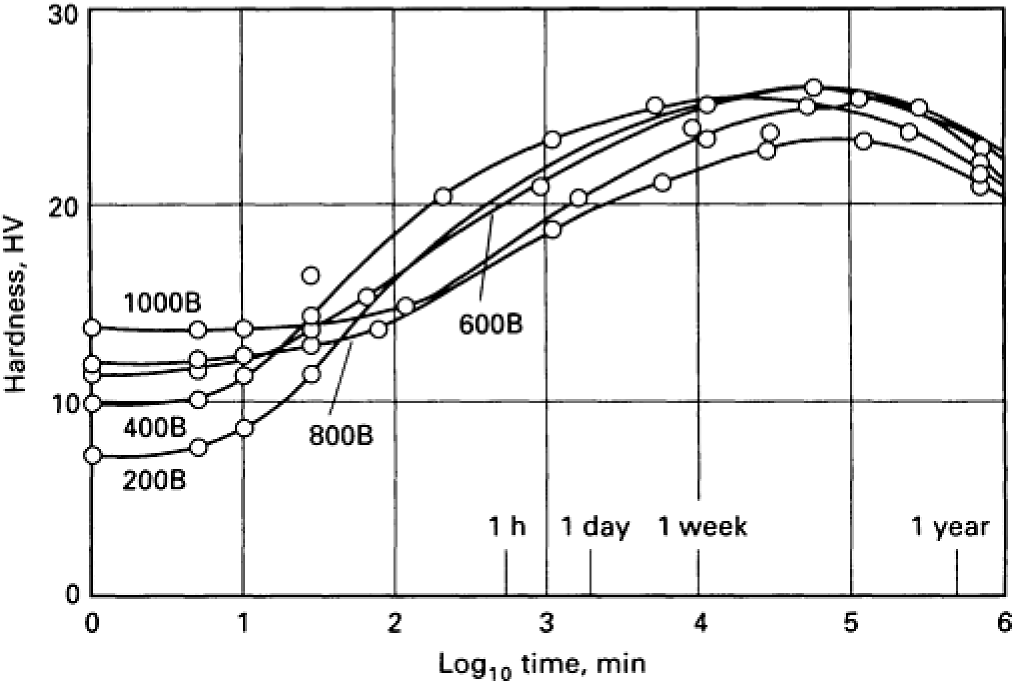

Fig. 2 Age hardening of lead-antimony alloys, solution treated 4 h at 250 °C (480 °F) and water quenched

Figures 3 and 4 show that both the rate and the extent of hardening are increased by addition of 0.15% As. As shown in Fig. 4, increases in hardness of the solution-treated hypoeutectic alloys are pronounced in the first 10 min.

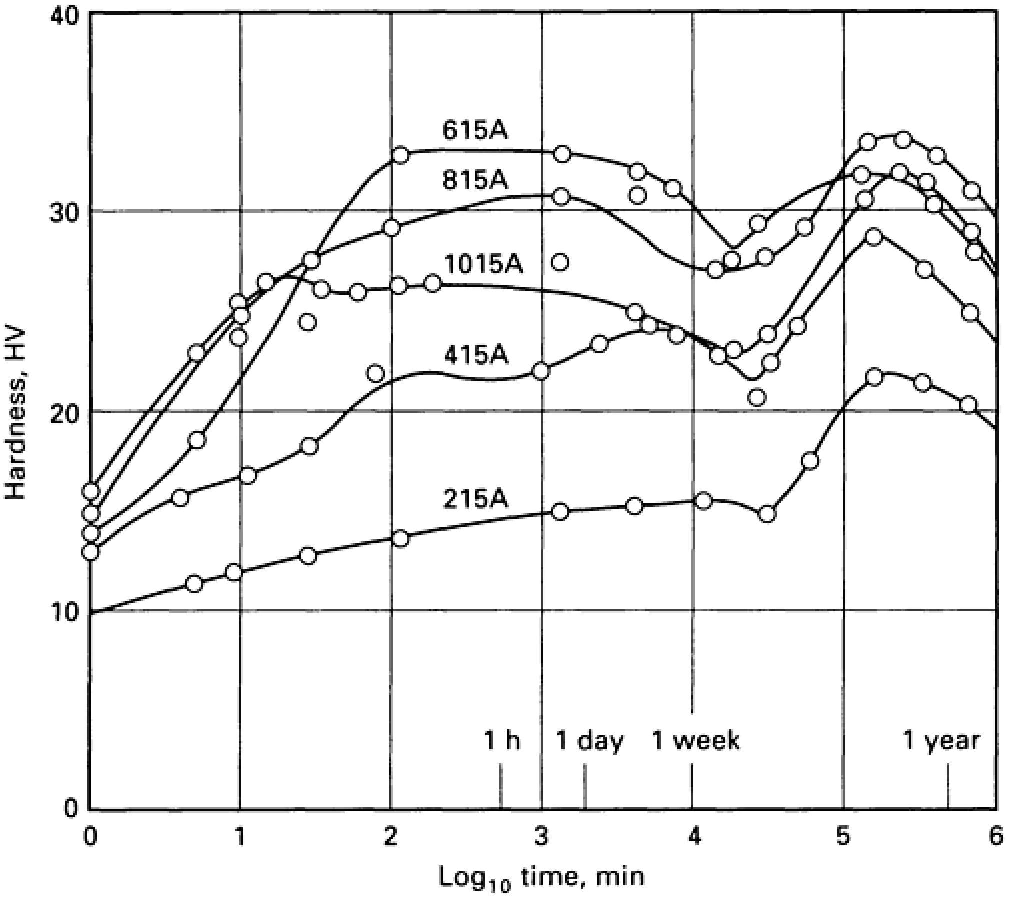

Fig. 3 Age hardening of lead-antimony-arsenic alloys, solidified and water quenched

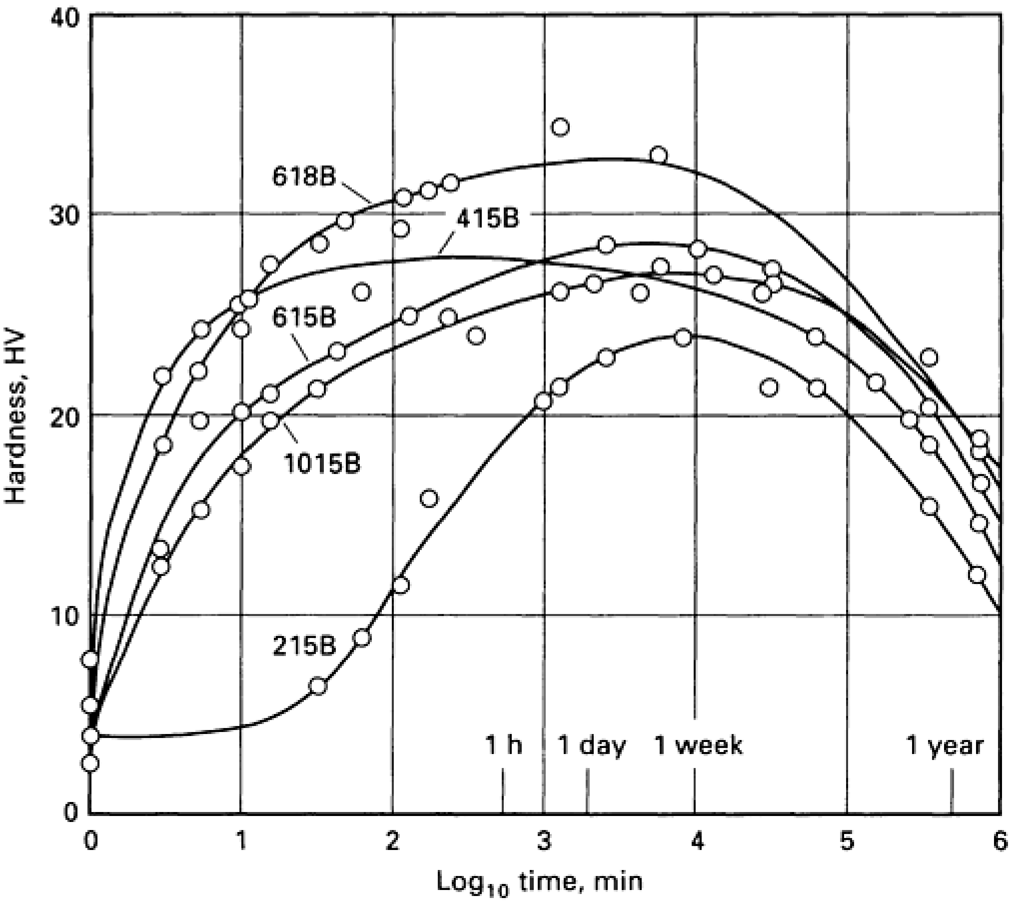

Fig. 4 Age hardening of lead-antimony-arsenic alloys, solution treated 4 h at 250 °C (480 °F) and water quenched

Hardness Stability. For any given alloy, both heat treatments result in somewhat comparable hardnesses after 1 min and after 2 years, as indicated in Fig. 1, 2, 3, and 4. For most of the two-year period, the solution-treated specimens were harder than the quench-cast specimens. Other investigations have also shown that alloys cooled slowly after casting are always softer than quenched alloys. As shown in Fig. 3, the alloys with 2 and 4% Sb harden comparatively slowly, and the alloy containing 6% Sb appears to undergo optimum hardening.

Application. Because of the detrimental effect of antimony on charge retention, the effort to reduce antimony contents of the positive plates in lead-acid storage batteries has led to the trend of replacing eutectic alloys with a Pb-6Sb-0.15As alloy. Battery grids made of this arsenical alloy will age harden slowly after casting and air cooling. However, storing grids for several days constitutes unproductive use of floor space and results in undesirable interruptions in manufacturing sequences.

Although large-scale solution treatment of battery grids might be difficult to justify economically or to achieve without some distortion, quenching of grids cast from arsenical lead-antimony alloys offers an attractive alternative method of effecting improvements in strength. The suitability of quench-cast grids can be assessed by comparing the values given in Fig. 3 with the hardness level that battery grids require in order to withstand industrial handling (about 18 HV, the hardness of the eutectic alloy). The alloy containing 2% Sb clearly does not respond sufficiently to be considered as a possible alternative. The 4% Sb alloy, however, attains a hardness of 18 HV after 30 min, and the alloys that contain 6, 8, and 10% Sb could be handled almost immediately. Furthermore, the values given in Fig. 3 for hardness after two years are superior in all instances to those for air-cooled alloys of similar composition. Hardness curves decline steadily after two years, and full evaluation of these alloys for use in the battery industry would require battery performance tests.

Reference cited in this section

1. J.D. Williams, The Effect of Arsenic on the Age-Hardening of Lead-Antimony Alloys, *Metallurgia*, Vol 74 (No. 443), Sept 1966, p 105-108

Dispersion Hardening

Another mechanism for strengthening of lead alloys involves elements that have low solubilities in solid lead, such as copper and nickel. Alloys that contain these elements can be processed so that no homogenization results; most of the strengthening that occurs is developed through dispersion hardening, with some solid-solution hardening taking place as a secondary effect. The resulting structure is more stable than those developed by other hardening processes. Dispersion strengthening also has been achieved through powder metallurgy methods in which lead oxide, alumina, or similar materials are dispersed in pure lead.

Fabrication

Although alloy selection is important, care must be taken in fabrication as well. Castings should be cooled rapidly to a temperature below that at which the structure breaks down, or a coarse structure will be obtained. Age-hardening alloys should be extruded at a temperature above the breakdown temperature, and extrusions should not be allowed to cool slowly. Rolled alloys often are processed at insufficient temperatures; when this occurs, homogenization after rolling is required if age hardening is to produce a beneficial response.

Cold Storage

Cold storage has been shown to improve the response of lead-antimony alloys to age hardening. Cooling a homogenized Pb-2Sb alloy to -10 °C (15 °F) and holding for one or two days prior to room-temperature aging results in increases in both the rate of age hardening and the maximum hardness attained. This behavior has been explained as the result of a reduction in the mobility of quenched-in free vacancies and a consequent reduction in their annihilation. The process allows the vacancies to form complexes with solute atoms, and these complexes improve the efficiency of nucleation during aging.

Service Temperatures

Service temperatures for lead alloys must be kept low to prevent overaging. Some cable-sheathing alloys, for example, have retained most of their creep resistance for up to 20 years, but exposure to elevated temperatures could have reduced this performance substantially. Even the normally stable age-hardened lead-antimony and lead-calcium alloys can be altered detrimentally by high service temperatures or excessive working.

Heat Treating of Uranium and Uranium Alloys

Revised by Gerard M. Ludtka and E.L. Bird, Materials Engineering Department, Development Division, Martin Marietta Energy Systems, Inc.

Introduction

THE MAJOR APPLICATIONS of depleted uranium (DU) and its alloys are those for which density is an important, if not an overriding, consideration (at 19.05 g/cm^3, unalloyed depleted uranium is one of the densest of all elements). Among these applications are kinetic energy penetrators for military use, aircraft and missile counter-weights, radiation shielding, gyrorotors, high energy physics calorimeters, and ballast. Dilute alloys containing 0.75 wt% Ti or 2 wt% Mo are used in production of kinetic energy penetrators (the largest single application of DU) because superior mechanical properties can be developed in these alloys, and their corrosion resistance can be improved, by heat treatment.

Although most DU was originally produced in cast form and used without heat treatment, current material requirements usually call for heat treated, wrought DU for property consistency. Ingot breakdown and primary fabrication processes, such as forging, rolling, and extruding, can be readily carried out between 550 and 640 °C (1020 and 1180 °F) or between 800 and 900 °C (1470 and 1650 °F). The 650 to 780 °C (1200 to 1435 °F) range is avoided because cracking commonly occurs at these temperatures. Secondary fabrication processes such as rolling, swaging, and straightening are commonly done between room temperature and 500 °C (930 °F). Following heat treatment, machining to final dimensions can be

carried out by most conventional cutting and grinding techniques. This article focuses on the heat treatment of uranium alloys. Additional information on processing, including heat treatment, is also provided in Volume 2 of *ASM Handbook*, formerly 10th Edition *Metals Handbook* and in the Selected References at the end of this article.

Metallurgical Characteristics of Depleted Uranium

In processing of uranium, several considerations must be addressed: hydrogen embrittlement and hydride formation; ready oxidation in air, attack by hot water; and dissolution by acids. In addition, fine particles of uranium metal are pyrophoric and can ignite spontaneously at room temperature.

The metal uranium is obtained from uranium hexafluoride (UF_6) tailings from the uranium enrichment process that provides U-235 uranium for the nuclear industry. In typical production of depleted uranium, UF_6 tailings are reduced to uranium tetrafluoride (UF_4), called "green salt," which is further reduced to derby uranium metal by a thermite-type bomb reduction with magnesium metal. Calcium metal has also been used to reduce UF_4 to derby metal. Typical derby chemical analysis ranges (in ppm) are 5 to 50 Cu, 8 to 40 Al, 30 to 150 Fe, 10 to 50 Ni, 10 to 100 Si, 1 to 10 Mg, 10 to 50 C, 15 to 40 O, 8 to 40 N, and 4 to 18 H. Minor high-vapor-pressure contaminants can be removed by volatilization during subsequent vacuum melting operations, while the other listed elemental contaminants remain. These impurities should be monitored and controlled to ensure expected metallurgical response to processing. Typical chemical and gas analyses for vacuum-induction-melted depleted uranium are shown in Table 1. In general, hardness varies directly, and ductility varies inversely, with impurity content.

Table 1 Typical chemical and gas analyses for vacuum-induction-melted DU

Element	Average analysis, ppm (by wt)
Carbon	180
N_2	15
O_2	40
Bulk H_2	2
Aluminum	25
Copper	15
Iron	85
Manganese	15
Nickel	20
Lead	4
Silicon	120

Phase Changes. Chemically and metallurgically, DU is identical with natural uranium. Transformation from the alpha phase (orthorhombic) to the beta phase (tetragonal) occurs at 662 °C (1224 °F). The beta phase is stable up to 773 °C (1423 °F), where it transforms to the high-temperature gamma phase (body-centered cubic). The latter is stable to the melting point, 1132 °C (2070 °F). The gamma phase in unalloyed DU cannot be retained to room temperature by commercial quench rates.

Phase changes in DU and its alloys are accompanied by significant changes in volume. Volumetric shrinkage from the high-temperature gamma phase to the low-temperature phase is 1.8%. Changes in linear dimensions are influenced by preferred orientation. For a random orientation, linear shrinkage is 0.6%. Because shrinkage cannot be predicted accurately, these dimensional changes make it impossible to machine (DU) to final dimensions before heat treatment. In rough machining for heat treatment, an envelope at least 0.4 to 0.5 mm (0.015 to 0.020 in.) thick should be allowed for final machining.

Grain Size and Orientation Control

The grains of cast DU or of DU worked in the gamma region are quite large, typically 2 to 3 mm (0.08 to 0.12 in.) in diameter. Large grain sizes are undesirable for material that is to be worked because they result in rough machined surfaces and variations in mechanical properties. On a macroscale, grain size can be refined considerably by multiple beta quenching. In workpieces more than 25 mm (1 in.) thick, however, refinement is limited to an outer layer of grains because the cooling rates at greater depths are too low. Generally, the rim of fine-grain material is sufficiently thick to produce a smooth surface after subsequent working.

Beta treatment is also used as a heat treatment for DU worked in the high alpha temperature range. Beta treatment consists of heating the DU into the beta range, holding for a suitable time and cooling at a rapid rate. A common temperature range is 720 to 730 °C (1330 to 1350 °F). The purpose of this heat treatment is to eliminate the preferred orientation that develops during working.

The final alpha grain size is insensitive to temperature within the beta range and to variations in holding time. Times from 1 min to 1 h at temperatures greater than 700 °C (1290 °F) have no effect on final alpha grain size. Cooling rate, however, has a significant effect. Water-quenched material has a significantly finer grain size, and the grains have scalloped edges which are indicative of the massive transformation which occurs during rapid beta quenching. Air-cooled grains have more uniform boundaries. Extremely low cooling rates, such as those obtained in a furnace-cool cycle, produce large alpha grains. Also, detrimental grain growth to as-cast grain sizes can occur in wrought DU through an extended alpha anneal.

High cooling rates such as those achieved by water quenching produce high residual stresses in beta-treated material. In thin sections, these residual stresses can produce appreciable plastic deformation in the alpha phase. This alpha phase can be recrystallized, and sometimes grain refined, by an anneal in the alpha range. Alpha annealing after beta treatment will not produce recrystallization at the center of a thick section, because the center does not cool rapidly enough for sufficient straining of the lattice to occur.

When DU is water quenched from the beta phase, high stresses develop due to the combination of (a) the radial temperature gradient and (b) volume contraction during beta-to-alpha transformation. These stresses are compressive at the surface and tensile at the center. The tensile stresses are high enough to produce failure near the centerline. Large numbers of repetitive quenches from the beta phase can produce sponginess, cracks, or holes in the center section of the workpiece.

Grain growth is extremely sensitive to orientation as well as to differences in metal purity, to prior deformation, and to heat treatments that affect the dispersions of contaminant second phase. Those contaminants that are in solution tend to delay recrystallization and often result in mixed, or incomplete, recrystallized structures. Those elements having uranium compounds that show limited solubility, thereby existing as inclusions, do not delay recrystallization appreciably.

The amount of work that exists in uranium metal prior to heat treatment has an important effect on final grain size. A 1 to 2% strain in uranium constitutes critical strain. Recrystallization of material with this amount of strain results in very large grains. Consequently, a plate prepared for forming operations is produced with 10 to 15% warm work to ensure that no areas of critical strain exist in the final wrought product. As the amount of work in the metal to be annealed is increased, the temperature needed for uniform recrystallization is lowered. For most formed parts made from relatively pure material, recrystallization will not occur below 400 °C (750 °F) with annealing times of up to 10 h.

Cold Working

Alpha uranium is slightly softer than steel and is considered to be malleable and ductile. Alpha uranium is readily worked at room temperature; however, directionality and texture persist because of a pronounced anisotropy. Aside from the complication of directionality, the tensile strength of uranium can be greatly enhanced by cold working, as shown in Table 2; hardness also can be increased significantly, as shown in Table 3.

Table 2 Typical mechanical properties of DU as functions of amount of cold work

Cold work, %	Ultimate tensile strength		Tensile yield strength[(a)]		Compressive yield strength		Elongation[(b)], %	Hardness[(c)], HV
	MPa	ksi	MPa	ksi	MPa	ksi		
0[(d)]	1060	154	375	54	405	58	15	294
15	1140	165	525	76	500	72	17	352
25	1190	173	600	87	575	83	14	354
40	1280	186	660	96	605	87	13	359

(a) At 0.2% offset.

(b) In 50 mm (2 in.).

(c) 1-kg load.

(d) This material is highly directional and was not beta heat treated.

Table 3 Hardness data for cold-worked uranium rod

Cold work, %	Hardness									
	HR15N		HR30N		HR30T		HR45T		HV[(a)]	
	Average	Range[(b)]	Average	Range	Average	Range	Average	Range	Average	Range[(c)]
0	72	71-74	43	42-44	79	77-82	68	67-69	294	281-308
15	73	71-74	46	42-49	81	79-82	72	69-73	352	335-366

25	75	74-76	47	43-49	81	79-83	73	71-74	354	348-361
40	76	75-77	50	47-52	83	81-85	73	69-75	359	339-376
55	78	76-79	56	55-58	85	83-86	79	78-80	397	376-423

(a) 1-kg load.

(b) Results of five indentations.

(c) Results of eight indentations across the diametral cross-section of the bar

Annealing

Annealing of cold-worked DU is similar to that in other metals. The first stage is recovery, in which there is a slight decrease in hardness, a small decrease in electrical resistivity and a pronounced sharpening of x-ray line shape. Recovery is followed by recrystallization. The variation of recrystallization temperature as a function of cold work is shown in Fig. 1 for an annealing time of $1\frac{1}{2}$ h. Recrystallization begins at 400 °C (750 °F) and is complete at 450 °C (840 °F) in material cold worked 90 to 94%. Light cold working (about 4%) causes recrystallization to begin at 525 °C (975 °F), but recrystallization is not complete after $1\frac{1}{2}$ h at 600 °C (1110 °F).

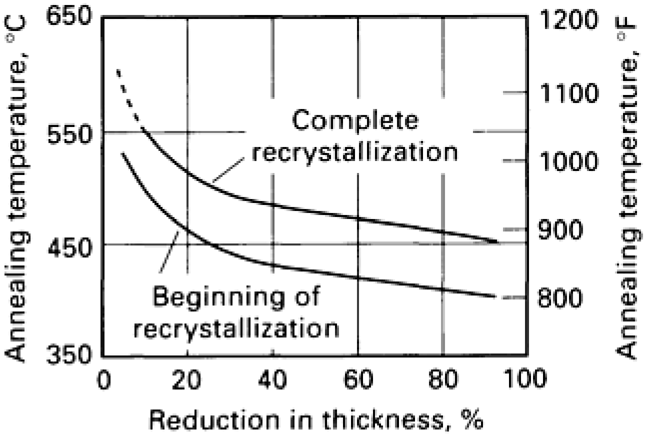

Fig. 1 Recrystallization temperature as a function of cold work for rolled depleted uranium of moderate purity. Annealing time, $1\frac{1}{2}$ h. Source: Ref 1

The grain size of cold-worked and annealed DU depends upon a variety of factors: annealing time and temperature; amount and homogeneity of the cold work strain; cold working temperature; and volume, size, and dispersion of inclusions. Cold or warm working of DU often results in a banded or duplex structure; this persists as a duplex grain size after recrystallization. The average grain size for material rolled to 50% reduction at 300 °C (570 °F) is illustrated in Fig. 2. This shows the effect of annealing temperature (annealing time, 1 h) on materials of various purities. Grain size is about 0.01 to 0.015 mm (0.0004 to 0.0006 in.) for impure uranium and as large as 0.04 mm (0.0015 in.) for high-purity metal.

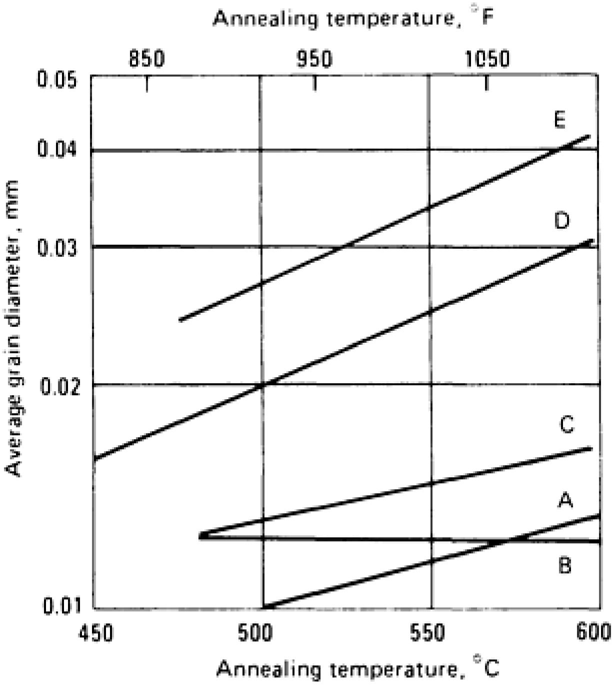

Fig. 2 Average grain size of depleted uranium as a function of annealing temperature. 1-h anneals after 50% reduction by rolling at 300 °C (570 °F). A and B are impure metal; C, D, and E are high-purity uranium in decreasing order of submicroscopic inclusion content. Source: Ref 2

Table 4 presents typical mechanical properties of uranium in various conditions. These data are not precise values and are intended for use only as guidelines for selection of heat treatments.

Table 4 Typical room-temperature mechanical properties of uranium in various conditions

Fabrication history	Yield strength[(a)]		Tensile strength		Elongation[(b)],%	Reducton in area, %
	MPa	ksi	MPa	ksi		
Cast	207	30	448	65	5	10
Gamma extruded	172	25	552	80	10	12
Beta rolled	207	30	586	85	12	. . .
Alpha extruded, 600 °C (1080 °F)	207	30	621	90	15	
Alpha rolled at:						
300 °C (570 °F)	759	110	1172	170	7	14
500 °C (930 °F)	414	60	897	130	20	. . .

600 °C (1080 °F)	276	40	759	110	20	. . .
Annealed, after rolling at:						
300 °C (570 °F)	345	50	759	110	5	. . .
500 °C (930 °F)	276	40	690	100	15	. . .
Beta treated after alpha rolling:						
Water quenched	241	35	586	85	10	12
Slow cooled	207	30	414	60	7	. . .

(a) At 0.2% offset.

(b) In 50 mm (2 in.)

The following heat treating procedure can be followed to produce fine-grain material. It is best to start with a relatively pure material that has very small amounts of inclusion-producing impurities. Following a hot breakdown of the rolling ingot at 630 °C (1165 °F), rolling operations are performed at 300 to 400 °C (570 to 750 °F). After 40 to 60% warm work, the material is given a short recrystallization anneal (about 30 min per inch of thickness) at 630 °C (1165 °F). The rolling stock is cooled from the annealing temperature to below 400 °C (750 °F) and given further warm work. This process is repeated as often as final stock thickness will allow.

If the rolled stock is to be used in subsequent forming operations, the final rolling procedure should leave 15 to 20% warm work in the plate. Forming operations should be carried out warm at temperatures not exceeding 375 °C (705 °F). A final anneal at 630 °C (1165 °F) for 30 min per inch of thickness (minimum, 6 to 8 min) will produce parts with a grain size of ASTM 6 to 10, depending on the amount of warm rolling possible. Intermediate anneals at temperatures below the suggested 630 °C (1165 °F) will help develop the finer grain size. Test specimens will be required to establish the times necessary at these lower temperatures to effect complete recrystallization.

Alpha recrystallization annealing will not remove the anisotropy of the crystal structure produced by the rolling and forming processes. The stock for most forming operations is produced by "square rolling," or by giving the rolled plate essentially equal reductions in the longitudinal and transverse directions. This process produces a plate with relatively uniform properties in the plane of the plate. Equal reductions taken at 45° to the standard longitudinal and transverse directions will produce even more uniform forming stock.

Cast Uranium. The grain size of cast uranium is difficult to define because the large cast grains all have well-organized substructures (see Fig. 3). The cast microstructure and mechanical properties can be improved by beta heat treating (see Fig. 4). In this process, the casting is heated to about 740 °C (1365 °F), water quenched, and then given an alpha anneal. Grain refining occurs because of the presence of small levels of uranium-iron and uranium-silicon compounds. These compounds are put into solution by the 740 °C (1365 °F) (or higher) beta heat treatment, kept in solution by the water quench, and then precipitated by the alpha anneal. If the alpha-anneal temperature is low, the precipitation of the compounds is fine and well dispersed.

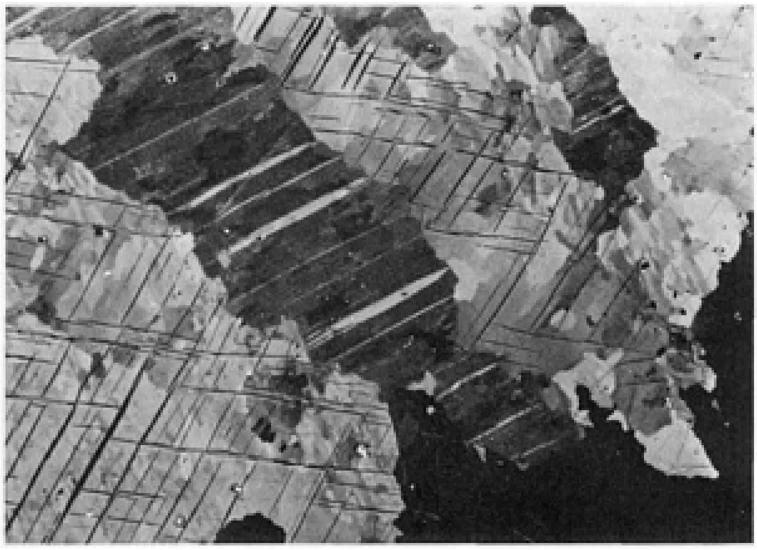

Fig. 3 Typical grain structure of cast depleted uranium

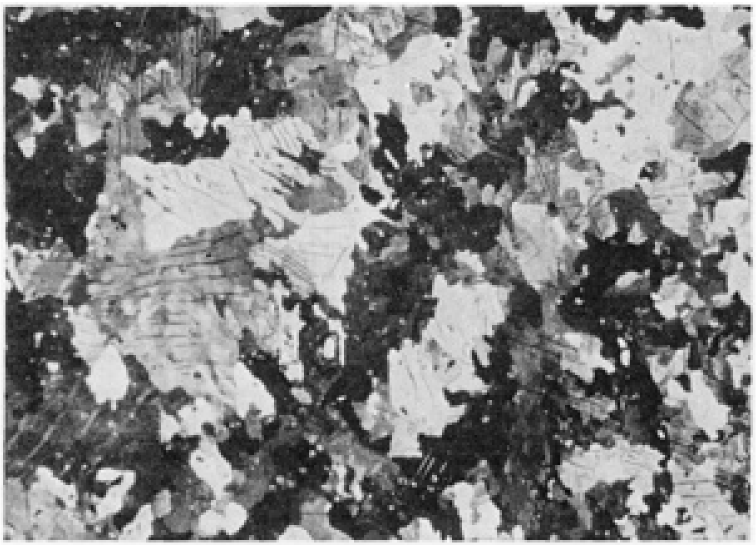

Fig. 4 Microstructure of cast depleted uranium refined by beta quenching

Figure 5(a) shows fine U_3Si precipitates in a U-400ppm Si-200ppm Fe alloy after a beta quench and 625 °C (1160 °F) anneal. Finer precipitation is evident in a U-200ppm Fe alloy annealed at 600 °C (1110 °F) as exhibited in Fig. 5(b). After this fine precipitate dispersion is achieved, a second beta quench can be more effective as a grain refining step. Two beta quenches and two alpha annealing cycles will produce the desired grain structure in stock as thick as 32 mm, or 1.25 in. (see Fig. 4).

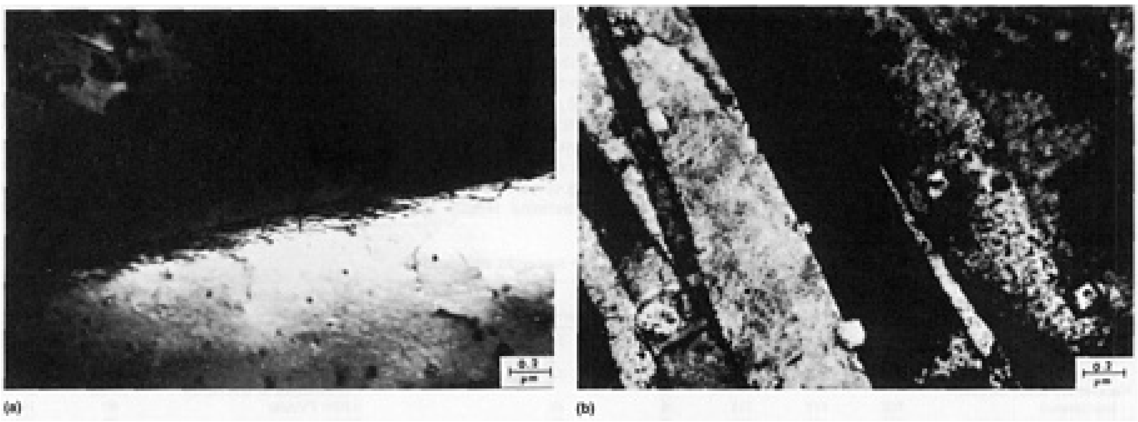

Fig. 5 Micrographs showing precipitates in dilute-impurity uranium alloys after beta solution treatment of 730 °C (1345 °F) for 30 min followed by water quenching and an aging treatment. (a) U_3Si precipitates in a U-400 ppm Si-200 ppm iron alloy after a beta quench followed by an aging treatment of 625 °C (1160 °F) with furnace cool. (b) Fine precipitation in a U-200 ppm iron alloy after a beta quench followed by an aging treatment of 600 °C (1110 °F) for 20 h with a furnace cool

The specific details of the recommended beta heat treatment--such as temperature, time, quenching procedure, and furnace conditions--are dictated by the final metallurgical condition desired. When beta heat treating is followed by water quenching, the uranium lattice undergoes heavy strain as a result of the beta-to-alpha transformation. This transformation can occur by diffusion, massive, or martensitic mechanisms depending on the severity of quenching. At slower cooling rates, the beta-to-alpha transformation occurs by diffusion. A massive transformation mechanism has been shown to dominate at intermediate quench rates of 20 to 100 °C (35 to 180 °F/s), whereas a martensitic reaction has been observed for the most rapid quench rates in the dilute impurity alloys. In general, to relieve the residual stresses induced by beta quenching and to precipitate a fine dispersion of secondary compounds, an annealing temperature of 575 °C (1065 °F) is used. Typical tensile properties that can be developed by various heat treatments in cast and wrought uranium are shown in Tables 5 and 6, respectively.

Table 5 Typical tensile properties versus heat-treating methods for cast uranium

Heat-treating methods	Tensile strength		Yield strength[a]		Elongation[b], %	Reduction in area, %	J-integral		Tearing modulus	Charpy impact energy	
	MPa	ksi	MPa	ksi			J/mm^2	in. · lb/in.^{2}		J	ft · lbf
As cast	420	61	205	30	6	. . .	. . .	. . .	. . .	. . .	. . .
Vacuum heat treated, 640 °C (1185 °F), 1 h	450	65	215	31	5	. . .	. . .	. . .	. . .	. . .	. . .
Vacuum heat treated, 650 °C (1200 °F), 2 h, then 630 °C(1195 °F),24 h	565	82	185	27	13	. . .	. . .	. . .	. . .	. . .	. . .
Salt annealed	450	65	215	31	8	. . .	. . .	. . .	. . .	. . .	. . .

Beta quenched, vacuum annealed	785	114	295	43	22	17	0.034 0.016	192 90	35 11	~14[d] ~7[c]	~10[c] ~5[d]

(a) At 0.2% offset.

(b) In 50 mm (2 in.).

(c) 21 °C.

(d) 54 °C

Table 6 Typical tensile properties versus heat-treating methods for wrought uranium

Method of heat treating	Tensile strength		Yield strength[a]		Elongation[b], %	Reduction in area, %
	MPa	ksi	MPa	ksi		
Vacuum heat treated	800	116	270	39	31	28
Salt annealed or short vacuum heat treated	655	95	272	39	12	12
Vacuum arc melt, vacuum heat treated	780	113	215	31	49	. . .
Vacuum heat-treated plate	835	121	273	40	40	. . .

(a) At 0.2% offset.

(b) In 50 mm (2 in.)

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Dilute Alloys of Depleted Uranium

Dilute alloys that are heat treated in larger quantities are DU-(0.70-0.85) wt% Ti and DU-2 wt% Mo. Both are used as cores in kinetic energy penetrators. The ability of these alloys to age harden is related to the fact that titanium and molybdenum have extended solid solubility in the high-temperature gamma phase and essentially complete insolubility in

the low-temperature alpha phase. On rapid quenching, the gamma transforms martensitically to supersaturated alpha prime. A fine dispersion of intermetallic compound develops during subsequent aging at temperatures above 300 °C (570 °F).

Figure 6 shows the microstructure of water-quenched 36 mm (1.4 in.) diam U-0.75Ti bar. The outside of the bar (Fig. 6a) has transformed completely to lenticular alpha prime. The fineness of this structure increases with increasing quench rate. The grain boundaries visible in the structure are those of the prior gamma grains. The U-0.75Ti alloy is shallow hardening, however. At the center of the bar, transformation to alpha phase plus U_2Ti starts at prior grain boundaries (Fig. 6b). Similar structures are found in 18 mm (0.7 in.) diam bar oil quenched from the gamma phase. Aging to peak hardness produces no detectable change in structure.

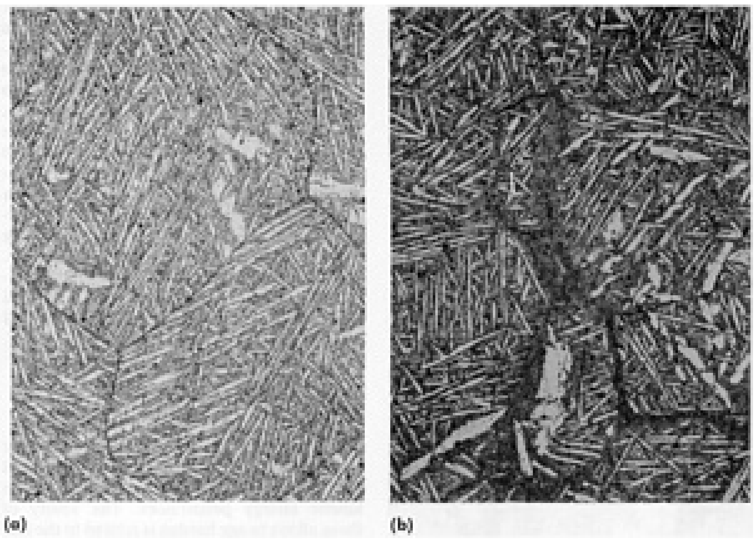

Fig. 6 Microstructure of solution treated and quenched U-0.75Ti. Bar 36 mm (1.4 in.) in diameter and quenched into water at 455 mm/min (18 in./min). Chrome-acetic electroetch. 100×. (a) Edge. (b) Center

Solution Treating and Aging. Heat treating for improved hardness and mechanical properties in dilute DU alloys consists of solution treating in the gamma-phase temperature range of 800 to 850 °C (1470 to 1560 °F), quenching to room temperature, and aging in the alpha temperature range. Solution heat treatment is usually done in vacuum or an argon atmosphere for oxidation control and hydrogen outgassing. Alternatively, interrupted quenching in a molten metal or salt bath held at the appropriate temperature can be used.

A completely gamma phase microstructure can be produced in a very short time, 2 to 5 min, depending on the thickness. Longer solution heat treatment times of 4 to 8 h are generally used for thicker components and for hydrogen outgassing. Excessive soak times lead to unfavorable, large gamma grain sizes which influence the final martensite lathe size obtained upon water quenching.

An important consideration in the selection of conditions for gamma solution treatment is the hydrogen level required in the final product. Although hydrogen is detrimental to ductility in the U-0.75Ti alloy, acceptable ductility with occasional low values can be achieved with H_2 levels below nominally 1 ppm. However, higher and more consistent properties (less scatter) are best obtained when H_2 levels are maintained at 0.1 ppm or less.

Erratic ductile behavior in U-0.8Ti can be offset by controlling the effects of hydrogen by reducing the internal hydrogen content from 0.36 ppm to 0.02 ppm H_2 and testing in dried air containing less than 10% relative humidity. A recent study (Fig. 7) showed a 50% improvement in ductility with no loss in strength. Scanning electron microscopic evaluation of the fractured tensile specimens revealed a correlation of premature failures originating at inclusion clusters, identified as titanium carbides and/or uranium oxides. These results indicate that as the hydrogen content increases, there is a greater likelihood of premature or erratic fracture at an inclusion cluster or other defect. As expected, large defects or inclusion clusters cause a significant loss in ductility regardless of the hydrogen level. Unalloyed uranium and uranium alloys are sensitive to hydrogen and for maximum material properties require extensive outgassing. The literature should be consulted before selecting conditions for these alloys.

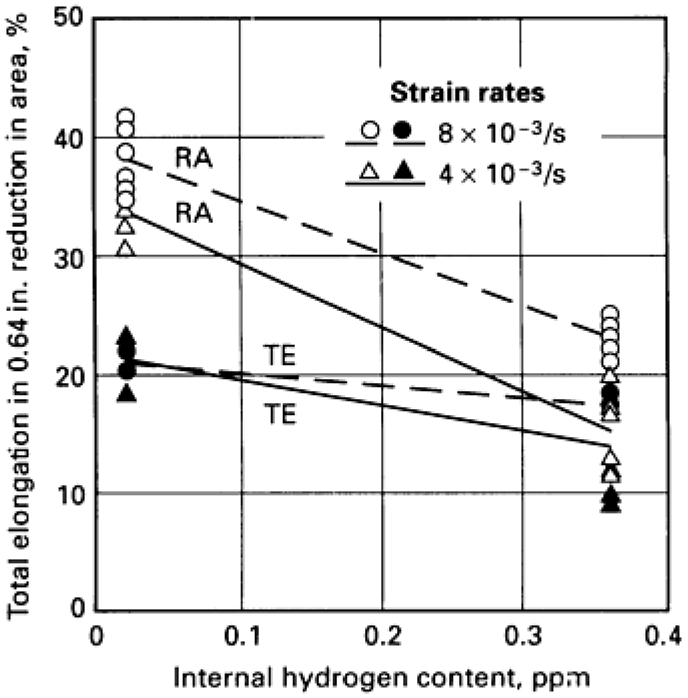

Fig. 7 Effect of hydrogen content and strain rate on the ductility of a conventional tensile test for the U-0.8Ti alloy. RA, reduction in rate; TE, total elongation in 16.3 mm gage length

Quenching. Table 7 gives the rates at which DU-0.75Ti cools when quenched in various media. The test slugs used for measuring these rates were 22 mm (0.875 in.) in diameter by 21 mm (0.845 in.) long. Cooling rates for other DU alloys should be similar. Because DU-Ti alloys are quench rate sensitive (shallow hardening), higher quench rates are needed to achieve uniform hardening response in large diameter bars or thicker plates.

Table 7 Cooling rates for DU-0.75Ti in various quench media

Media	Quench rate	
	°C/s	°F/s
Flowing argon	3.8	6.8
Conventional or soluble oil	38-40	68-72
0.05% PVA[a]	80	145
Water	98	175

(a) Polyvinyl alcohol

Effect of Quench Rate on Microstructures. Figure 8 shows the effect of quench rate on the microstructures developed during quenching. A truly 100% martensitic microstructure can be obtained only in very thin, rapidly quenched samples (<3 mm) as shown in Fig. 8(a). Even after excessive etching (as evidenced by pitting at the grain boundaries), the α' martensite is not resolvable in bright field optical micrographs but is easily detected under polarized light conditions. As the quench rate is reduced (or the quenching blank becomes more massive), some equilibrium α+ δ is formed preferentially at prior γ grain boundaries and along martensite lathe interfaces.

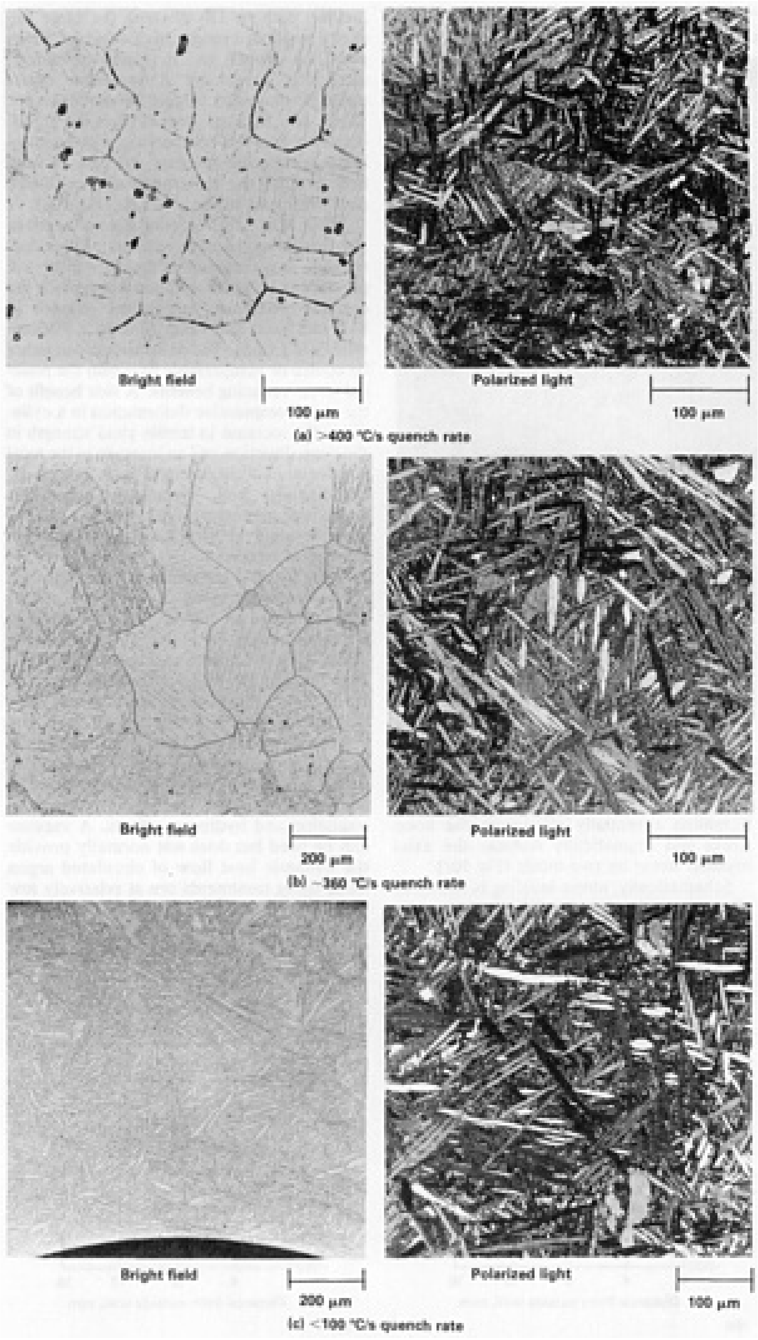

Fig. 8 Effect of quench rate on the microstructure of a U-0.8Ti alloy as seen in bright field and polarized light optical micrographs. (a) 100% α' martensite microstructure for a quench rate >400 °C/s (> 720 °F/s). (b) Microstructure developed at a cooling rate of ~360 °C/s (~650 °F/s) with <100% α'. (c) Approximately 90% α ' martensite developed at a <100 °C/s (<180 °F/s) quench rate

Figure 8(c) represents typical acceptable microstructures in a satisfactorily quenched U-0.8Ti alloy sample. The martensite lathes are visible in bright field due to the interface decoration by the equilibrium α+ δ. Despite the rapid phase decomposition upon quenching, acceptable properties can be achieved in aged U-0.8Ti alloy components with up to 50%

of the α + δ transformation products within the interior of the test specimens. On the other hand, the U-6Nb alloy is not a quench rate sensitive alloy. The α" martensite microstructure and desirable properties can be obtained after a gamma solution heat treatment even at cooling rates as slow as 10 °C/s (20 °F/s).

Void Formation. Small-diameter bars and plates can be plunge quenched, but larger diameter bars (greater than 19 mm, or 0.75 in.) develop centerline voids if plunge quenched. These voids pose a particularly serious problem. Once they are formed, there is no easy way to heal them. Void formation is related to the stresses caused by the large volume change associated with the gamma-to-alpha prime transformation and high radial thermal gradients. Centerline voids can be minimized by end quenching--that is, by lowering the bars, end on, at a controlled rate, into the quench media. Bars 36 mm (1.4 in.) in diameter have acceptable levels of centerline voids when quenched in this way, 18 at a time, into circulating water at 455 mm/min (18 in./min). The number and size of centerline voids, as detected by ultrasonic techniques, are substantially lower in bars end quenched at 255 mm/min (10 in./ min). A typical quench crack in the U-0.8Ti alloy that occurred during a sluggish quenching operation is shown in Fig. 9. Note the lack of α' martensite platelets along the surface where the crack originated. The aging response of the more slowly quenched bars is identical with those quenched at 455 mm/min (18 in./min).

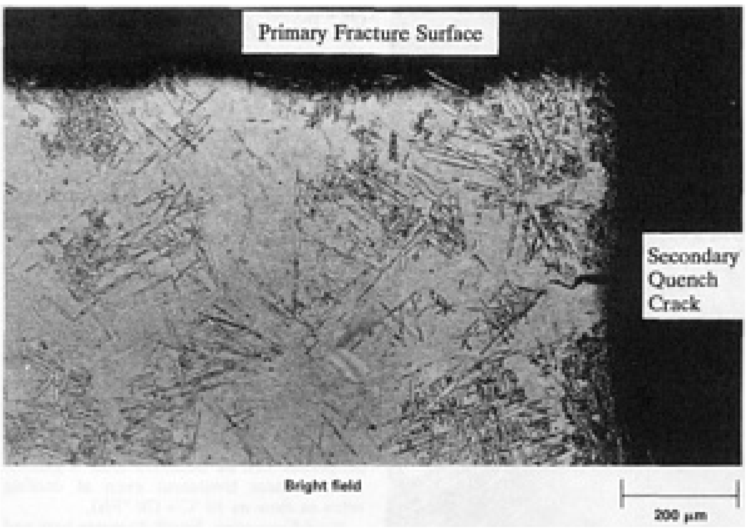

Fig. 9 A poorly transformed microstructure developed by a sluggish quench can result in a quench crack for the U-0.8Ti alloy. Acicular needles are the desired, α' martensite microstructure while the grayish regions are the undesirable, equilibrium α+ δ microstructure.

Quenching-Induced Residual Stresses and Stress Leveling. Quenching high-strength uranium alloys results in extremely high residual stresses which approach, and in some instances exceed, the yield strength of the base material. The large thermal gradients during quenching coupled with the significant difference in yield strength between the parent (γ) and product phases (either α ' or α + δ), and the phase transformation related volume contractions, induce these large residual stresses. The former are responsible for approximately 80 to 90% of the residual stresses while the latter contribute only between 10 to 20% of the quenched-in residual stresses. These latent residual stresses can be detrimental in terms of delayed fracture through stress corrosion or by significant distortion during subsequent machining operations. At times, elaborate machining procedures must be followed to obtain a final part which will meet drawing tolerances.

An example of the residual stresses obtained in a U-0.8Ti alloy cylinder after immersion water quenching is shown in Fig. 10(a). Essentially, a biaxial stress state is obtained with very high surface compressive and interior tensile residual stresses being reached. Several approaches have been used to reduce these stresses prior to final machining operations. These include thermal stress relief by aging and stress leveling through plastic deformation. Figure 10(b) shows that a typical aging heat treatment (385 °C, or 725 °F, for 4 h + water quench) after water quenching can reduce residual stresses by approximately one-third. On the other hand, stress leveling by imparting 1.5% permanent, plastic axial deformation essentially eliminates the hoop stress and dramatically reduces the axial residual stress by two-thirds (Fig. 10c).

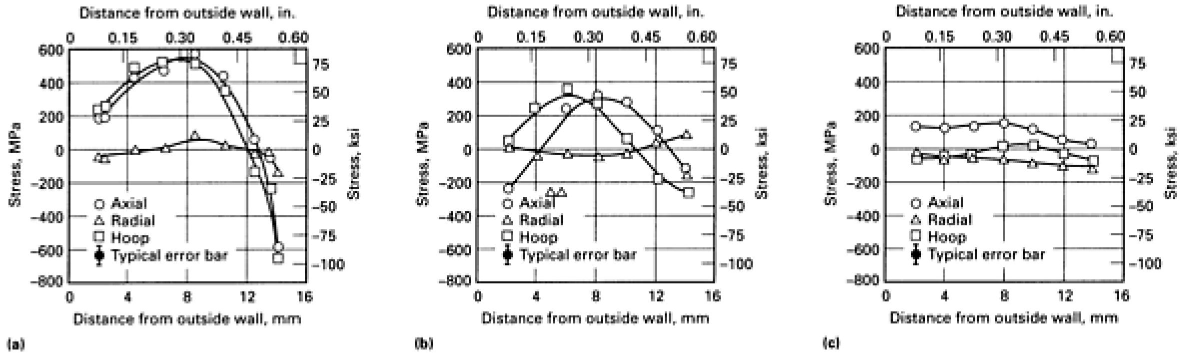

Fig. 10 Residual stresses measured by a neutron diffraction technique in a U-0.8Ti alloy cylinder. (a) After a gamma solution heat treatment and water immersion quench, a biaxial stress state is observed with very large surface compressive and interior tensile residual stresses. (b) Aging after a gamma solution heat treatment and water quench provides only a moderate reduction in the residual stresses from the original quenched values. (c) Stress leveling with 1.5% permanent, axial compressive deformation significantly reduces the residual stresses in a quenched U-0.8Ti alloy cylinder. Source: Ref 3

Schematically, stress leveling is shown in Fig. 11 for a compressive deformation cycle. Upon compressive loading, the very high tensile residual stress point 1A follows the loading path to 1B whereas the large (already yielded) compressive residual stress point 2A moves to 2B. Upon unloading, after this permanent deformation cycle, point 1B moves to 1C and 2B moves to 2C. These new residual stress values are significantly reduced in comparison with the original quenched-in residual stresses as verified through the experimentally measured data presented in the example (Fig. 10c).

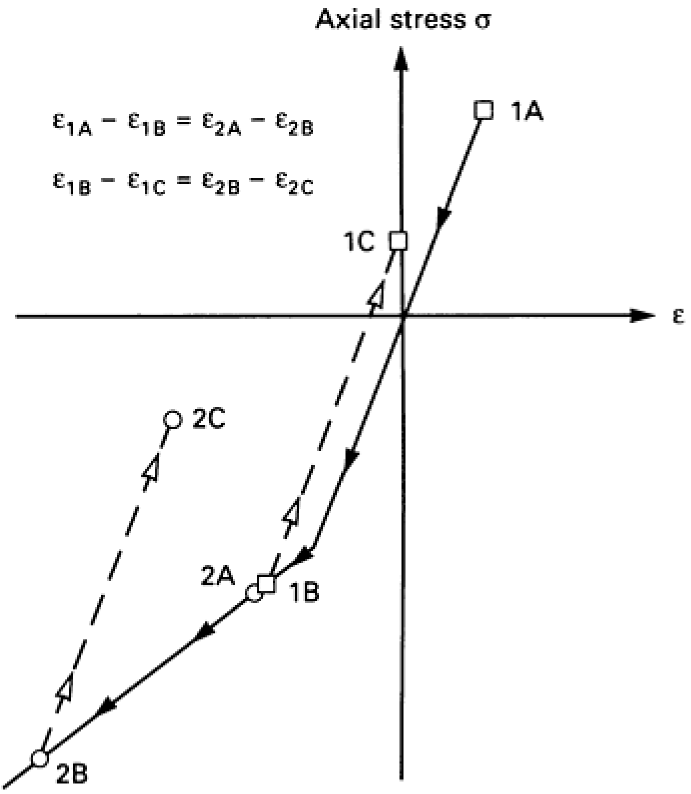

Fig. 11 Schematic of the principles of stress leveling method of residual stress reduction

Aging after stress leveling did not result in any further appreciable reduction in residual stresses. A general rule of thumb is that ~2% permanent, axial deformation will provide the optimum reduction in residual stresses in both the axial and hoop (due to a Poisson effect) directions. The deformation can either be tensile or compressive to obtain the residual stress reducing benefits. A side benefit of the axial compressive deformation in a cylinder is the increase in tensile yield strength in the hoop direction and an increase in the axial compressive yield strength with essentially no ductility loss. Geometric constraints (specimen geometry) limit the use of the stress leveling method of reducing quenched-in residual stresses.

Aging Results. Hardness and strength levels achieved on aging of dilute DU alloys are illustrated in Fig. 12, 13, and 14. The hardness curves for U-0.75Ti apply equally well to oil-quenched and water-quenched material (Fig. 12). The scatter band is caused by nominal differences in titanium and trace element contents of the alloys; iron and copper, even at low levels, contribute to the hardening response. Silicon is reported to retard hardening. Aging is usually done in an inert atmosphere like argon to minimize oxidation and hydrogen effects. A vacuum can be used but does not normally provide the dynamic heat flow of circulated argon since aging treatments are at relatively low temperatures where thermal radiation (α T^4-dependence) is not as effective for heat transfer as conduction and convection.

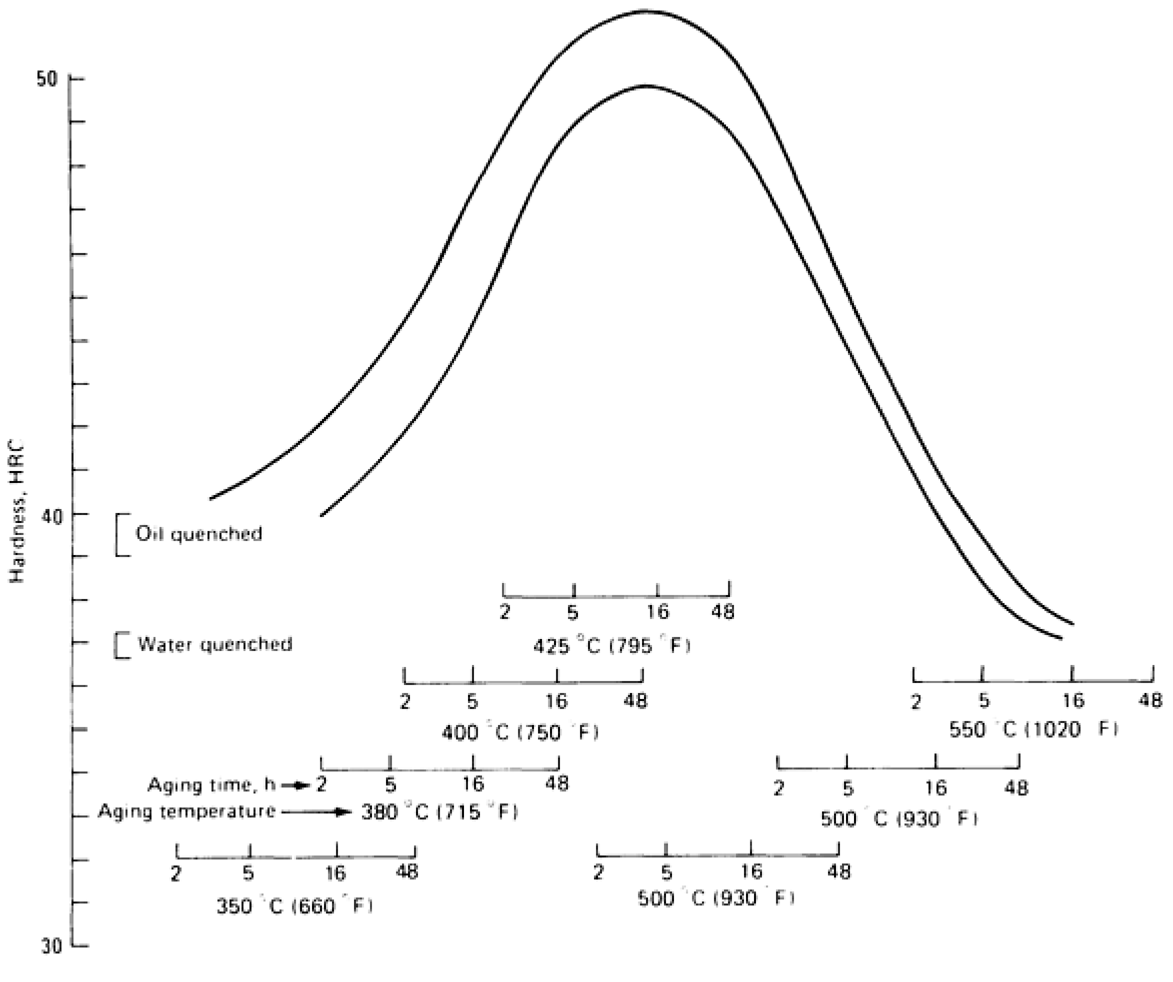

Fig. 12 Effects of aging time and temperature on hardness of U-0.75Ti

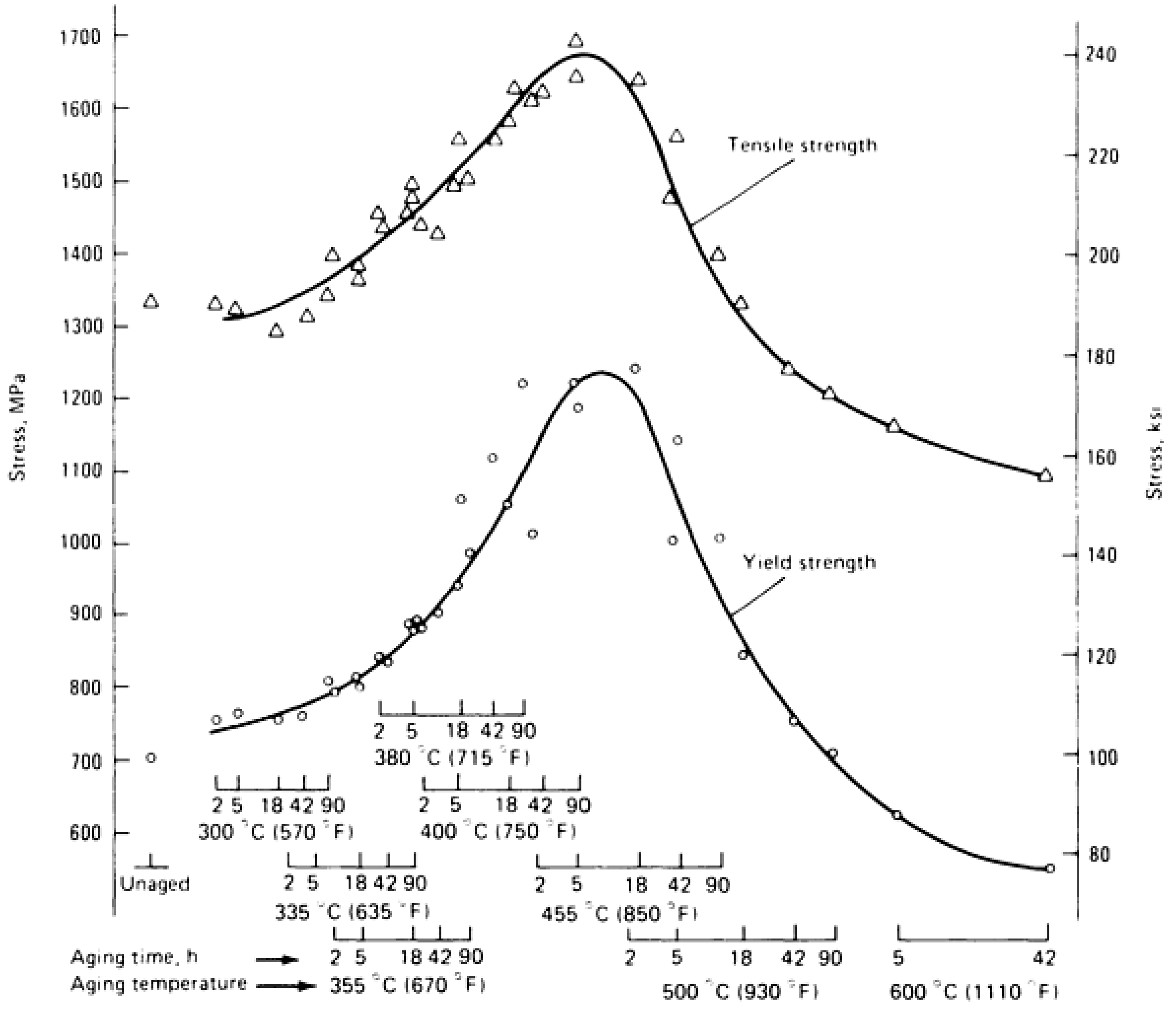

Fig. 13 Effects of aging time and temperature on tensile and yield strengths of U-0.75Ti. Source: Ref 4

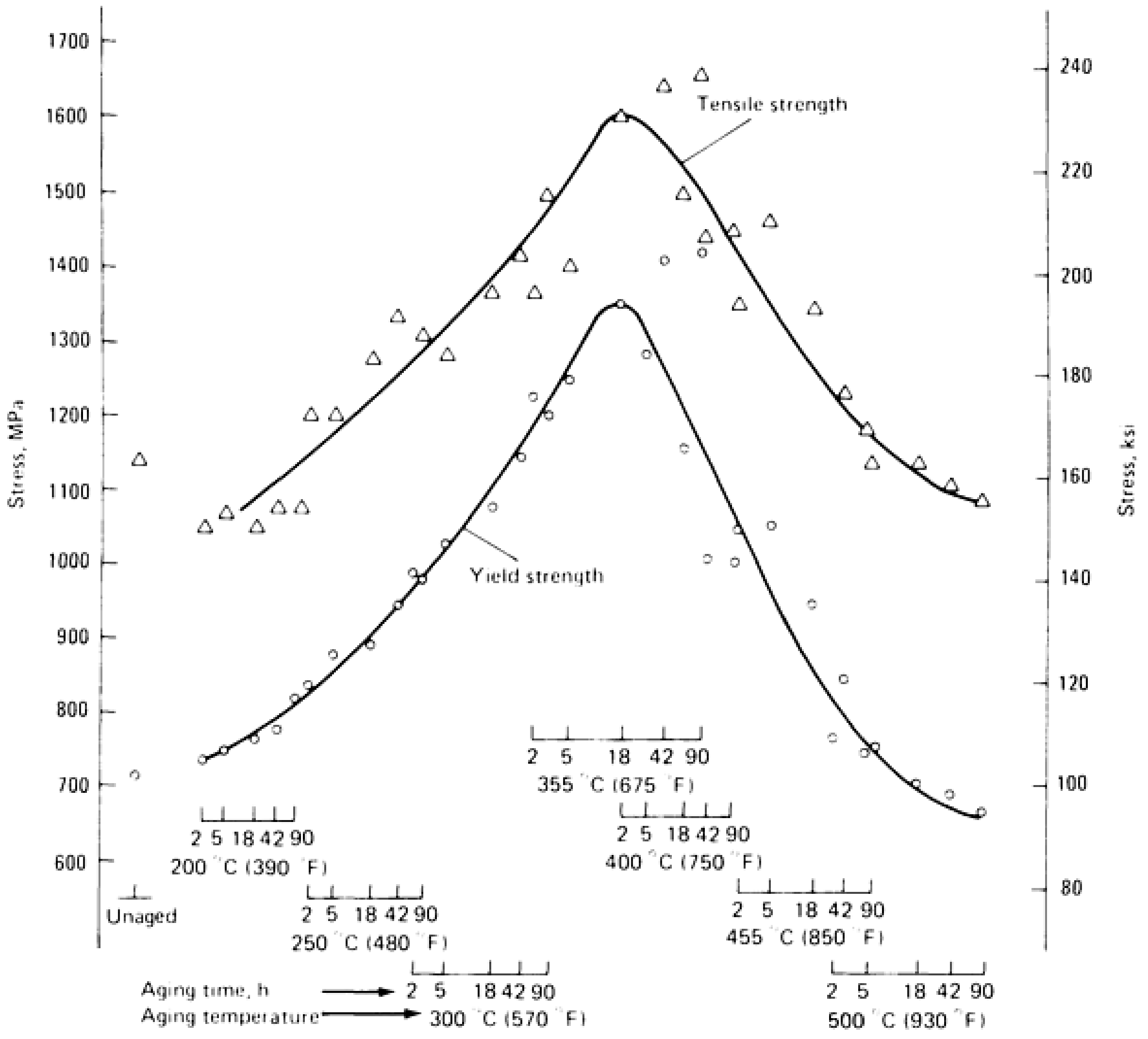

Fig. 14 Effects of aging time and temperature on tensile and yield strengths of U-2.0Mo

The heat treater has a wide selection of time-temperature options to achieve specified combinations of hardness and strength. For example, U-0.75Ti can be hardened to 45 HRC by any of the following treatments: 16 h at 380 °C (720 °F); 5 h at 400 °C (750 °F); or $1\frac{3}{4}$ h at 420 °C (790 °F). For production runs, conditions are selected to optimize equipment utilization.

Uranium alloys can differ significantly in their aging response as shown in Fig. 15. Whereas the U-2Mo alloy develops better strength/ductility combinations in the overaged condition, the U-0.8Ti alloy must be used in the underaged condition since the overaged condition exhibits poor ductility. A semicontinuous film of brittle intermetallic (U_2Ti) forms along the prior α' martensite plate boundaries during overaging of the U-0.8Ti alloy. In contrast for the U-2Mo alloy, the banded α' martensite plate boundaries do not act as preferential sites for the brittle intermetallic during overaging and so higher ductility is achievable in overaged microstructures.

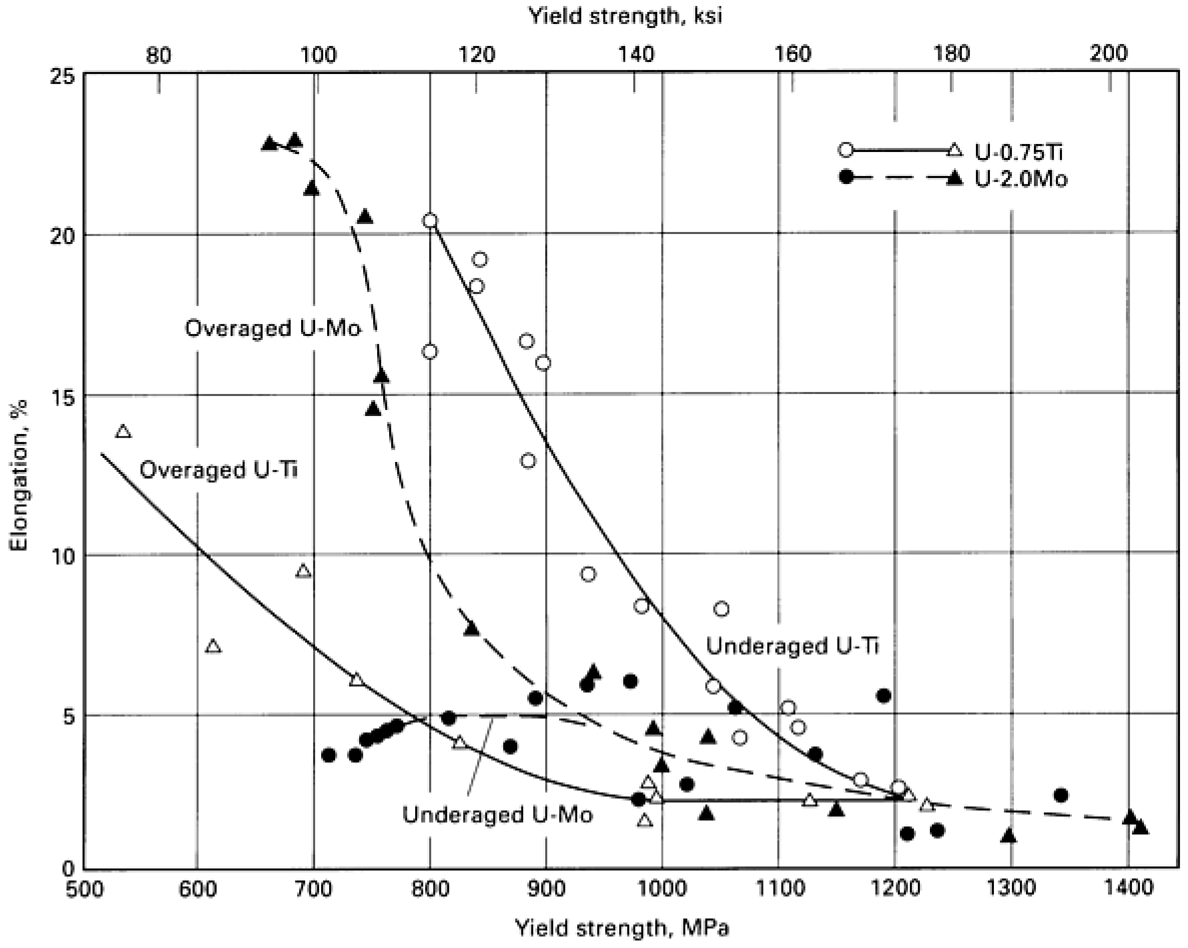

Fig. 15 A comparison between the aging responses of the U-2Mo and U-0.75Ti alloys

A general comment on the heat treatment of uranium alloys is that the elastic moduli (tensile and shear) can be varied significantly (over 100%) through heat treatment. This fact has been used as the basis for a quality control method through measurement of elastic ultrasonic wave response to verify heat treatment. This ability to vary modulus is opposite in behavior to conventional ferrous alloys which yield the same moduli independent of heat treatment.

Mechanical Testing. External hydrogen can lead to premature failures in U-0.8Ti. Ideally, the test atmosphere should be one with low relative humidity such as dried air, vacuum, or immersed in a suitable oil. Strain rate also plays a role in determining mechanical properties, especially ductility. Faster strain rates tend to improve reduction-in-area values significantly (Fig. 7). Fracture morphologies change from a mixed mode of quasi-cleavage and microvoid coalescence to one of predominantly dimpled rupture.

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Metastable High Alloys

Heat treatment of DU alloys with 4.0 wt% or more molybdenum or equivalent is similar to that for dilute alloys. The treatment starts with a gamma-phase solution treatment of 1 h at about 800 °C (1470 °F). This is followed by either quenching to room temperature followed by aging in the alpha region or quenching directly to the aging temperature and holding to achieve the desired properties. For higher ductilities, it may be necessary to cold work the U-6 wt% Nb alloy prior to heat treatment. Swaging of rods at room temperature prior to heat treatment resulted in a slightly smaller grain size along with a 20% improvement in yield strength. Special care must be taken in heat treating large sections. Cracking has occurred in billets of U-6 wt% Nb 200 mm (8 in.) in diameter (or larger) that were water quenched from 800 °C (1470 °F).

Processing and Equipment

Generally, three basic furnace designs are used for heating or heat treating of unalloyed uranium: molten baths, inert-atmosphere furnaces, and vacuum furnaces. The type of furnace chosen depends primarily on desired final properties and material quality.

Uranium has been heated in molten lead for 50 h at 350 °C (660 °F) with no appreciable reaction. Longer periods and/or temperatures of 800 to 1000 °C (1470 to 1830 °F), however, have caused uranium to be completely penetrated. Molten salts are the most common heating media used in industry for preheating uranium prior to fabrication operations and for final heat treatment. Table 8 shows corrosion results for six heat-treating mixtures of salts. The main disadvantage of molten salt baths is the potential for hydrogen contamination. Consequently, any planned use of molten salt baths for heating of uranium should include a design for removing the hydrogen from the bath, such as sparging the bath with CO_2 gas. Hydrogen, which is particularly deleterious to uranium, drastically reduces its tensile elongation, as shown in Fig. 16.

Table 8 Corrosion of uranium in molten salts at 595 °C (1100 °F)

Salt mixture	Time, h	Observed attack
$44Na_2CO_3$-$30K_2CO_3$-$26Li_2CO_3$	$\frac{1}{2}$-2	No corrosion
	4	Surface pitting
$74K_2CO_3$-$26Li_2CO_3$	$\frac{1}{2}$-2	No corrosion
	4	Pitted
$47Na_2CO_3$-$32K_2CO_3$-$21Li_2CO_3$	$\frac{1}{2}$-2	No corrosion
	2	Pits beginning
	4	Badly pitted
$53K_2CO_3$-$46.6Li_2CO_3$	$\frac{1}{2}$-1	No corrosion
	2	Surface pits

20NaOH-30K_2CO_3-50Na_2CO_3	$\frac{1}{2}$ -4	Surface etching
47Na_2CO_3-47K_2CO_3-6Li_2CO_3	$\frac{1}{2}$	Scaling, 0.24% weight loss
	2	Scaling, 1.0% weight loss
	4	Scaling, 1.3% weight loss

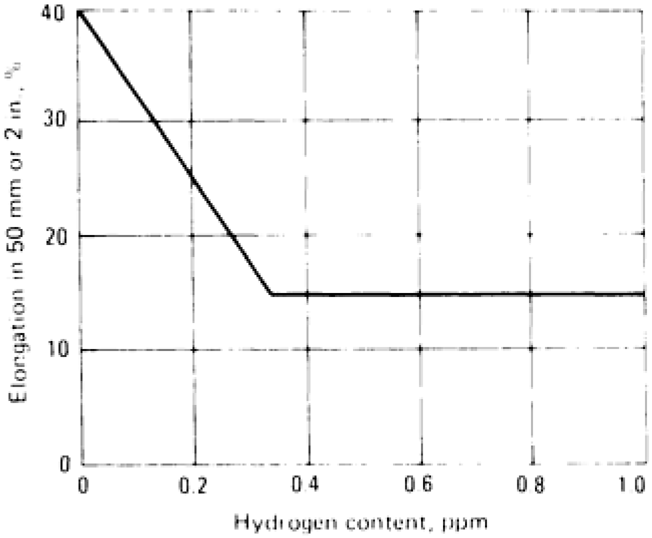

Fig. 16 Elongation versus hydrogen content for wrought depleted uranium

Furnace Atmospheres. No appreciable attack on uranium occurs in dry furnace atmosphere of helium, argon, carbon monoxide, carbon dioxide, or hydrocarbon gases at temperatures up to 500 °C (930 °F). However, relatively slight amounts of water vapor in any of these gases can cause extensive corrosion. Uranium reacts with water, in either liquid or vapor form, to produce UO_2 and hydrogen. The UO_2 spreads over the entire surface area as a black powder and, depending on the amount of exposure and purity of the metal, can result in excessive pitting and surface cratering. Thus, in heat treating of uranium in atmospheres of commercial inert gases, furnaces should be equipped with gas line dryers to dry the gas thoroughly before it is used.

Vacuum Treatment. Vacuum heat treating of uranium provides the best over-all environment for obtaining maximum tensile properties and high-quality metal surfaces. The principal advantage of vacuum-furnace heat treating is the potential for removing hydrogen from the metal.

Figure 17 shows the time required for vacuum heat treating uranium stock of different thicknesses to achieve maximum ductility. This illustration assumes an initial hydrogen concentration within the part of 2 ppm, which is typical of material processed through carbonate preheating baths, and it can be used for cast material.

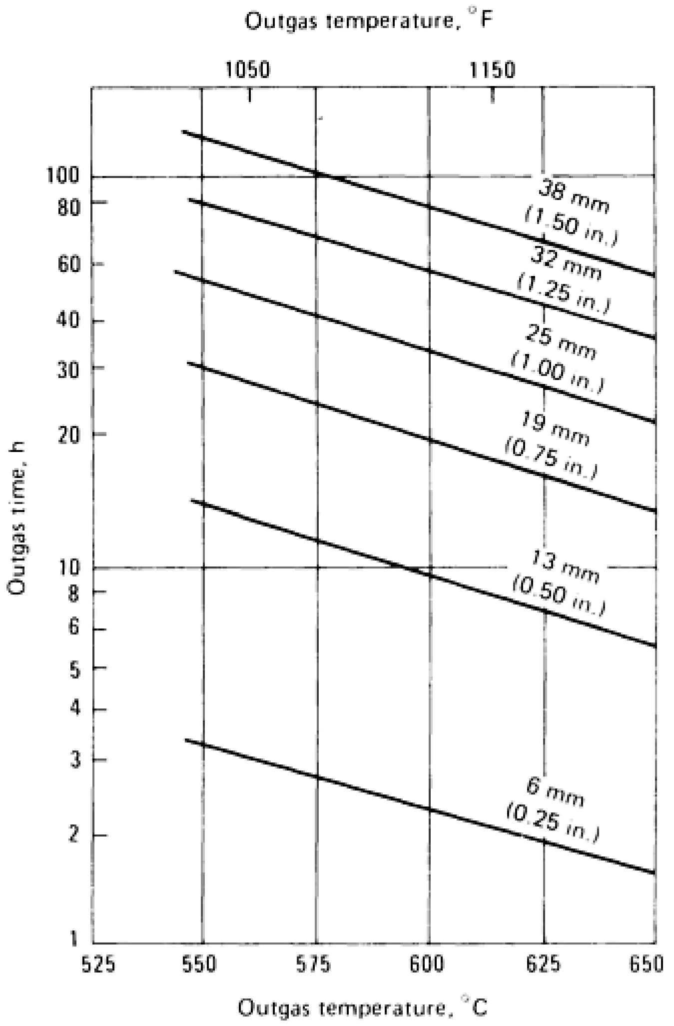

Fig. 17 Time required to achieve maximum ductility in depleted uranium plate of various thicknesses under a vacuum of 10^{-4} torr

A vacuum of 40 kPa (300 torr) limits oxidation to an acceptable level while maintaining the hydrogen at its initial level. A vacuum of 10^{-3} Pa (10^{-5} torr) is needed for significant lowering of the hydrogen level.

Cleaning. Surfaces of parts to be heat treated should be free of moisture, grease, and cutting lubricants. Heavier oxides that form on DU and its alloys can be removed by pickling for about $\frac{1}{2}$ h in a 1:1 mixture of nitric acid and water at 25 °C (75 °F). Copper, which is often used as cladding during fabrication, can also be removed with 1:1 nitric acid. U-0.8Ti should be coated with a suitable oil such as MIL-C-16173D, Grade 3 or stored in a dry environment to mitigate the deleterious effects of hydrogen.

Caution: U-Nb and U-Zr alloys can produce explosions during pickling in nitric acid. The problem can be eliminated by adding 1 to 2 vol % of hydrofluoric acid to the pickling solution.

Quenching. The oil-quench media can be contained within the vacuum chamber. Following solution treating, the furnace is backfilled with argon or helium. The work is then transferred to a position directly over the quench tank and lowered at a controlled rate into the quench media.

The high vapor pressure of water precludes incorporation of water-based quench media into the furnace. Specially designed bottom-loading furnaces have been used successfully with separate quench tanks. The sequence of events is as follows. At the end of solution treating, the quench tank is moved under the furnace. The furnace is then backfilled with

argon or helium, the power turned off, and the bottom door removed. The load is dropped rapidly to a position 50 to 75 mm (2 to 3 in.) above the water level and then is dropped at a controlled rate until all of the workpiece is submerged.

Fixtures. Neither DU nor its alloys are especially strong at gamma-solution treating temperatures. Low strength coupled with a high density places special requirements on fixturing to provide proper support and thus prevent sagging. If possible, rods and irregular-shape pieces should be placed with the long axis in a vertical position and supported every 150 mm (6 in.); spans for horizontal pieces should be limited to 75 to 100 mm (3 to 4 in.).

Figure 18 shows a fixture used for solution treating of bars 36 mm (1.4 in.) in diameter by 380 mm (15 in.) long. This basket is made of Inconel 600. Tantalum shims are often used at points of contact between DU and the basket material if the basket alloy contains a metallic element like iron, which forms a eutectic at 725 °C (1335 °F). Other common eutectics found in heat treating DU include nickel at 740 °C (1364 °F), chromium at 860 °C (1580 °F), and copper at 950 °C (1742 °F). Molten-metal attack would result in extensive local wastage of the DU and welding to the fixture.

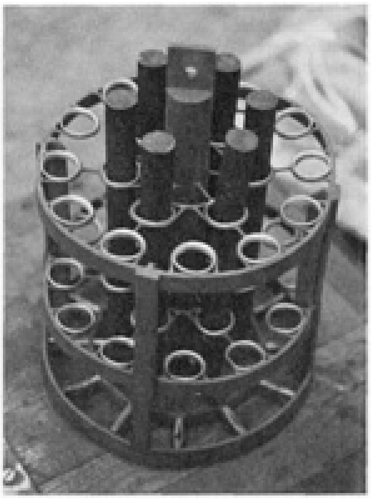

Fig. 18 Fixture for solution treating and end quenching of 18 depleted uranium bars

Salt Baths. If a salt bath is used for solution treating, the times should be kept as short as possible, not only to minimize hydrogen pickup but also to limit corrosive attack. Pieces exposed to molten chloride salts ($BaCl_2$, KCl, and NaCl eutectic) and molten carbonate salts (35% Li_2CO_3 and 65% K_2CO_3) at 730 °C (1350 °F) have lost 0.08 mm (0.003 in.) of thickness in 1 h. Such attack would be significantly more severe at 850 °C (1560 °F).

Aging treatments can be carried out in recirculating inert gas furnaces, lead baths, lead-tin baths, or molten salt baths. Because the aging reactions are temperature sensitive, the temperature should be controlled to within +5 °C (+9 °F) and preferably to within +2 °C (+4 °F). Following aging, the pieces should be either furnace cooled to 100 °C (212 °F) or water quenched. Oxidation of DU is exothermic, and the heat generated can make the reaction self-sustaining. *Caution: Rods 18 mm (0.7 in.) in diameter have reached red heat when they were not water quenched after being aged at 425 °C (795 °F) in a lead pot.*

Examples of Heat Treatment

The following procedures are examples of heat treatment used to meet certain specifications of ultimate tensile strength (UTS), yield strength (YS), and elongation. Other work related to the heat treating of specific uranium alloys is given in Ref 5, 6, 7, and 8.

Example 1: U-0.8Ti Alloy.

A U-0.8Ti alloy is to be extruded and heat treated to produce components with 1240 MPa (180 ksi) ultimate tensile strength, 895 MPa (130 ksi) yield strength at 0.85% extension, 16% total elongation with less than 0.3 ppm internal hydrogen.

- Billet is preheated in molten salt bath at 630 °C (1165 °F) and extruded
- Extruded billet is machined into blank that is solution heat treated at 800 °C (1475 °F) for 8 h in vacuum and water quenched
- Blank is aged at 385 °C (725 °F) for 4.5 h in argon and water quenched

Example 2: U-0.75Ti.

Bars of DU-0.75Ti alloy, 36 mm (1.4 in.) in diameter are to be heat treated to the following specifications: hardness, 38 to 44 HRC; minimum 0.2% yield strength, 725 MPa (105 ksi); minimum elongation, 12%; and maximum hydrogen content, 1 ppm. The procedure is to:

- Cut extruded bar stock to length
- Pickle in 1:1 nitric acid to remove copper sheath
- Rinse and air dry
- Place rods vertically in a basket
- Solution treat $2\frac{1}{2}$ h at 850 °C (1560 °F) in a vacuum of 7×10^{-3} Pa (5×10^{-5} torr), or better
- Quench into circulating water at 455 mm/ min (18 in./min)
- Air dry
- Age 16 h at 350 °C (660 °F) in an inert gas recirculating furnace

Example 3: U-6Nb Alloy.

A U-6 Nb alloy is to be formed into a hemisphere with the following mechanical properties: ultimate tensile strength, 770 MPa (112 ksi) min; yield strength at 0.2% offset, 360 to 485 MPa (52 to 70 ksi); and total elongation, 25% min.

- Billet is preheated to 800 to 850 °C (1475 to 1560 °F) and forged
- Forged billet is homogenized at 1000 °C (1830 °F) for 4 h in vacuum
- Forged billet is preheated to 850 °C (1560 °F) in molten salt bath and cross rolled into plate
- Plate is preheated in argon furnace to 850 °C (1560 °F) and formed into a hemisphere
- Hemisphere is solution heat treated to 800 °C (1475 °F) for 1 to 2 h in vacuum and water quenched
- Hemisphere is aged in argon at 200 °C (400 °F) for 2 h

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8. G.H. Llewellyn, G.A. Aramayo, G.M. Ludtka, J.E. Park, M. Siman-Tov, "Experimental and Analytical Studies in Quenching Uranium-0.75% Titanium Alloy Cylinders," Y-2397, Martin Marietta Energy Systems, Inc., Feb 1989

Licensing and Health and Safety Requirements

Possession of more than 15 lb (6.8 kg) of depleted uranium in any form requires a license from the U.S. Nuclear Regulatory Commission. Title 10, Part 40, of Federal Regulations describes the steps necessary and the requirements to obtain such a license. In addition, all other local, state, and federal regulations are effective as applicable.

The greatest potential source of contamination in the heat-treating area is uranium oxide. The area should be isolated from the remainder of the plant, and everyone entering should be required to wear disposable protective footwear. Smoking and eating should be restricted.

Caution: The toxicity of depleted uranium if it enters the blood stream may result in poisoning similar to that caused by lead, arsenic, mercury, or any other heavy metal.

A more detailed discussion about health and safety requirements is provided in Volume 2 of *ASM Handbook*, formerly 10th Edition *Metals Handbook.* The important fact to remember is that each new operation or procedure involving uranium alloys should be individually evaluated to determine the correct protective clothing and equipment, dosimetry, and handling requirements for that particular job. The prior processing history of the heat treatment samples is likewise important in this consideration since operations which change the state of the uranium, like casting, can make concerns about daughter-product beta radiation more important than normal low-level alpha radiation associated with depleted uranium.

Annealing of Precious Metals

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Introduction

THE PRECIOUS METAL GROUP consists of silver, gold, platinum, palladium, rhodium, iridium, ruthenium, and osmium. Significant production of wrought product forms is limited to the first four elements and their alloys. The last four elements become increasingly intractable or less ductile and consequently cannot be practically fabricated into engineering products. Because of the dissimilarities of the physical metallurgy of elements within the precious metal group, the annealing practice for each member of the group will be considered separately. For each element and its alloys, a brief description of the compositions, uses, annealing practices, and nominal annealing effects on key properties is given.

Silver and Silver Alloys

Consumption of silver and silver alloys in wrought product form is large and exceeds that of any other members of the precious metal group. Because of the extensive use of silver, data on annealing practice and the effects of annealing on mechanical properties are more available for silver than for the remainder of the precious metal group.

Commercially Pure Fine Silver

Commercially pure fine silver contains, by definition, at least 99.9% Ag. It is widely used in the electrical and electronics industries as contacts and conductors and in the chemical industry as linings for reactors and process/storage vessels, particularly caustic evaporators and crystallizers.

Annealing Practice. Commercially pure fine silver is typically annealed between 300 and 350 °C (570 and 660 °F) following at least 50% cold work. However, data exists in the literature for annealing times up to 1.5 h at temperatures as high as 565 °C (1050 °F). Most annealing of silver, however, is done at approximately 500 °C (930 °F). Under extreme conditions of cold work, ultra-pure (99.99% pure) silver can recrystallize at temperatures as low as room temperature. Silver is typically annealed in air at temperatures below 350 °C (660 °F) without adverse effects. However, higher annealing temperatures (550 to 650 °C, or 1020 to 1200 °F) can result in oxygen adsorption due to the high solubility and diffusion rate (under 0.025 mm at >800 °C/h, or 1440 °F/h) of oxygen in silver. Very pure silver has a hardness of 25 HV after a hydrogen anneal at 650 °C (1200 °F) and 27 HV after annealing in air at the same temperature. Oxygen present in silver tends to react with impurities and has the beneficial effect of inhibiting grain growth. Silver containing oxygen will become embrittled when annealed in hydrogen. Hydrogen annealing of thin material sections of silver can cause the formation of blisters. This effect is similar to that known to occur when tough pitch copper, that is, copper refined in a reverberatory furnace to adjust the oxygen content to 0.2 to 0.5%, is annealed in hydrogen. Thus, deoxidized silver is essential where hydrogen annealing is practiced.

Effect of Annealing Temperature on Mechanical Properties. The effect of annealing temperature on the tensile strength and elongation of wire cold drawn 49% prior to annealing is presented in Fig. 1. Ductility is maximized at

approximately 370 °C (700 °F). Higher temperatures reduce ductility and ultimately increase tensile strength as grain growth and perhaps oxygen adsorption begin to adversely influence tensile properties. Comparable data are presented in Table 1 for commercially pure fine silver sheet, 0.81 mm (0.032 in.) thick. Data on the deep-drawing characteristics of commercially pure fine silver as a function of annealing temperature are given in Table 2. Annealing lowers Poisson's ratio to 0.37 from 0.39 for hard-drawn material. The most frequently reported room-temperature value for the elastic modulus of commercially pure fine silver is 71 GPa (10.3×10^6 psi). This value was determined on material strained 5% and then annealed 0.5 h at 350 °C (660 °F). Cold work and annealing temperature, as well as compositional variations, apparently can affect the elastic modulus. The shear modulus is reduced by annealing from the cold worked state from 26.9 GPa (3.90×10^6 psi) for hard-drawn material to 26.6 GPa (3.86×10^6 psi) for annealed commercially pure fine silver at 20 °C (68 °F).

Table 1 Effect of annealing temperature on room-temperature tensile properties of commercially pure fine silver cold rolled 50% to 0.81 mm (0.032 in.) thickness

Annealing condition (held $\frac{1}{2}$ h)		**Tensile strength**		**Elongation, %**
°C	**°F**	**MPa**	**ksi**	
As rolled 50%		374	54.3	2.4
205	400	183	26.5	43.7
315	600	172	25.0	51.6
425	800	172	25.0	51.5
540	1000	166	24.1	50.3
650	1200	158	22.9	53.9
760	1400	155	22.5	48.4

Table 2 Cup depth at room temperature as a function of annealing temperature for commercially pure fine silver sheet 0.81 mm (0.032 in.) thick

Annealing temperature		**Cup depth**	
°C	**°F**	**mm**	**in.**
95	200	3.56	0.140
205	400	7.65	0.301

315	600	8.33	0.328
425	800	8.43	0.332
540	1000	8.38	0.330
650	1200	8.41	0.331
760	1400	8.31	0.327

Source: Ref 2

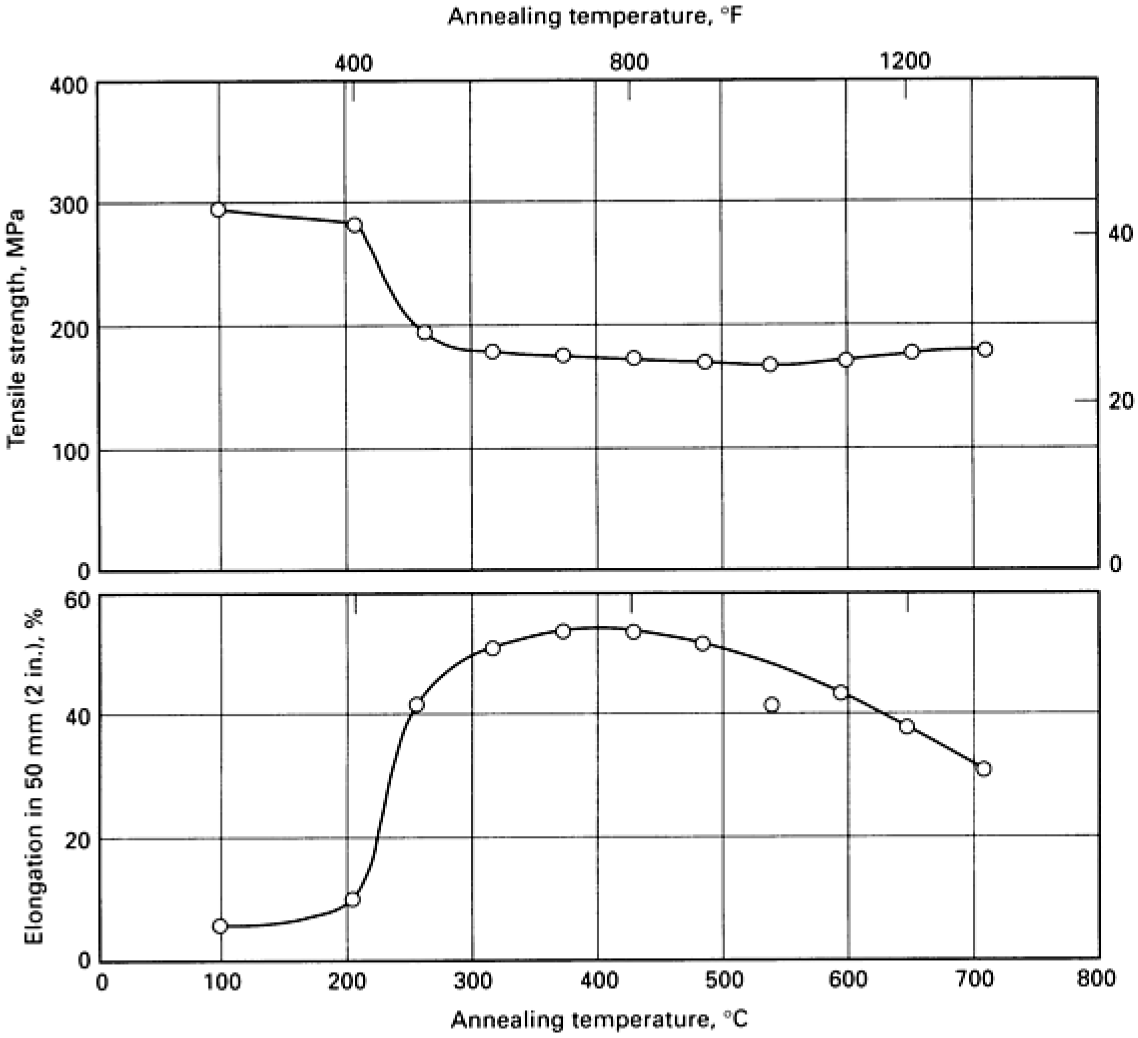

Fig. 1 Tensile properties of commercially pure fine silver 2.3 mm (0.091 in.) diam wire

Effect of Cold Work on Recovery and Recrystallization. Data for the onset of softening (recovery) for commercially pure fine silver as a function of the degree of cold rolling at 20 °C (68 °F) are shown in Table 3. Commercially pure fine silver that has been cold worked extensively, that is, greater than about 95%, can recrystallize at relatively low temperatures. The effect of small amounts of a second element has been found to measurably influence the recrystallization temperature under these conditions. A brief summary of these observations is given in Table 4. Because

of the uncertainty of overall purity and whether the temperature given is the start or finish of recrystallization, these data are only indicative of a general trend.

Table 3 Effect of cold work on the softening temperature of commercially pure fine silver

Reduction by rolling at 20 °C (68 °F), %	Softening temperature	
	°C	°F
10	250	480
50	100	210
90	65	150

Table 4 Effect of second elements on the recrystallization temperature of commercially pure fine silver that has been extensively cold worked

Element	Nominal composition, wt%	Recrystallization temperature	
		°C	°F
. . .	. . .	150	300
Aluminum	0.200	190	370
Copper	0.012	200	390
Copper	0.037	175	350
Copper	0.303	230	450
Gold	0.100	110	230
Gold	0.200	110	230
Iron	0.035	110	230
Iron	0.055	20	70
Iron	0.065	20	70

Lead	0.059	145	290
Nickel	0.100	140	280
Palladium	0.100	110	230
Zinc	0.119	145	290

Source: Ref 4

Silver-Copper Alloys

The most common silver-copper alloys are sterling silver (92.5% Ag minimum), coin silver (Ag-10% Cu), and the eutectic alloy containing 28.1% Cu. Sterling silver is normally alloyed only with copper because other elements have proved to be less effective hardeners. Sterling silver is typically used for flat and hollow tableware and in the manufacture of jewelry. Coin silver is used for coins and in certain electrical contacts where pure silver is deemed too soft and prone to pitting. Spring-type electrical contacts are made from the eutectic alloy.

Effect of Annealing Temperature on Mechanical Properties. Figure 2 shows the effect of annealing temperature on the strength and elongation of cold drawn 2.3 mm (0.091 in.) diam sterling silver and eutectic alloy wire. Commercial silver-copper alloys are typically annealed between 480 and 535 °C (900 and 1000 °F) followed by furnace cooling under protective atmosphere, which can result in some age hardening. Process annealing can be conducted at temperatures as high as 675 °C (1250 °F) usually in a steam atmosphere or salt bath. However, at the higher temperature, quenching is required for producing full softness. Alternating between oxidizing and reducing atmospheres during annealing is damaging to this alloy compositional range. Where light oxidation has occurred, pickling in a hot (approximately 50 °C, or 120 °F) sulfuric acid solution (5 to 10%) is suitable.

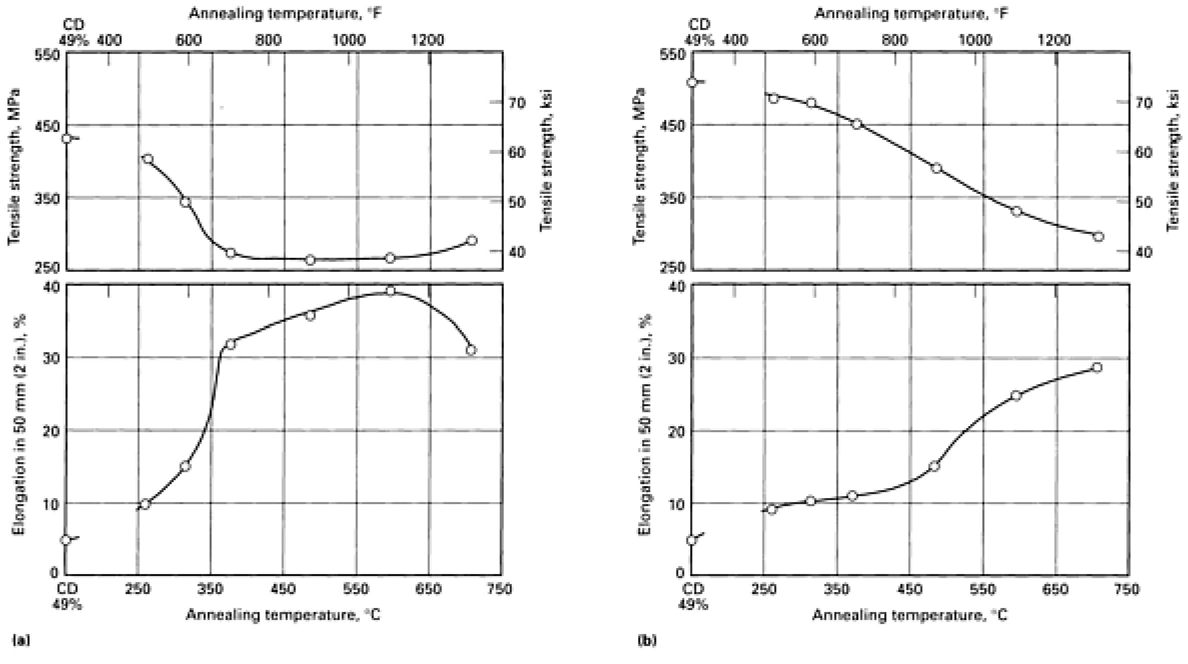

Fig. 2 Tensile properties and electrical conductivity of silver-copper alloys. 2.3 mm (0.091 in.) diam wire, cold drawn (CD) 49% before annealing. (a) Sterling silver (92.5Ag-7.5Cu). (b) Eutectic alloy (72Ag-28Cu)

Figure 3 records the nominal electrical resistivity of annealed as well as annealed/aged silver-copper wire as a function of copper content. The silver-copper alloys can be age hardened as depicted in Fig. 4. The solubility of copper in silver at 650 °C (1200 °F) is about 4% and at 730 °C (1350 °F) about 6%, thus sterling silver annealed at these temperatures is duplex with small amounts of the copper-rich phase scattered through the silver-rich matrix. Aging treatments cause precipitation of the copper-rich phase and, if prolonged, increase the electrical conductivity considerably. Coin silver will remain duplex after any annealing treatment, and ages in much the same manner as sterling silver. Both alloys respond to aging at 280 °C (535 °F) (Fig. 4). The mechanical properties of sterling silver and coin silver are virtually the same after the usual annealing treatment at about 650 °C (1200 °F) because the composition of the silver-rich phase is essentially the same. Alloys containing 20 to 30% Cu have much more of the copper-rich phase and show less age hardening.

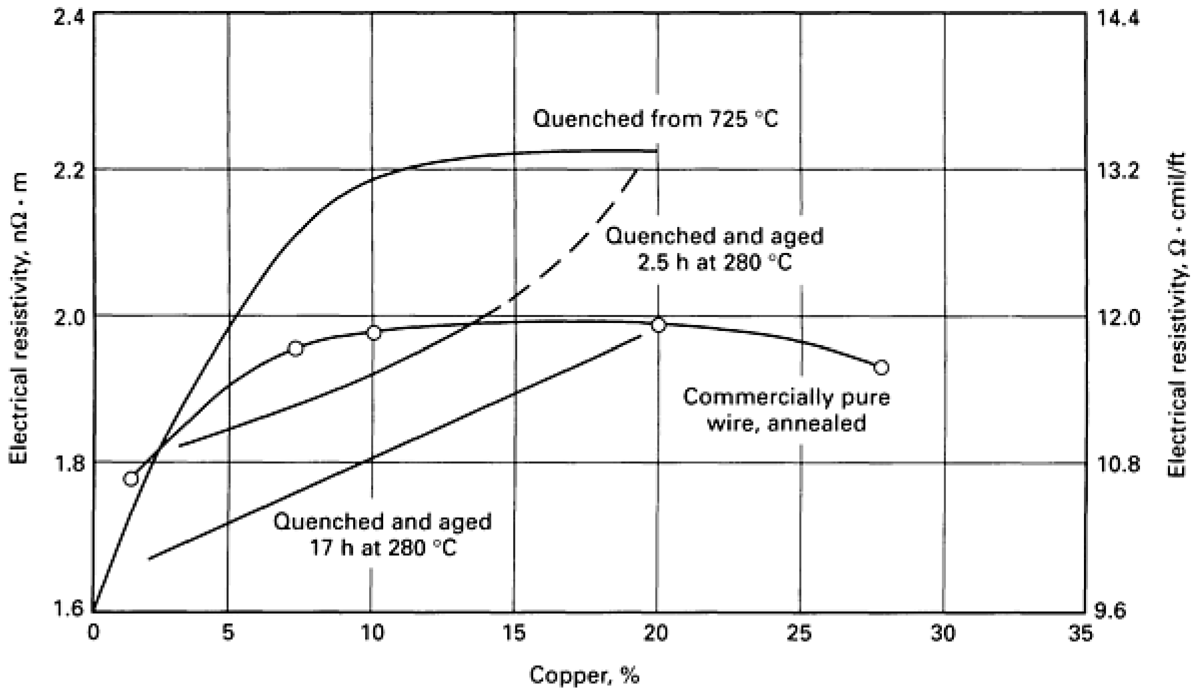

Fig. 3 Effect of copper content on the electrical resistivity of annealed silver-copper alloys and annealed/aged silver-copper alloys

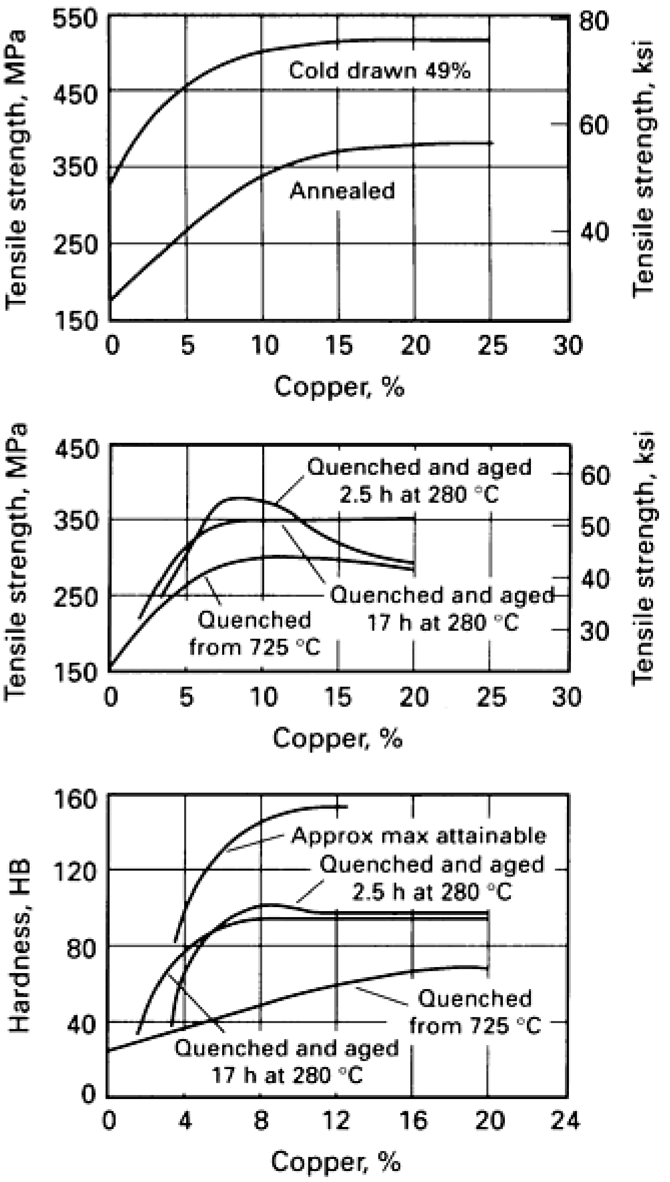

Fig. 4 Effect of copper content on properties of silver-copper alloys

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Gold and Gold Alloys

There are a number of types of pure and alloy gold systems of commercial significance each with different annealing practices. Included here will be annealing information on pure gold, color and white gold, gold-platinum, gold-palladium-iron, and cast and wrought gold alloys for dentistry.

Pure Gold

The usual grade of refined gold is 99.99% pure and is suitable for jewelry and dental applications. Coin gold contains 89.9 to 91.7% Au, with the balance being copper.

Annealing Practice. Pure gold can be annealed in air at 305 °C (580 °F) to control grain size but it is usually not required because pure gold easily recrystallizes at room temperature. Wrought annealed pure gold has a room temperature tensile strength of 131 MPa (19 ksi), 45% elongation, and a hardness of 25 HB. The elastic modulus is 80 GPa (11.6×10^6 psi).

Color Gold Alloys

Most of the commercially important color gold alloys are based on the gold-silver-copper system although zinc and nickel are frequent modifiers. The composition of typical color gold alloys is given in Table 5. These alloys are used principally in jewelry; slip rings and bushings in electrical devices; and in dental applications.

Table 5 Chemical composition of typical color gold alloys

Alloy, k	Color	Nominal composition, wt%			
		Au	Cu	Ag	Zn
10	Yellow	41.7	43.8	5.5	9.0
10	Yellow	41.7	48.0	6.6	3.7
10	Yellow	41.7	40.8	11.7	5.8
10	Green	41.7	9.1	48.9	0.3
14	Yellow	58.3	31.3	4.0	6.4
14	Yellow	58.3	29.2	8.3	4.2
14	Yellow	58.3	39.7	10.0	2.0
14	Yellow	58.3	25.0	16.5	0.2
14	Yellow	58.3	16.8	24.8	0.1
14	Green	58.3	6.5	35.0	0.2
18	Yellow	75.0	10.0	15.0	. . .

Annealing Practice. Typical annealing temperatures for the color gold alloys are in the range of 500 to 700 °C (930 to 1290 °F) depending on the exact composition. It is recommended that color gold alloys be quenched in water after annealing to avoid age hardening. This has the secondary effect of removing any oxide scale that may have formed during

annealing in air. Commercially, most annealing of color gold alloys is done in a 7% H_2-N_2 atmosphere with slow cooling instead of quenching.

However, nickel-containing white gold alloys should be air cooled as quenching introduces high residual stress levels in these alloys. Aging of the two-phase alloys is customarily done at 260 to 315 °C (500 to 600 °F).

Effect of Annealing and Aging on Hardness. Figure 5 depicts the effect of annealing, followed by quenching, on the hardness of the color gold alloys. Also shown is the effect of aging at 260 to 315 °C (500 to 600 °F) as a function of silver content. Age hardening temperatures can vary from between 100 °C (210 °F) and 425 °C (800 °F) depending upon the alloy that is being used. Aging times can vary from 5 min to 2 h, with increasing time associated with increasing strength and lower ductility. Longer aging times may result in overaging and subsequent decreasing hardness. In Fig. 5, note the lack of an aging response for the extremes of the silver content for the 10 and 14 k alloys, where k is karats.

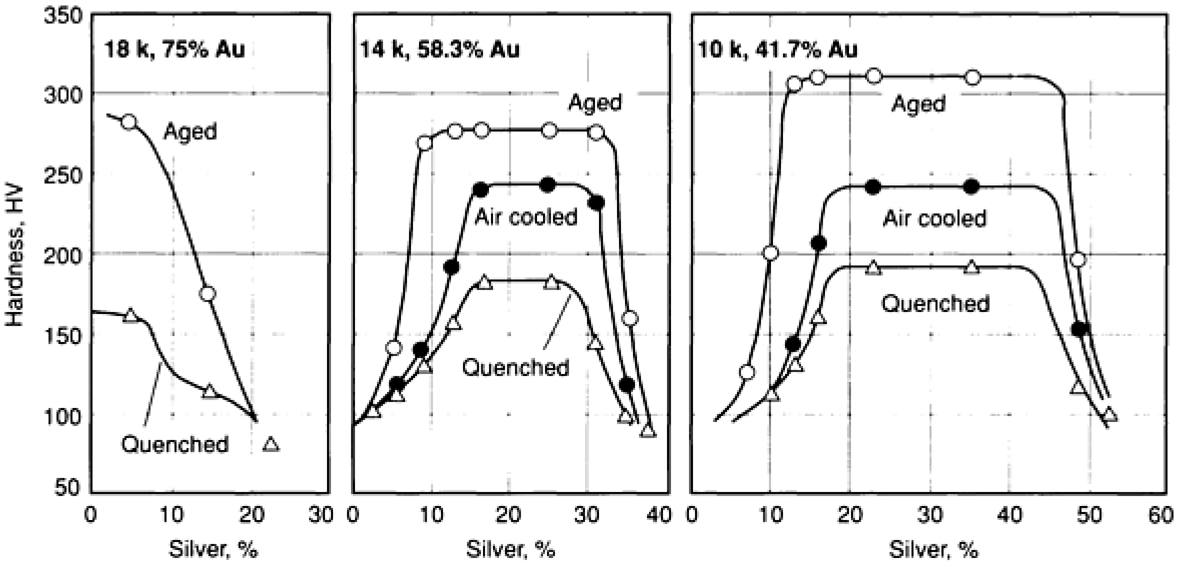

Fig. 5 Variation of hardness with silver content for gold-silver-copper alloys

Gold Alloys in Dentistry

A large number of alloys are used in dentistry in the form of wrought plate and wire, casting, and solder. These alloys require high strength and corrosion resistance. Both requirements are met by complex alloys of gold, platinum, palladium, silver, copper, and zinc. These alloys age harden readily. Typical compositional limits of wrought alloys are given in Table 6 and for cast alloys in Table 7.

Table 6 Compositions and colors of wrought precious-metal alloys used in high-strength dental wires

Alloy[(a)]	Composition[(b)], %							Color
	Au	Pt	Pd	Ag	Cu	Ni	Zn	
1	25-30	40-50	25-30	. . .	. . .	. . .	. . .	Platinum
2	54-60	14-18	1-8	7-11	11-14	1 max	2 max	Platinum
3	45-50	8-12	20-25	5-8	7-12	. . .	1 max	Platinum

4	62-64	7-13	6 max	9-16	7-14	2 max	1 max	Light gold
5	64-70	2-7	5 max	9-15	12-18	2 max	1 max	Gold
6	56-63	5 max	5 max	14-25	11-18	3 max	1 max	Gold
7	10-28	25 max	20-37	6-30	14-21	2 max	2 max	Platinum
8	. . .	1 max	42-44	38-41	16-17	1 max	. . .	Platinum

(a) Numbers are for identification in this article only.

(b) Fractional percentages of iridium, indium, and rhodium are omitted here.

Table 7 Composition limits of alloys used in dental castings

Alloy[(a)]	Type	Composition, wt%					
		Au	Ag	Cu	Pd	Pt	Zn
9	I[(b)]-soft	79-92.5	3-12	2-4.5	0.5 max	0.5 max	0.5 max
10	II[(b)]-medium	75-78	12-14.5	7-10	1 to 4	1 max	0.5
11	III[(b)]-hard	62-78	8-26	8-11	2 to 4	3 max	1
12	IV[(b)]-partial	60-71.5	4.5-20	11-16	5 max	8.5 max	1-2
13	Porcelain	83-88	0-1.3	. . .	4.5-6	4.0-16	. . .
14	Porcelain	49-52.5	12-16	. . .	25-30	. . .	. . .

(a) Numbers are for identification in this article only.

(b) American Dental Association Specification No. 5

Annealing Practice. The wrought alloys are typically annealed and quenched from 705 to 870 °C (1300 to 1600 °F). Aging of these alloys can be accomplished by cooling slowly and uniformly from 450 to 250 °C (840 to 480 °F). Manufacturer recommendations for each alloy must be carefully followed for specific mechanical properties. The cast gold alloys used in dentistry are annealed by heating to 705 °C (1300 °F) for 10 min and quenching in water. Reheating to

450 °C (840 °F) in about 30 min will produce maximum strength and hardness with loss of considerable ductility. Surface discoloration can be removed by pickling in 15% HC1 or hot 50% H_2SO_4.

Effect of Annealing and Aging. The annealed and aged physical and mechanical properties of wrought gold alloys for dental applications are presented in Table 8. The properties for the cast gold alloys are given in Table 9.

Table 8 Physical and mechanical properties of wrought high-strength precious-metal dental wires

See Table 6 for chemical compositions.

Alloy[(a)]	Tensile strength[(b)]				Proportional limit			
	Soft[(c)]		Hard[(d)]		Soft		Hard	
	MPa	ksi	MPa	ksi	MPa	ksi	MPa	ksi
1	860-1240	125-180	[(f)]	[(f)]	550-1035	80-150	[(f)]	[(f)]
2	760-895	110-130	1105-1280	160-186	495-705	72-102	895-1040	130-151
3	965-1035	140-150	1105-1170	160-170	760-825	110-120	895-965	130-140
4	620-795	90-115	825-1140	120-165	380-550	55-80	585-965	85-140
5	565-825	82-120	895-1140	130-165	365-505	53-73	710-960	103-139
6	580-690	84-100	660-1085	96-157	360-400	52-58	485-855	70-124
7	660-1020	96-148	1035-1325	150-192	415-795	60-115	760-1105	110-160
8	690-760	100-110	895-1170	130-170	435-600	63-87	740-875	107-127

Alloy[(a)]	Elongation, % (8-in. gage)		Hardness, HB[(e)]		Fusion temperature (wire method)		Specific gravity	
	Soft	Hardened	Soft	Hardened	°C	°F	g/cm^3	lb/in.^{3}
1	14-15	[(f)]	200-245	[(f)]	1500-1530	2730-2790	16.9-17.6	0.611-0.636
2	12-22	5-10	150-190	240-285	1005-1100	1840-2010	15.0-18.5	0.542-0.668
3	8-10	7-9	210-230	250-270	1065-1120	1950-2050	15.5-15.8	0.560-0.571
4	14-26	2-8	166-195	240-295	945-1015	1730-1860	14.5-15.6	0.524-0.564

5	14-20	1-3	135-200	230-290	900-930	1650-1710	14.1-15.2	0.509-0.549
6	20-28	1-2	138-170	220-280	875-900	1610-1650	13.7-14.0	0.495-0.506
7	9-20	1-8	150-225	180-270	940-1080	1725-1975	11.5-15.6	0.415-0.564
8	16-24	8-15	150-200	235-270	1045-1075	1910-1970	10.7-11.2	0.387-0.405

(a) Numbers are for identification in this article only.

(b) Tension tests on wires 1.0 mm (0.040 in.) in diam. Most elongation data on 8-in. gage lengths.

(c) Quenched from 705 to 870 °C (1300 to 1600 °F) depending on type of alloy.

(d) Cooled slowly and uniformly from 450 to 250 °C (840 to 480 °F) in 30 min. This is a severe hardening treatment used in testing to determine the behavior of wire under adverse conditions. Manufacturers recommend hardening treatments for specific uses.

(e) Brinell hardness numbers obtained with the Baby Brinell testing machine.

(f) Not appreciably affected by heat treatment

Table 9 Physical and mechanical properties of gold-alloy castings used in dentistry

Modulus of elasticity of these alloys ranges from 76 to 125 GPa (11 to 18 × 10^6 psi). See Table 7 for compositions of alloys.

Alloy[(a)]	Treatment[(b)]	Hardness, HB	Tensile strength		Proportional limit		Elongation, %	Liquidus temperature	
			MPa	ksi	MPa	ksi		°C	°F
9	Q	45-70	205-310	30-45	55-105	8-15	20-35	950-1050	1740-1920
10	Q	80-90	310-380	45-55	140-170	20-25	20-35	930-970	1705-1780
11	Q	95-115	330-395	48-57	160-205	23-30	20-25	950-1000	1740-1830
11	A	115-165	415-565	60-82	200-400	29-58	6-20	950-1000	1740-1830
12	Q	130-160	415-515	60-75	240-325	35-47	4-25	970-985	1600-1805
12	A	210-235	690-830	100-120	415-635	60-92	1-6	870-985	1600-1805
13	Q	155-175	460-515	67-75	415-485	60-70	4-6	1150-1190	2100-2175

13	A	175-190	. . .	. . .	. . .	. . .	. . .	1150-1190	2100-2175
14	Q	190-210	620-760	90-110	515-585	75-85	8-12	1240-1280	2265-2335
14	A	212-230	. . .	. . .	. . .	. . .	. . .	1240;-1280	2265-2335
15	Q	160-190	485-620	70-90	345-485	50-70	20-35	900-940	1650-1725
15	A	180-200	550-895	80-130	415-825	60-120	1-3	900-940	1650-1725

(a) Numbers are for identification in this article only.

(b) Q, quenched: A, aged

Gold-Palladium-Iron Alloys

Selected alloys within the gold-palladium-iron ternary system develop exceptionally high resistivity with proper heat treatment. There is a peak in the resistivity in the central area of the loops shown in Fig. 6. The maximum resistivity of 180 μ · cm (1100 · cmil/ft) is found after heat treatment at 49.5% Au, 40.5% Pd, and 10% Fe. These alloys are used primarily for potentiometer wire.

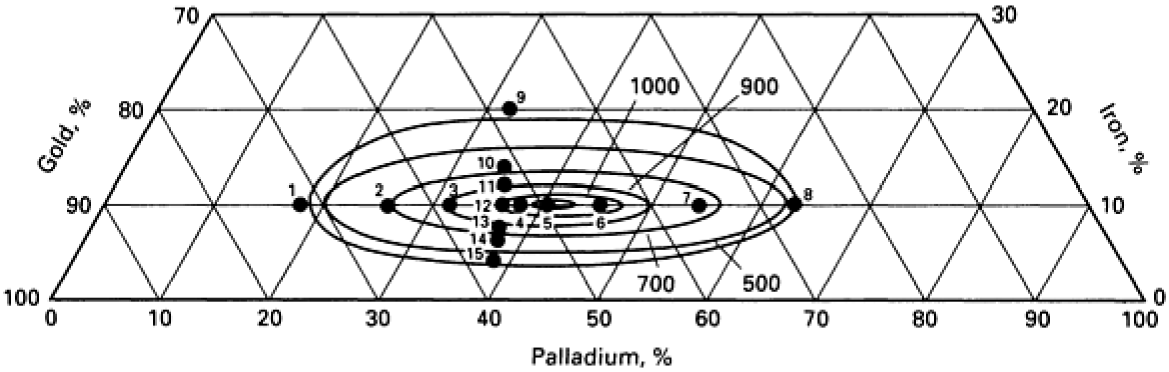

Fig. 6 Curves of equal resistivity for gold-platinum-iron alloys annealed 1 h at 500 °C (930 °F). Numbers from 1 to 15 refer to alloys for which resistivity is shown in Table 10. Numbers 500 to 1000 refer to resistivity values given in ohm · circular mils/ft

Annealing Practice. Peak resistivity is generally achieved by annealing cold worked material at 500 °C (930 °F) for 1 h. Higher temperatures result in lower resistivity values and lower temperatures require longer times to reach peak resistivity.

Effect of Annealing on Resistivity. Table 10 presents the resistivity of the alloys of Fig. 6 as cold worked (about 50%) and as annealed for 1 h at 500 °C (930 °F). The tensile strength of the peak resistivity alloy is 1380 MPa (200 ksi) as heat treated and 690 MPa (100 ksi) as cold worked.

Table 10 Electrical resistivity of gold-platinum-iron alloys shown in Fig. 6

Alloy	Cold worked		Annealed 1 h	
	μΩ· cm	Ω· cmil/ft	μΩ· cm	Ω· cmil/ft
1	71	430	75	455
2	76	460	110	670
3	76	460	155	920
4	76	460	174	1050
5	71	430	178	1070
6	70	420	174	1050
7	61	370	135	800
8	53	320	61	370
9	46	275	46	275
10	51	310	100	610
11	58	350	150	910
12	83	500	171	1030
13	78	470	145	860
14	74	445	90	545
15	61	365	65	390

Reference cited in this section

5. E.M. Wise, *Gold: Recovery, Properties, and Applications,* Van Nostrand, 1964, p 264

Platinum Group Elements and Alloys

The platinum group metals are used in a wide range of applications and product forms. Applications for wrought products include electrical contacts, brushes, precision potentiometer wire, laboratory ware, thermocouple alloys, catalysts, anodes, spinnerets, crucibles, sputter targets, spark plugs, igniters, fiberglass bushings, and magnets.

Platinum and Platinum Alloys

Platinum is the best known and least rare of the platinum group metals and has the widest range of uses because of its general corrosion resistance, high melting point, appearance, and ductility.

Annealing Practice. The annealing temperature range for platinum is 600 to 1000 °C (1110 to 1830 °F). The most common commercial annealing practice is torch annealing. The maintenance of oxidizing conditions throughout the anneal is essential to avoid contamination. Hot reducing atmospheres can contaminate pure platinum and contact with asbestos pads or charcoal is not recommended. Alumina supports work well. For high-purity wire and sheet, it is essential to remove iron contamination after processing and before annealing by pickling in hot hydrochloric acid. The entire range of platinum-palladium alloys can be annealed at 900 °C (1650 °F). However, the palladium-rich alloys should be annealed in inert or nitrogen atmospheres. Platinum-rhodium alloys containing 3.5 to 40% Rh are typically annealed between 900 and 1000 °C (1650 and 1830 °F). Platinum-iridium alloys containing 0.4 to 10% Ir are commonly annealed between 1000 and 1200 °C (1830 and 2190 °F). For alloys of higher iridium content, temperatures nearer 1400 °C (2550 °F) are recommended. Platinum alloys containing more than 10% Ir can be age hardened by quenching from 1700 °C (3090 °F) followed by heating to 805 °C (1480 °F). Pt-5% Ru can be annealed at 1000 °C (1830 °F) and Pt-10% Ru at 1100 °C (2010 °F).

Pt-23% Co and similar alloys close to the 50/50 atomic composition can be annealed by quenching from above the transformation temperature of 830 °C (1525 °F). Optimum magnetic properties can be developed in these materials by following quenching with a heat treatment designed to develop partial ordering in the system.

Effects of Annealing on Mechanical Properties. The hardness of commercially pure platinum (99.95% min) and chemically pure platinum (99.99% min) as a function of annealing temperature for various percent reductions is plotted in Fig. 7. The tensile strength and hardness of annealed and cold worked platinum-palladium compositions as a function of palladium content are given in Fig. 8 and 9. Table 11 presents the annealed and cold worked properties of the common platinum-rhodium alloys and Table 12 presents these properties for the common platinum-iridium alloys. Figure 10 shows the tensile strength of platinum-ruthenium alloys in the annealed and cold worked condition as a function of ruthenium content.

Table 11 Typical properties of platinum-rhodium alloys

% Rhodium and temper	Tensile strength		Elongation[a], %	Hardness, HB	Density		Electrical resistivity[b]		Temperature coefficient[c], per °C
	MPa	ksi			g/cm^3	lb/in.^{3}	nΩ · m	Ω· cmil/ft	
3.5% annealed	170	25	35	60	20.90	0.755	166	100	0.0022
3.5% hard[d]	415	60	. . .	120					
5.0% annealed	205	30	35	70	20.65	0.746	175	105	0.0020
5.0% hard[d]	485	70	. . .	130					
10% annealed	310	45	35	90	19.97	0.722	192	116	0.0017
10% hard[d]	620	90	2	165					
20% annealed	485	70	33	120	18.74	0.677	208	125	0.0014

20% hard[(d)]	895	130	2	210					
30% annealed	540	78	30	132	17.62	0.637	194	117	0.0013
30% hard[(d)]	1060	154	0.5	238					
40% annealed	565	82	30	150	16.63	0.601	175	105	0.0014
40% hard[(d)]	1255	182	0.5	290					

(a) In 50 mm (2 in.).

(b) At 20 °C (68 °F).

(c) Of electrical resistivity at 20 to 100 °C (68 to 212 °F).

(d) Hard, as cold worked, 75% reduction

Table 12 Typical properties of platinum-iridium alloys

Iridium, %	**Temper**	**Tensile strength**		**Hardness, HB**	**Density**		**Electrical resistivity**		**Temperature coefficient[(a)], per °C**
		MPa	**ksi**		**g/cm^3**	**lb/in.^{3}**	**nΩ · m**	**Ω· cmil/ft**	
5	Annealed	275	40	90	21.49	0.776	190	115	0.00188
5	Hard	485	70	140					
10	Annealed	380	55	130	21.53	0.778	250	150	0.00126
10	Hard	620	90	185					
15	Annealed	515	75	160	21.57	0.779	285[(b)]	170[(b)]	0.00102
15	Hard	825	120	230					
20	Annealed	690	100	200	21.61	0.781	310	185	0.00081
20	Hard	1000	145	265					

25	Annealed	860	125	240	21.66	0.783	330	200	0.00066
25	Hard	1170	170	310					
30	Annealed	1105	160	280	21.70	0.784	350	210	0.00058
30	Hard	1380	200	360					
35	Annealed	. . .	. . .	. . .	21.79	0.787	360	215	0.00058
35	Hard	. . .	. . .	. . .					

(a) Of electrical resistivity at 0 to 160 °C (32 to 320 °F).

(b) By interpolation

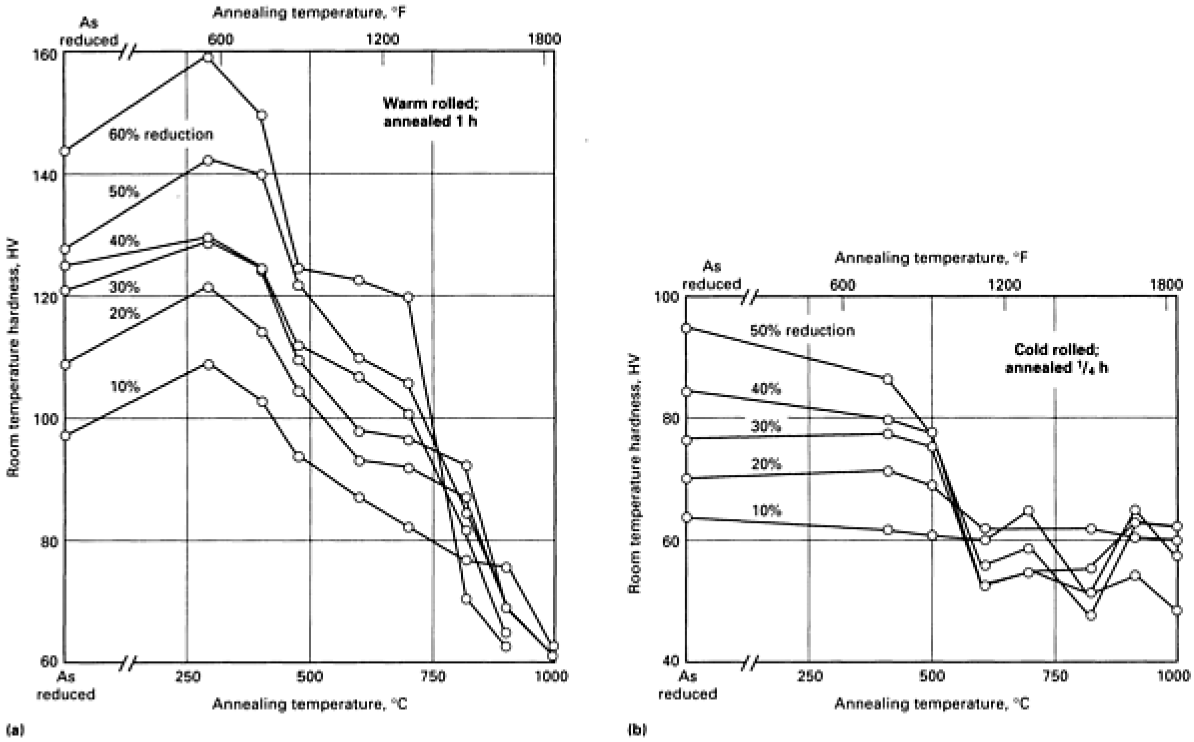

Fig. 7 The hardness of platinum as a function of annealing temperature and percent reduction. (a) Commercially pure (99.85% min). (b) Chemically pure (99.99% min)

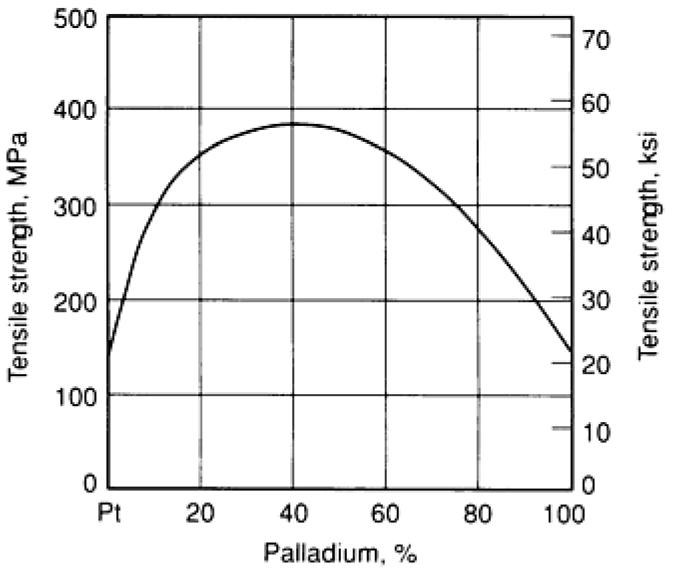

Fig. 8 Tensile strength of annealed platinum-palladium alloys as a function of palladium content

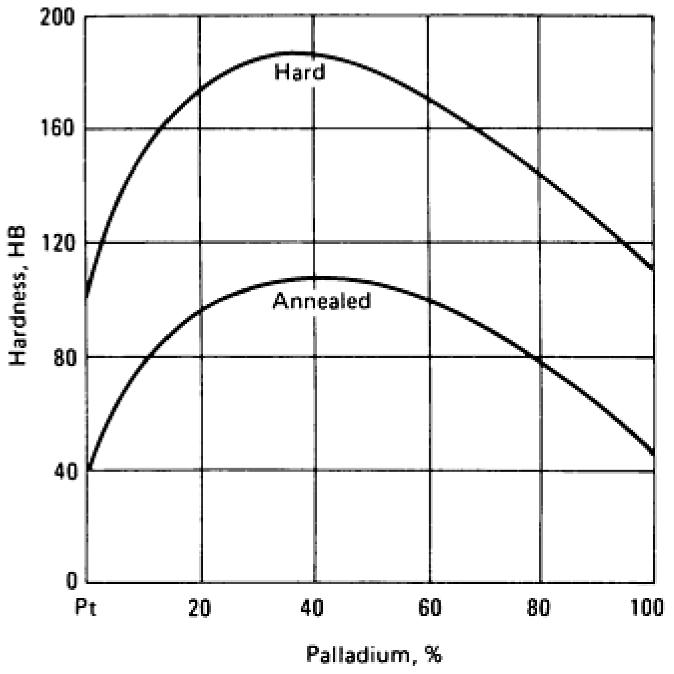

Fig. 9 Hardness of platinum-palladium alloys as a function of palladium content

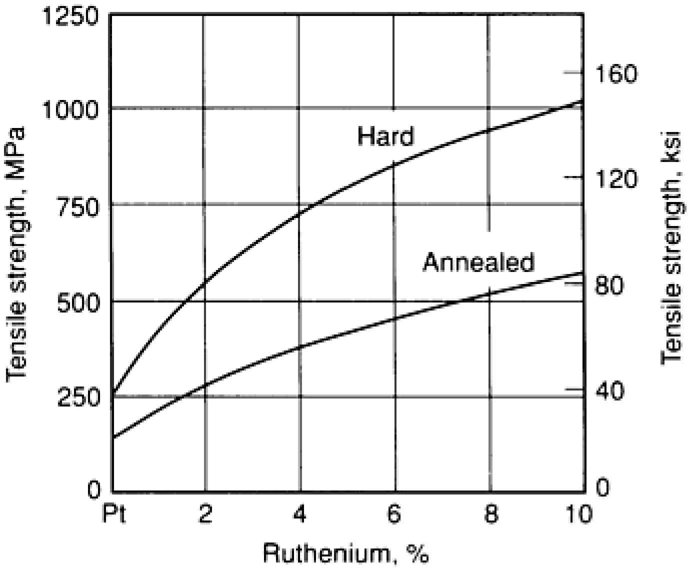

Fig. 10 Tensile strength of platinum-ruthenium alloys as a function of ruthenium content. Alloys initially reduced by 75%, then annealed 15 rain at 1000 to 1100 °C (1830 to 2010 °F)

Palladium and Palladium Alloys

While palladium resembles platinum in appearance and tensile properties, its corrosion resistance and melting point are lower. The major use of palladium and its alloys has been for contacts in light-duty relays, where its freedom from tarnish and cold fusion provides extreme reliability and noise-free transmission. Palladium hardened with ruthenium provides an all precious metal white jewelry alloy that sets off diamonds to advantage.

Palladium dental casting alloys have, to a great extent, replaced the high gold dental casting alloys as the material of choice for porcelain bonding and other dental restoration work. Palladium-silver alloys are used for the production of high-purity hydrogen by taking advantage of the selective high diffusion rate of this gas through the alloy.

Annealing Practice. Commercially pure palladium (99.85% min) can be annealed at about 800 °C (1470 °F). Nitrogen-hydrogen mixtures, nitrogen, argon, or steam provide a suitable annealing atmosphere. Slow cooling in air from 815 °C (1500 °F) to 425 °C (800 °F) will cause a blue oxide film to form. To avoid this, the metal should be quenched in water or cooled in a nitrogen atmosphere. Cooling in hydrogen will cause a phase change to occur with accompanying distortions. Alloys in the palladium-silver-copper system can be annealed at about 800 °C (1470 °F) in nitrogen. The age hardenable alloys in this system (see Fig. 11) should be cooled fairly rapidly for maximum softness. If much zinc is present, oil quenching may be required. Treatment for $\frac{1}{4}$ to 5 h between 400 and 500 °C (750 and 930 °F) hardens most of these alloys effectively. Alloys in the palladium-silver-gold system can be annealed at 850 °C (1560 °F) in nitrogen. Pd-4.5% Ru is effectively annealed in a N_2-36.7% H_2 atmosphere at 900 °C (1650 °F).

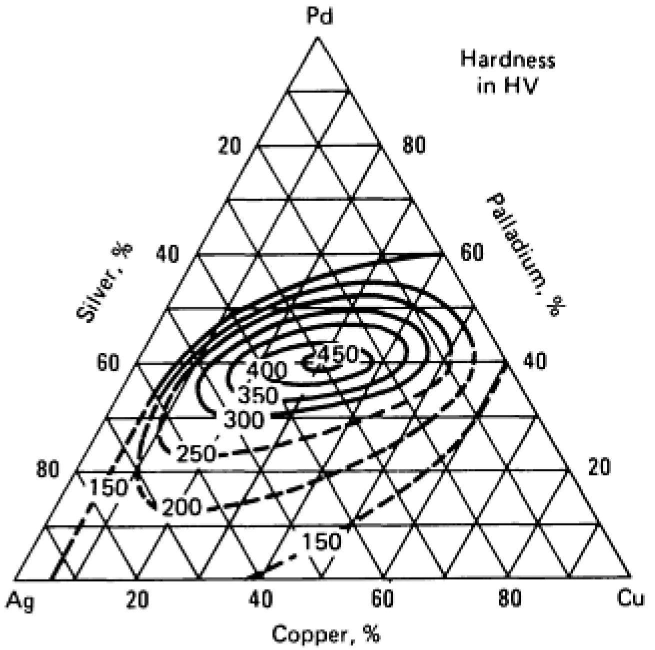

Fig. 11 Maximum hardness of aged palladium-silver-copper alloys

Effect of Annealing on Mechanical Properties. The tensile properties of cold drawn deoxidized palladium as a function of annealing temperature are presented in Fig. 12. The hardness of commercially pure (99.85% min) and chemically pure (99.99% min) palladium versus annealing temperature are given in Fig. 13 for various degrees of reduction. The tensile strength and hardness of annealed and cold worked palladium-silver alloys as a function of silver content are shown in Fig. 14. The maximum hardness of aged palladium-silver-copper alloys is shown in Fig. 15. The effect of annealing temperature on the tensile properties of Pd-4.5% Ru are shown in Fig. 16.

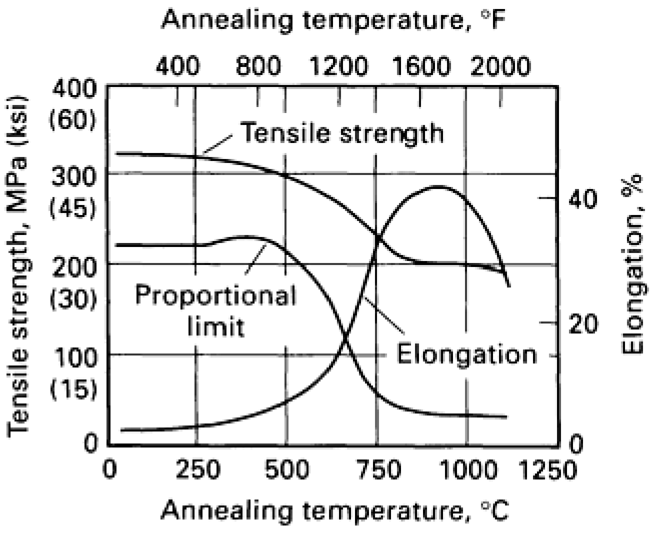

Fig. 12 Tensile properties of cold drawn deoxidized palladium as a function of annealing temperature (held for 5 min)

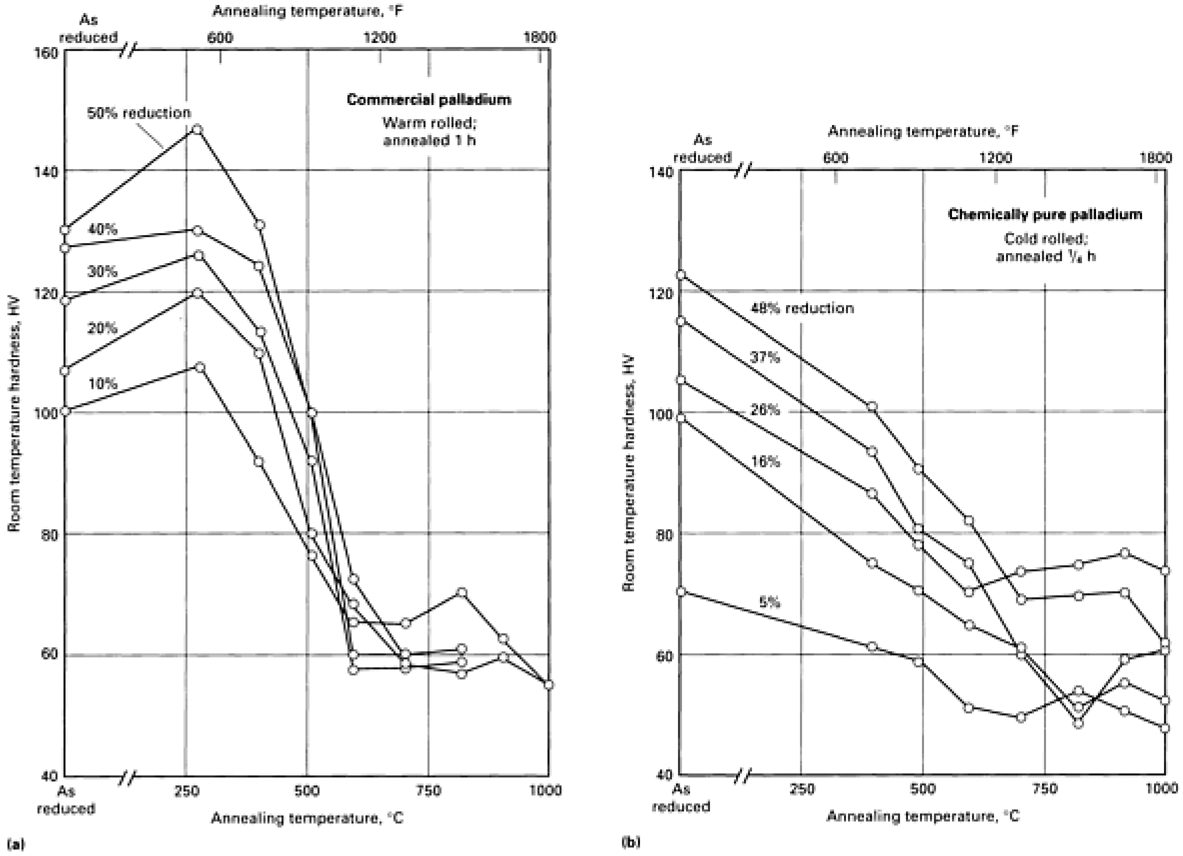

Fig. 13 The hardness of palladium as a function of annealing temperature and percent reduction. (a) Commercially pure (99.85% min). (b) Chemically pure (99.99% min)

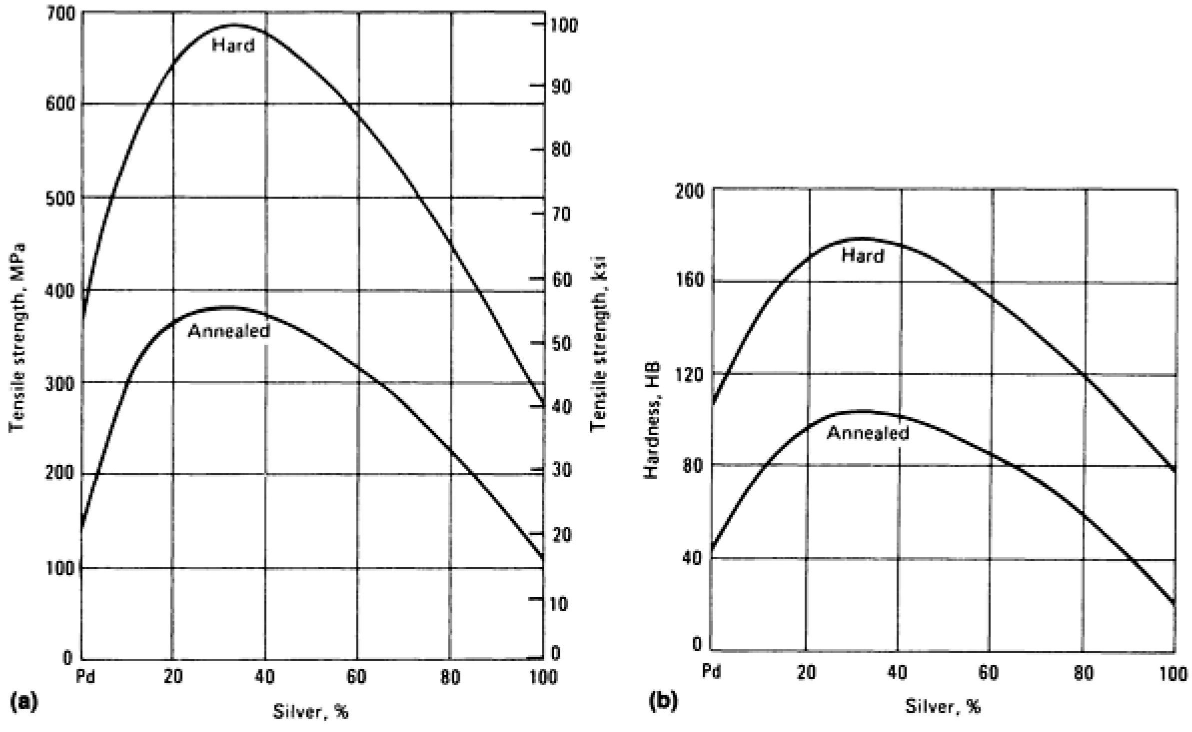

Fig. 14 Plot of mechanical properties of palladium-silver alloys as a function of silver content. (a) Tensile

strength. (b) Hardness

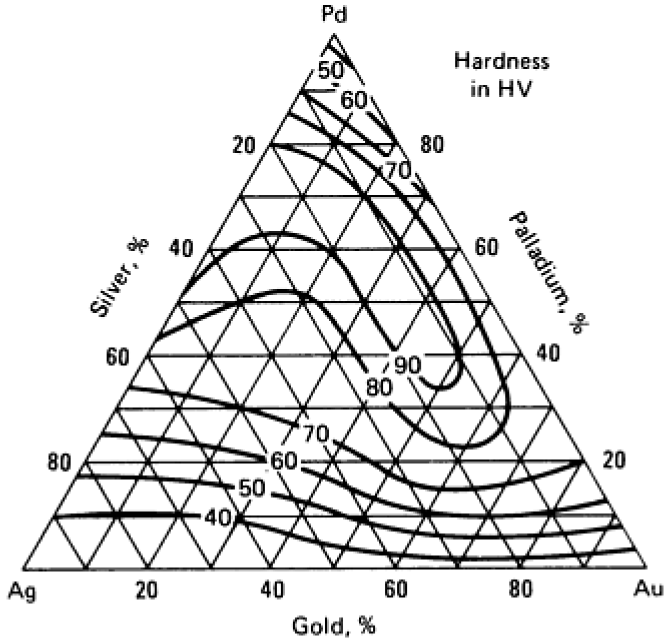

Fig. 15 Maximum hardness of annealed palladium-silver-gold alloys

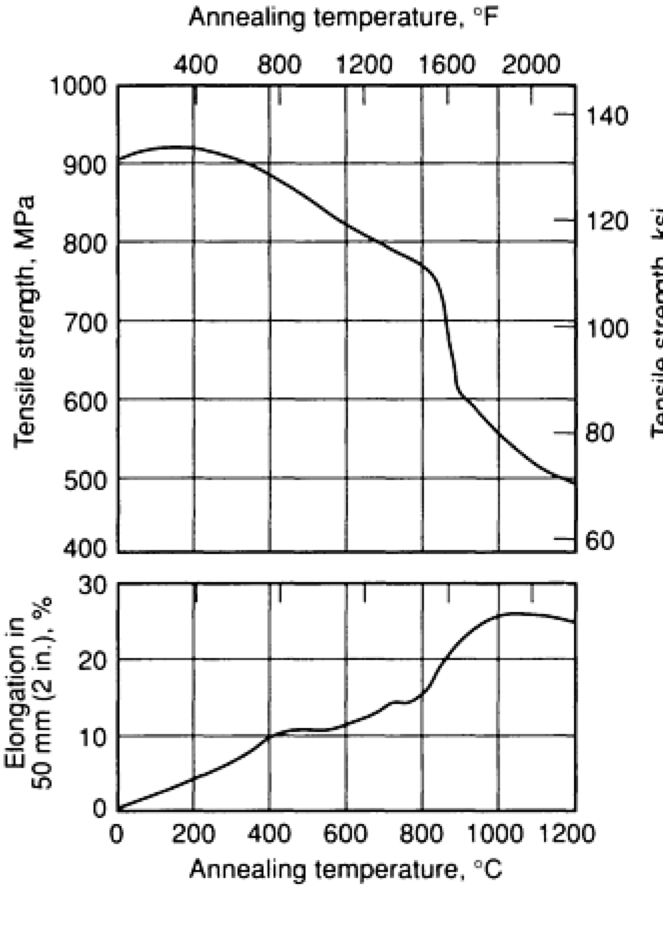

Fig. 16 Effect of annealing temperature on the tensile properties of Pd-4.5Ru

Rhodium, Iridium, and Ruthenium

Wrought products of these elements are produced although not to the extent that platinum and palladium are produced. Iridium and rhodium can be produced using arc melting and electron-beam (EB) furnaces. These elements can be produced using powder metallurgy, although generally only ruthenium is fabricated via powder metallurgy.

Annealing Practice. These elements must be annealed in an inert atmosphere or vacuum to prevent oxidation. Commercial iridium and ruthenium can be annealed at 1315 °C (2400 °F).

Effect of Annealing on Hardness. The hardness of commercial rhodium, iridium, and ruthenium as a function of annealing temperature for varying degrees of cold work is given in Fig. 17.

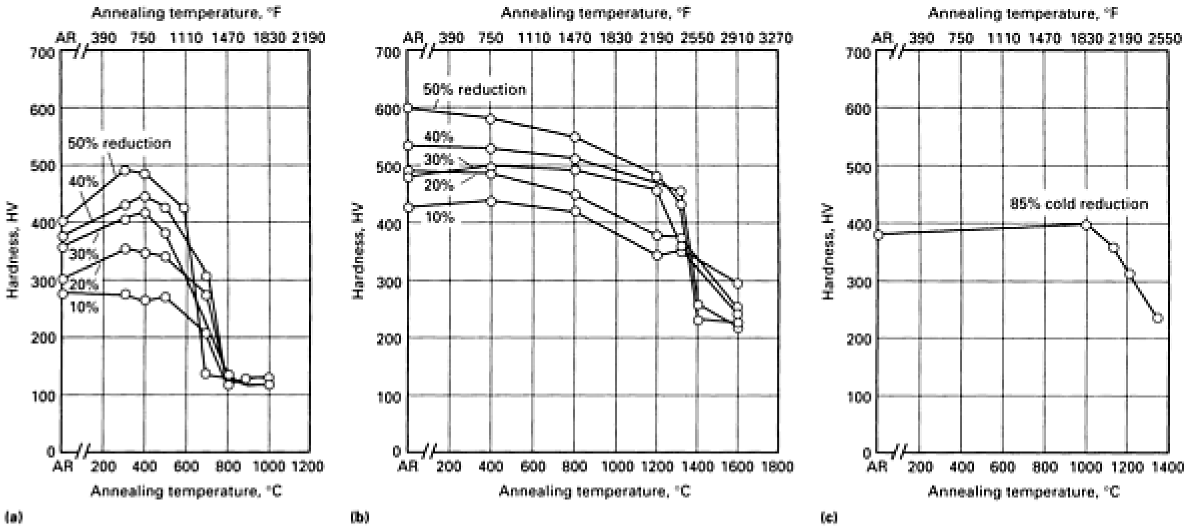

Fig. 17 Plot of hardness versus annealing temperature (held for 1 h) for varying degrees of cold work of selected noble metals. (a) Commercial rhodium. (b) Commercial iridium. (c) Electron-beam-melted ruthenium. AR, as-rolled. Source: Ref 6

Reference cited in this section

6. R.W. Douglass, C.A. Krier, and R.I. Jaffee, Report from Battelle Memorial Institute to Office of Naval Research, 31 August 1961

Introduction

It is common and long-time knowledge that steel heated in contact with air at temperatures in the tempering range takes on various temper colors due to the formation of a thin oxide film. There is, however, little detailed information on this phenomenon in the readily available literature. As an example, the 1948 ASM *Metals Handbook* gives the following table:

Heating temperature, °F	Color
400	Faint straw
440	Straw
475	Deep straw
520	Bronze
540	Peacock
590	Full blue
640	Light blue

Temper Colors

In the course of a research program at the Illinois Institute of Technology, it became desirable to have more detailed information on temper colors for plain carbon steel, especially on the effect of time and temperature. This was obtained using 16 mm ($\frac{5}{8}$ in.) diam hot-rolled bars of a standard SAE 1035 steel. Samples that were 50 mm (2 in.) long were cut from the bars and carefully machined and cleaned to give smooth, bright surfaces. They were then heated for various times at several temperatures in air-circulating furnaces controlled to within ±3 °C (±5 °F) of the desired temperatures. The results of this study are shown in Fig. 1.

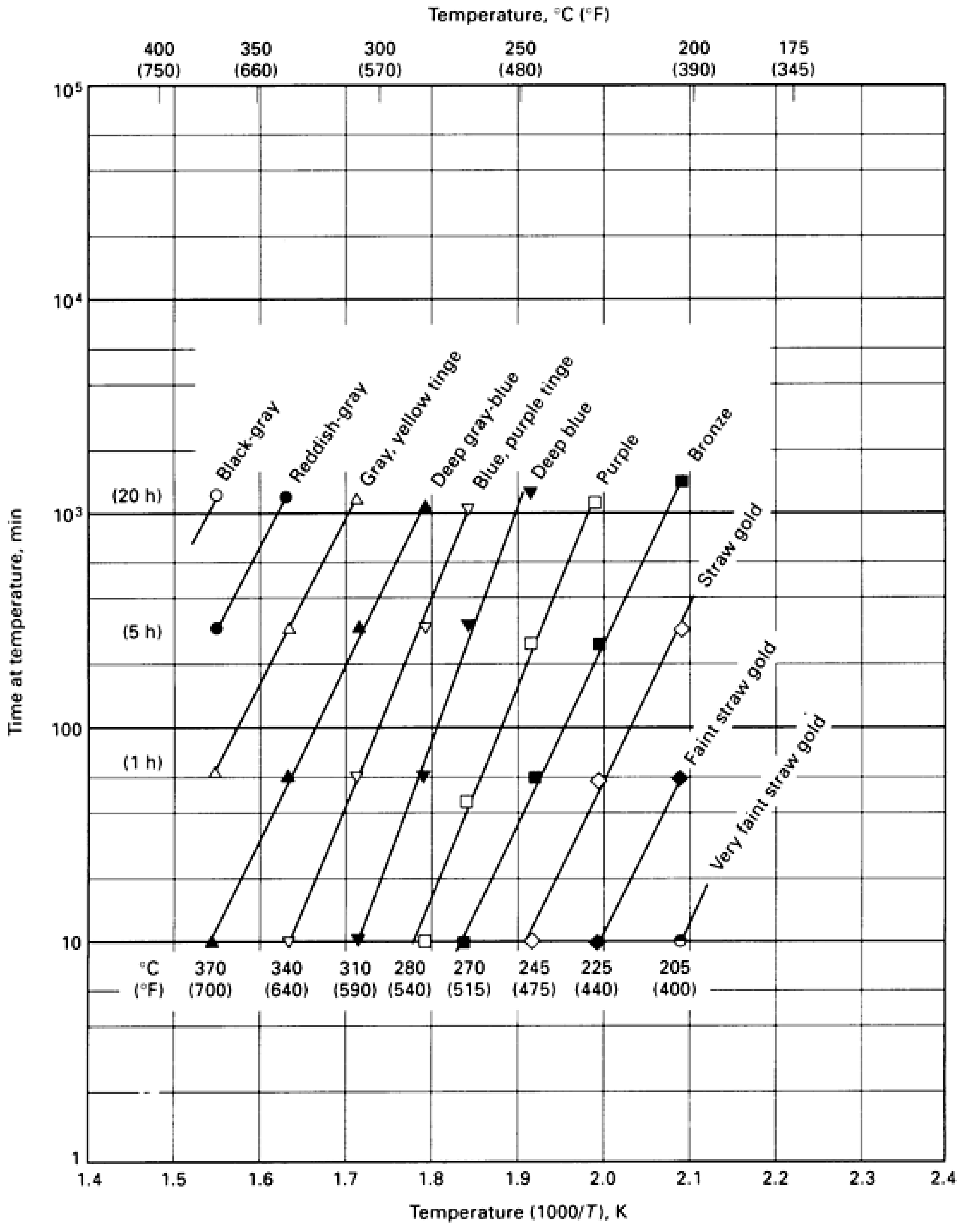

Fig. 1 Temper colors after heating 1035 steel in circulating air (atmospheric pressure)

Austenitizing Temperatures for Steels

Introduction

Temperatures recommended for austenitizing carbon and low-alloy steels prior to hardening are given in Table 1 (for direct-hardening grades) and Table 2 (for carburized steels). Table 2 is applicable to carburized steels that have been cooled slowly from the carburizing temperature and are to be furnace hardened in a subsequent operation.

Table 1 Austenitizing temperatures for direct-hardening carbon and alloy steels (SAE)

Steel	Temperature	
	°C	°F
Carbon steels		
1025	855-900	1575-1650
1030	845-870	1550-1600
1035	830-855	1525-1575
1037	830-855	1525-1575
1038[(a)]	830-855	1525-1575
1039[(a)]	830-855	1525-1575
1040[(a)]	830-855	1525-1575
1042	800-845	1475-1550
1043[(a)]	800-845	1475-1550
1045[(a)]	800-845	1475-1550
1046[(a)]	800-845	1475-1550
1050[(a)]	800-845	1475-1550
1055	800-845	1475-1550
1060	800-845	1475-1550
1065	800-845	1475-1550
1070	800-845	1475-1550
1074	800-845	1475-1550

1078	790-815	1450-1500
1080	790-815	1450-1500
1084	790-815	1450-1500
1085	790-815	1450-1500
1086	790-815	1450-1500
1090	790-815	1450-1500
1095	790-815[a]	1450-1500[b]
Free-cutting carbon steels		
1137	830-855	1525-1575
1138	815-845	1500-1550
1140	815-845	1500-1550
1141	800-845	1475-1550
1144	800-845	1475-1550
1145	800-845	1475-1550
1146	800-845	1475-1550
1151	800-845	1475-1550
1536	815-845	1500-1550
1541	815-845	1500-1550
1548	815-845	1500-1550
1552	815-845	1500-1550
1566	855-885	1575-1625

Alloy steels		
1330	830-855	1525-1575
1335	815-845	1500-1550
1340	815-845	1500-1550
1345	815-845	1500-1550
3140	815-845	1500-1550
4037	830-855	1525-1575
4042	830-855	1525-1575
4047	815-855	1500-1575
4063	800-845	1475-1550
4130	815-870	1500-1600
4135	845-870	1550-1600
4137	845-870	1550-1600
4140	845-870	1550-1600
4142	845-870	1550-1600
4145	815-845	1500-1550
4147	815-845	1500-1550
4150	815-845	1500-1550
4161	815-845	1500-1550
4337	815-845	1500-1550
4340	815-845	1500-1550

50B40	815-845	1500-1550
50B44	815-845	1500-1550
5046	815-845	1500-1550
50B46	815-845	1500-1550
50B50	800-845	1475-1550
50B60	800-845	1475-1550
5130	830-855	1525-1575
5132	830-855	1525-1575
5135	815-845	1500-1550
5140	815-845	1500-1550
5145	815-845	1500-1550
5147	800-845	1475-1550
5150	800-845	1475-1550
5155	800-845	1475-1550
5160	800-845	1475-1550
51B60	800-845	1475-1550
50100	775-800[c]	1425-1475[c]
51100	775-800[c]	1425-1475[c]
52100	775-800[c]	1425-1475[c]
6150	845-885	1550-1625
81B45	815-855	1500-1575

8630	830-870	1525-1600
8637	830-855	1525-1575
8640	830-855	1525-1575
8642	815-855	1500-1575
8645	815-855	1500-1575
86B45	815-855	1500-1575
8650	815-855	1500-1575
8655	800-845	1475-1550
8660	800-845	1475-1550
8740	830-855	1525-1575
8742	830-855	1525-1575
9254	815-900	1500-1650
9255	815-900	1500-1650
9260	815-900	1500-1650
94B30	845-885	1550-1625
94B40	845-885	1550-1625
9840	830-855	1525-1575

(a) Commonly used on parts where induction hardening is employed. All steels from SAE 1030 up may have induction hardening applications.

(b) This temperature range may be employed for 1095 steel that is to be quenched in water, brine, or oil. For oil quenching, 1095 steel may alternatively be austenitized in the range 815 to 870 °C (1500 to 1600 °F).

(c) This range is recommended for steel that is to be water quenched. For oil quenching, steel should be austenitized in the range 815 to 870 °C (1500 to 1600 °F).

Table 2 Reheating (austenitizing) temperatures for hardening of carburized carbon and alloy steels (SAE)

Carburizing is commonly carried out at 900 to 925 °C (1650 to 1700 °F); slow cooled and reheated to given austenizing temperature.

Steel	**Temperature**	
	°C	**°F**
Carbon steels		
1010	760-790	1400-1450
1012	760-790	1400-1450
1015	760-790	1400-1450
1016	760-790	1400-1450
1017	760-790	1400-1450
1018	760-790	1400-1450
1019	760-790	1400-1450
1020	760-790	1400-1450
1022	760-790	1400-1450
1513	760-790	1400-1450
1518	760-790	1400-1450
1522	760-790	1400-1450
1524	760-790	1400-1450
1525	760-790	1400-1450
1526	760-790	1400-1450
1527	760-790	1400-1450
Free-cutting carbon steels		

1109	760-790	1400-1450
1115	760-790	1400-1450
1117	760-790	1400-1450
1118	760-790	1400-1450
Alloy steels		
3310	790-830	1450-1525
4320	830-845	1525-1550
4615	815-845	1500-1550
4617	815-845	1500-1550
4620	815-845	1500-1550
4621	815-845	1500-1550
4626	815-845	1500-1550
4718	815-845	1500-1550
4720	815-845	1500-1550
4815	800-830	1475-1525
4817	800-830	1475-1525
4820	800-830	1475-1525
8115	845-870	1550-1600
8615	845-870	1550-1600
8617	845-870	1550-1600
8620	845-870	1550-1600

8622	845-870	1550-1600
8625	845-870	1550-1600
8627	845-870	1550-1600
8720	845-870	1550-1600
8822	845-870	1550-1600
9310	790-830	1450-1525

For most applications, the rate of heating to the austenitizing temperature is less important than other factors in the hardening process, such as maximum temperature attained throughout the section, temperature uniformity, time at temperature, and rate of cooling. The thermal conductivity of the steel, the nature of the furnace atmosphere (scaling or nonscaling), thickness of section, method of loading (spaced or stacked), and the degree of circulation of the furnace atmosphere all influence the rate of heating of the steel part to the required temperature selected from Tables 1 and 2.

Temperature Rise

The difference in temperature rise within thick and thin sections of articles of varying cross section is a major problem in practical heat-treating operations. When temperature uniformity is the ultimate objective of the heating cycle, this is more safely attained by slowly heating than by rapidly heating. Furthermore, the maximum temperature in the austenite range should not exceed that required to achieve the necessary extent of solution of carbide. The temperatures listed in Tables 1 and 2 conform with this requirement. When heating with significant cross-section variations, provisions should be made for slower heating to minimize thermal stresses and distortions.

Glossary of Terms

- **A**

- **A_{cm}, A_1, A_3, A_4**
  - Same as Ae_{cm}, Ae_1, and Ae_3 and Ae_4.
- **Ac_{cm}, Ac_1, Ac_3, Ac_4**
  - Defined under transformation temperature .
- **acicular ferrite**
  - A highly substructured non-equiaxed ferrite that forms upon continuous cooling by a mixed diffusion and shear mode of transformation that begins at a temperature slightly higher than the temperature transformation range for upper bainite. It is distinguished from bainite in that it has a limited amount of carbon available; thus, there is only a small amount of carbide present.
- **Ae_{cm}, Ae_1, Ae_3, Ae_4**
  - Defined under transformation temperature .
- **aerated bath nitriding**
  - A type of liquid nitriding in which air is pumped through the molten bath creating agitation and increased chemical activity.
- **age hardening**
  - Hardening by aging, usually after rapid cooling or cold working. See aging .
- **age softening**
  - Spontaneous decrease of strength and hardness that takes place at room temperature in certain strain hardened alloys, especially those of aluminum.

- **aging**
  - A change in the properties of certain metals and alloys that occurs at ambient or moderately elevated temperatures after hot working or a heat treatment (quench aging in ferrous alloys, natural or artificial aging in ferrous and nonferrous alloys) or after a cold working operation (strain aging). The change in properties is often, but not always, due to a phase change (precipitation), but never involves a change in chemical composition of the metal or alloy. See also age hardening , artificial aging , interrupted aging , natural aging , overaging , precipitation hardening , precipitation heat treatment , progressive aging , quench aging , step aging .
- **air-hardening steel**
  - A steel containing sufficient carbon and other alloying elements to harden fully during cooling in air or other gaseous mediums from a temperature above its transformation range. The terms should be restricted to steels that are capable of being hardened by cooling in air in fairly large sections, about 2 in. (50 mm) or more in diameter. Same as self-hardening steel.
- **allotropy**
  - A near synonym for polymorphism . Allotropy is generally restricted to describing polymorphic behavior in elements, terminal phases, and alloys whose behavior closely parallels that of the predominant constituent element.
- **alpha ferrite**
  - See ferrite .
- **alpha iron**
  - The body-centered cubic form of pure iron, stable below 910 °C (1670 °F).
- **annealing**
  - A generic term denoting a treatment, consisting of heating to and holding at a suitable temperature followed by cooling at a suitable rate, used primarily to soften metallic materials, but also to simultaneously produce desired changes in other properties or in microstructure. The purpose of such changes may be, but is not confined to: improvement of machinability, facilitation of cold work, improvement of mechanical or electrical properties, and/or increase in stability of dimensions. When the term is used without qualification, full annealing is implied. When applied only for the relief of stress, the process is properly called stress relieving or stress-relief annealing.

    In ferrous alloys, annealing usually is done above the upper critical temperature, but the time-temperature cycles vary widely in both maximum temperature attained and in cooling rate employed, depending on composition, material condition, and results desired. When applicable, the following commercial process names should be used: black annealing , blue annealing , box annealing , bright annealing , cycle annealing , flame annealing , full annealing , graphitizing , intercritical annealing , isothermal annealing , malleablizing , order hardening , process annealing , quench annealing , spheroidizing , subcritical annealing .

    In nonferrous alloys, annealing cycles are designed to: (a) remove part or all of the effects of cold working (recrystallization may or may not be involved); (b) cause substantially complete coalescence of precipitates from solid solution in relatively coarse form; or (c) both, depending on composition and material condition. Specific process names in commercial use are final annealing , full annealing , intermediate annealing , partial annealing , recrystallization annealing , stress relieving ,anneal to temper .
- **annealing carbon**
  - Fine, apparently amorphous carbon particles formed in white cast iron and certain steels during prolonged annealing. Also called temper carbon.
- **annealing twin**
  - A twin form in a crystal during recrystallization.
- **anneal to temper**
  - A final partial anneal that softens a cold worked nonferrous alloy to a specified level of hardness or tensile strength.
- **Ar_{cm}, Ar_1, Ar_3, Ar_4, Ar', Ar''**
  - Defined under transformation temperature .
- **artificial aging**
  - Aging above room temperature. See aging . Compare with natural aging .

- **athermal transformation**
  - A reaction that proceeds without benefit of thermal fluctuations; that is, thermal activation is not required. In contrast, a reaction that occurs at constant temperature is an isothermal transformation ; thermal activation is necessary in this case and the reaction proceeds as a function of time.
- **ausforming**
  - Thermomechanical treatment of steel in the metastable austenitic condition below the recrystallization temperature followed by quenching to obtain martensite and/or bainite.
- **austempering**
  - A heat treatment for ferrous alloys in which a part is quenched from the austenitizing temperature at a rate fast enough to avoid formation of ferrite or pearlite and then held at a temperature just above M_s until transformation to bainite is complete. Although designated as bainite in both austempered steel and austempered ductile iron (ADI), austempered steel consists of two phase mixtures containing ferrite and carbide, while austempered ductile iron consists of two phase mixtures containing ferrite and austenite.
- **austenite**
  - A solid solution of one or more elements in face-centered cubic iron. Unless otherwise designated (such as nickel austenite), the solute is generally assumed to be carbon.
- **austenitic grain size**
  - The size attained by the grains of steel when heated to the austenitic region; may be revealed by appropriate etching of cross sections after cooling to room temperature.
- **austenitizing**
  - Forming austenite by heating a ferrous alloy into the transformation range (partial austenitizing) or above the transformation range (complete austenitizing). When used without qualification, the term implies complete austenitizing.
- **B**
- **bainite**
  - A metastable aggregate consisting of dispersed carbide in ferrite resulting from the transformation of austenite at temperatures below the pearlite range but above M_s. Its appearance is in the form of relatively coarse ferrite laths between which carbides are precipitated as platelets if formed in the upper part of the bainite transformation range; acicular, resembling tempered martensite, if formed in the lower part.
- **bainitic hardening**
  - Quench-hardening treatment resulting principally in the formation of bainite .
- **batch furnace**
  - A furnace used to heat treat a single load at a time. Batch-type furnaces are necessary for large parts such as heavy forgings and are preferred for complex alloy grades requiring long cycles. See car furnace , horizontal batch furnace .
- **belt furnace**
  - A continuous-type furnace which uses a mesh-type or cast-link belt to carry parts through the furnace.
- **beta annealing**
  - Producing a beta phase by heating certain titanium alloys in the temperature range of which this phase forms followed by cooling at an appropriate rate to prevent its decomposition.
- **black annealing**
  - Box annealing or pot annealing ferrous alloy sheet, strip, wire to impart a black color to the oxidized surface. See box annealing .
- **black oxide**
  - A black finish on a metal produced by immersing it in hot oxidizing salts or salt solutions.
- **blank carburizing**
  - Simulating the carburizing operation without introducing carbon. This is usually accomplished by using an inert material in place of the carburizing agent, or by applying a suitable protective coating to the ferrous alloy.
- **blank nitriding**
  - Simulating the nitriding operation without introducing nitrogen. This is usually accomplished by using an inert material in place of the nitriding agent or by applying a suitable protective coating to the ferrous alloy.
- **blue annealing**

- Heating hot-rolled ferrous sheet in an open furnace to a temperature within the transformation range and then cooling in air, in order to soften the metal. The formation of a bluish oxide on the surface is incidental.

- **blue brittleness**
  - Brittleness exhibited by some steels after being heated to some temperature within the range of about 205 to 370 °C (400 to 700 °F), particularly if the steel is worked at the elevated temperature. Killed steels are virtually free of this kind of brittleness.
- **bluing**
  - Subjecting the scale-free surface of a ferrous alloy to the action of air, steam, or other agents at a suitable temperature, thus forming a thin blue film of oxide and improving the appearance and resistance to corrosion. Note: This term is ordinarily applied to sheet, strip, or finished parts. It is used also to denote the heating of springs after fabrication to improve their properties.
- **boriding**
  - Thermochemical treatment involving the enrichment of the surface layer of an object with borides. This surface-hardening process is performed below the Ac_1 temperature.
- **boronizing**
  - See boriding .
- **box annealing**
  - Annealing a metal or alloy in a sealed container under conditions that minimize oxidation. In box annealing a ferrous alloy, the charge is usually heated slowly to a temperature below the transformation range, but sometimes above or within it, and is then cooled slowly; this process is also called close annealing or pot annealing. See black annealing .
- **breaks**
  - Creases or ridges usually in "untempered" or in aged material where the yield point has been exceeded. Depending on the origin of the break, it may be termed a cross break, a coil break, an edge break, or a sticker break.
- **bright annealing**
  - Annealing in a protective medium to prevent discoloration of the bright surface.
- **bright nitriding**
  - Nitriding in a protective medium to prevent discoloration of the bright surface. Compare with blank nitriding .
- **brine quenching**
  - A quench in which brine (salt water-chlorides, carbonates, and cyanides) is the quenching medium. The salt addition improves the efficiency of water at the vapor phase or hot stage of the quenching process.
- **brittle fracture**
  - Separation of a solid accompanied by little or no macroscopic plastic deformation. Typically, brittle fracture occurs by rapid crack propagation with less expenditure of energy than for ductile fracture .
- **burning**
  - (1) Permanently damaging a metal or alloy by heating to cause either incipient melting or intergranular oxidation. See overheating , grain-boundary liquation. (2) In grinding, getting the work hot enough to cause discoloration or to change the microstructure by tempering or hardening.
- **C**
- **calorizing**
  - Imparting resistance to oxidation to an iron or steel surface by heating in aluminum powder at 800 to 1000 °C (1470 to 1830 °F).
- **carbonitriding**
  - A case hardening process in which a suitable ferrous material is heated above the lower transformation temperature in a gaseous atmosphere of such composition as to cause simultaneous absorption of carbon and nitrogen by the surface and, by diffusion, create a concentration gradient. The process is completed by cooling at a rate that produces the desired properties in the workpiece.
- **carbonization**
  - Conversion of an organic substance into elemental carbon. (Should not be confused with car*bur*ization.)
- **carbon potential**

- A measure of the ability of an environment containing active carbon to alter or maintain, under prescribed conditions, the carbon level of the steel. Note: In any particular environment, the carbon level attained will depend on such factors as temperature, time, and steel composition.

- **carbon restoration**
  - Replacing the carbon lost in the surface layer from previous processing by carburizing this layer to substantially the original carbon level. Sometimes called recarburizing.
- **carburizing**
  - Absorption and diffusion of carbon into solid ferrous alloys by heating, to a temperature usually above Ac_3, in contact with a suitable carbonaceous material. A form of case hardening that produces a carbon gradient extending inward from the surface, enabling the surface layer to be hardened either by quenching directly from the carburizing temperature or by cooling to room temperature, then reaustenitizing and quenching.
- **carburizing flame**
  - A gas flame that will introduce carbon into some heated metals, as during a gas welding operation. A carburizing flame is a reducing flame , but a reducing flame is not necessarily a carburizing flame.
- **car furnace**
  - A batch-type furnace using a car on rails to enter and leave the furnace area. Car furnaces are used for lower stress relieving ranges.
- **case**
  - That portion of a ferrous alloy, extending inward from the surface, whose composition has been altered so that it can be case hardened. Typically considered to be the portion of the alloy (a) whose composition has been measurably altered from the original composition, (b) that appears dark on an etched cross section, or (c) that has a hardness, after hardening, equal to or greater than a specified value. Contrast with core .
- **case hardening**
  - A generic term covering several processes applicable to steel that change the chemical composition of the surface layer by absorption of carbon, nitrogen, or a mixture of the two and, by diffusion, create a concentration gradient. The processes commonly used are carburizing and quench hardening; cyaniding; nitriding; and carbonitriding. The use of the applicable specific process name is preferred.
- **caustic quenching**
  - Quenching with aqueous solutions of 5 to 10% sodium hydroxide (NaOH).
- **CCT diagram**
  - See continuous cooling transformation diagram .
- **cementation**
  - The introduction of one or more elements into the outer portion of a metal object by means of diffusion at high temperature.
- **cementite**
  - A compound of iron and carbon, known chemically as iron carbide and having the approximate chemical formula Fe_3C. It is characterized by an orthorhombic crystal structure. When it occurs as a phase in steel, the chemical composition will be altered by the presence of manganese and other carbide-forming elements.
- **checks**
  - Numerous, very fine cracks in a coating or at the surface of a metal part. Checks may appear during processing or during service and are most often associated with thermal treatment or thermal cycling. Also called check marks, checking, heat checks.
- **close annealing**
  - Same as box annealing .
- **coalescence**
  - Growth of grains at the expense of the remainder by absorption or the growth of a phase or particle at the expense of the remainder by absorption or reprecipitation.
- **coarsening**
  - An increase in the grain size, usually, but not necessarily, by grain growth .
- **coherent precipitate**
  - A crystalline precipitate that forms from solid solution with an orientation that maintains continuity between the crystal lattice of the precipitate and the lattice of the matrix, usually

accompanied by some strain in both lattices. Because the lattices fit at the interface between precipitate and matrix, there is no discernible phase boundary.

- **cold die quenching**
  - A quench utilizing cold, flat, or shaped dies to extract heat from a part. Cold die quenching is slow, expensive, and is limited to smaller parts with large surface areas.
- **cold dry die quenching**
  - Same as cold die quenching .
- **cold treatment**
  - Treatment carried out after quenching to transform retained austenite into martensite, involving cooling and holding at a temperature below ambient.
- **columnar structure**
  - A coarse structure of parallel elongated grains formed by unidirectional growth, most often observed in castings, but sometimes in structures resulting from diffusional growth accompanied by a solid-state transformation.
- **combined carbon**
  - The part of the total carbon in steel or cast iron that is present as other than free carbon .
- **conditioning heat treatment**
  - A preliminary heat treatment used to prepare a material for desired reaction to a subsequent heat treatment. For the term to be meaningful, the exact heat treatment must be specified.
- **congruent transformation**
  - An isothermal or isobaric phase change in which both of the phases concerned have the same composition throughout the process.
- **constitution diagram**
  - See phase diagram .
- **continuous cooling transformation (CCT) diagram**
  - Set of curves drawn using logarithmic time and linear temperature as coordinates, which define for each cooling curve the beginning and end of the transformation of the initial phase.
- **continuous precipitation**
  - Precipitation from a supersaturated solid solution in which the precipitate particles grow by long-range diffusion without recrystallization of the matrix. Continuous precipitates grow from nuclei distributed more or less uniformly throughout the matrix. They usually are randomly oriented, but may form a Widmanstätten structure. Also called general precipitation. Compare with discontinuous precipitation , localized precipitation .
- **continuous-type furnace**
  - A furnace used for heat treating materials that progress continuously through the furnace, entering one door and being discharged from another. See belt furnace , direct-fired tunnel-type furnace , rotary retort furnace , shaker-hearth furnace .
- **controlled cooling**
  - Cooling from an elevated temperature in a predetermined manner, to avoid hardening, cracking, or internal damage, or to produce desired microstructure or mechanical properties.
- **cooling curve**
  - A curve showing the relation between time and temperature during the cooling of a material.
- **cooling stresses**
  - Residual stresses resulting from nonuniform distribution of temperature during cooling.
- **core**
  - In a ferrous alloy prepared for case hardening , that portion of the alloy that is not part of the case . Typically considered to be the portion that (a) appears light on an etched cross section, (b) has an essentially unaltered chemical composition, or (c) has a hardness, after hardening, less than a specified value.
- **critical cooling rate**
  - The rate of continuous cooling required to prevent undesirable transformation. For steel, it is the minimum rate at which austenite must be continuously cooled to suppress transformations above the M_s temperature.
- **critical diameter**
  - (*D*) Diameter of the bar that can be fully hardened with 50% martensite at its center.
- **critical point**
  - (1) The temperature or pressure at which a change in crystal structure, phase or physical properties occurs. Same as transformation temperature . (2) In an equilibrium diagram, that

specific value of composition, temperature and pressure, or combinations thereof, at which the phases of a heterogeneous system are in equilibrium.

- **critical strain**
  - The strain just sufficient to cause recrystallization ; because the strain is small, usually only a few percent, recrystallization takes place from only a few nuclei, which produces a recrystallized structure consisting of very large grains.
- **critical temperature**
  - (1) Synonymous with critical point if the pressure is constant. (2) The temperature above which the vapor phase cannot be condensed to liquid by an increase in pressure.
- **critical temperature ranges**
  - Synonymous with transformation ranges , which is the preferred term.
- **cryogenic treatment**
  - See cold treatment .
- **Curie temperature**
  - The temperature of magnetic transformation below which a metal or alloy is ferromagnetic and above which it is paramagnetic.
- **cyaniding**
  - A case-hardening process in which a ferrous material is heated above the lower transformation range in a molten salt containing cyanide to cause simultaneous absorption of carbon and nitrogen at the surface and, by diffusion, create a concentration gradient. Quench hardening completes the process.
- **cycle annealing**
  - An annealing process employing a predetermined and closely controlled time-temperature cycle to produce specific properties or microstructures.
- D
- **dead soft**
  - A temper of nonferrous alloys and some ferrous alloys corresponding to the condition of minimum hardness and tensile strength produced by full annealing .
- **decalescence**
  - A phenomenon, associated with the transformation of alpha iron to gamma iron on the heating (superheating) of iron or steel, revealed by the darkening of the metal surface owing to the sudden decrease in temperature caused by the fast absorption of the latent heat of transformation. Contrast with recalescence .
- **decarburization**
  - Loss of carbon from the surface layer of a carbon-containing alloy due to reaction with one or more chemical substances in a medium that contacts the surface.
- **degrees of freedom**
  - The number of independent variables (such as temperature, pressure, or concentration within the phases present) that may be altered at will without causing a phase change in an alloy system at equilibrium; or the number of such variables that must be fixed arbitrarily to define the system completely.
- **delta ferrite**
  - See ferrite .
- **dew point**
  - The temperature and pressure at which a gas begins to condense to a liquid.
- **dew point analyzer**
  - An atmosphere monitoring device that measures the partial pressure of water vapor in an atmosphere.
- **differential heating**
  - Heating that intentionally produces a temperature gradient within an object such that, after cooling, a desired stress distribution or variation in properties is present within the object.
- **diffusion**
  - (1) Spreading of a constituent in a gas, liquid, or solid, tending to make the composition of all parts uniform. (2) The spontaneous movement of atoms or molecules to new sites within a material.
- **diffusion coefficient**
  - A factor of proportionality representing the amount of substance diffusing across a unit area through a unit concentration gradient in unit time.

- **dilatometer**
  - An instrument for measuring the linear expansion or contraction in a metal resulting from changes in such factors as temperature and allotropy.
- **direct-fired tunnel-type furnace**
  - A continuous-type furnace where the work is conveyed through a tunnel-type heating zone, and the parts are hung on hooks or fixtures to minimize distortion.
- **direct quenching**
  - (1) Quenching carburized parts directly from the carburizing operation. (2) Also used for quenching pearlitic malleable parts directly from the malleablizing operation.
- **discontinuous precipitation**
  - Precipitation from a supersaturated solid solution in which the precipitate particles grow by short-range diffusion, accompanied by recrystallization of the matrix in the region of precipitation. Discontinuous precipitates grow into the matrix from nuclei near grain boundaries, forming cells of alternate lamellae of precipitate and depleted (and recrystallized) matrix. Often referred to as cellular or nodular precipitation. Compare with continuous precipitation , localized precipitation .
- **dissociation**
  - As applied to heterogeneous equilibria, the transformation of one phase into two or more new phases of different composition. Compare with order-disorder transformation .
- **double aging**
  - Employment of two different aging treatments to control the type of precipitate formed from a supersaturated matrix in order to obtain the desired properties. The first aging treatment, sometimes referred to as intermediate or stabilizing, is usually carried out at higher temperature than the second.
- **double tempering**
  - A treatment in which a quench-hardened ferrous metal is subjected to two complete tempering cycles, usually at substantially the same temperature, for the purpose of ensuring completion of the tempering reaction and promoting stability of the resulting microstructure.
- **drawing**
  - A misnomer for *tempering*.
- **dry cyaniding**
  - (obsolete) Same as carbonitriding .
- **ductile cast iron**
  - A cast iron that has been treated while molten with an element such as magnesium or cerium to induce the formation of free graphite as nodules or spherulites, which imparts a measurable degree of ductility to the cast metal. Also known as nodular cast iron, spherulitic graphite cast iron and SG iron.
- **ductile fracture**
  - Fracture characterized by tearing of metal accompanied by appreciable gross plastic deformation and expenditure of considerable energy. Contrast with brittle fracture .
- **ductility**
  - The ability of a material to deform plastically without fracturing, measured by elongation or reduction of area in a tensile test, by height of cupping in an Erichsen test, or by other means.
- **E**
- **885 °F (475 °C) embrittlement**
  - Embrittlement of stainless steels upon extended exposure to temperatures between 400 and 510 °F). This type of embrittlement is caused by fine, chromium-rich precipitates that segregate at grain boundaries; time at temperature directly influences the amount of segregation. Grain-boundary segregation of the chromium-rich precipitates increases strength and hardness, decreases ductility and toughness, and changes corrosion resistance. This type of embrittlement can be reversed by heating above the precipitation range.
- **elastic limit**
  - The maximum stress that a material is capable of sustaining without any permanent strain (deformation) remaining upon complete release of the stress.
- **electron-beam heat treating**
  - A selective surface hardening process that rapidly heats a surface by direct bombardment with an accelerated stream of electrons.
- **embrittlement**

- The severe loss of ductility or toughness or both, of a material, usually a metal or alloy. Many forms of embrittlement can lead to brittle fracture . Many forms can occur during thermal treatment or elevated-temperature service (thermally induced embrittlement). Some of these forms of embrittlement, which affect steels, include blue brittleness , 885 °F (475 °C) embrittlement , quench-age embrittlement , sigma-phase embrittlement , strain-age embrittlement , temper embrittlement , tempered martensite embrittlement , and thermal embrittlement . In addition, steels and other metals and alloys can be embrittled by environmental conditions (environmentally assisted embrittlement). The forms of environmental embrittlement include acid embrittlement, caustic embrittlement, corrosion embrittlement, creep-rupture embrittlement, hydrogen embrittlement, liquid metal embrittlement, neutron embrittlement, solder embrittlement, solid metal embrittlement, and stress-corrosion cracking. These environmentally-related terms are defined elsewhere in this Handbook series.

- **enantiotropy**
  - The relation of crystal forms of the same substance in which one form is stable above a certain temperature and the other form stable below that temperature. Ferrite and austenite are enantiotropic in ferrous alloys, for example.
- **end-quench hardenability test**
  - A laboratory procedure for determining the hardenability of a steel or other ferrous alloy; widely referred to as the Jominy test . Hardenability is determined by heating a standard specimen above the upper critical temperature, placing the hot specimen in a fixture so that a stream of cold water impinges on one end, and, after cooling to room temperature is completed, measuring the hardness near the surface of the specimen at regularly spaced intervals along its length. The data are normally plotted as hardness versus distance from the quenched end.
- **equilibrium diagram**
  - A graphical representation of the temperature, pressure and composition limits of phase fields in an alloy system as they exist under conditions of complete equilibrium. In metal systems, pressure is usually considered constant.
- **eutectic**
  - (1) An isothermal reversible reaction in which a liquid solution is converted into two or more intimately mixed solids on cooling, the number of solids formed being the same as the number of components in the system. (2) An alloy having the composition indicated by the eutectic point on an equilibrium diagram. (3) An alloy structure of intermixed solid constituents formed by a eutectic reaction.
- **eutectic carbide**
  - Carbide formed during freezing as one of the mutually insoluble phases participating in the eutectic reaction of ferrous alloys.
- **eutectic melting**
  - Melting of localized microscopic areas whose composition corresponds to that of the eutectic in the system.
- **eutectoid**
  - (I) An isothermal reversible reaction in which a solid solution is converted into two or more intimately mixed solids on cooling, the number of solids formed being the same as the number of components in the system. (2) An alloy having the composition indicated by the eutectoid point on an equilibrium diagram. (3) An alloy structure of intermixed solid constituents formed by a eutectoid reaction.
- **extra hard**
  - A temper of nonferrous alloys and some ferrous alloys characterized by tensile strength and hardness about one-third of the way from full hard to extra spring temper.
- **extra spring**
  - A temper of nonferrous alloys and some ferrous alloys corresponding approximately to a cold-worked state above full hard beyond which further cold work will not measurably increase the strength and hardness.
- **F**
- **ferrite**
  - A solid solution of one or more elements in body-centered cubic iron. Unless otherwise designated (for instance, as chromium ferrite), the solute is generally assumed to be carbon. On some equilibrium diagrams, there are two ferrite regions separated by an austenite area. The

lower area is alpha ferrite; the upper, delta ferrite. If there is no designation, alpha ferrite is assumed.

- **ferritizing anneal**
  - A treatment given as-cast gray or ductile (nodular) iron to produce an essentially ferritic matrix. For the term to be meaningful, the final microstructure desired or the time-temperature cycle used must be specified.
- **final annealing**
  - An imprecise term used to denote the last anneal given to a nonferrous alloy prior to shipment.
- **finish annealing**
  - A subcritical annealing treatment applied to cold-worked low- or medium-carbon steel. Finish annealing, which is a compromise treatment, lowers residual stresses, thereby minimizing the risk of distortion in machining while retaining most of the benefits to machinability contributed by cold working. Compare with final annealing .
- **finishing temperature**
  - The temperature at which hot working is completed.
- **fixturing**
  - The placing of parts to be heat treated in a constraining or semiconstraining apparatus to avoid heat-related distortions. See racking .
- **flame annealing**
  - Annealing in which the heat is applied directly by a flame.
- **flame hardening**
  - A process for hardening the surfaces of hardenable ferrous alloys in which an intense flame is used to heat the surface layers above the upper transformation temperature, whereupon the workpiece is immediately quenched.
- **flame straightening**
  - Correcting distortion in metal structures by localized heating with a gas flame.
- **fluidized-bed heating**
  - Heating carried out in a medium of solid particles suspended in a flow of gas.
- **fog quenching**
  - Quenching in a fine vapor or mist.
- **forced-air quench**
  - A quench utilizing blasts of compressed air against relatively small parts such as a gear.
- **free carbon**
  - The part of the total carbon in steel or cast iron that is present in elemental form as graphite or temper carbon. Contrast with combined carbon .
- **free ferrite**
  - Ferrite that is formed directly from the decomposition of hypoeutectoid austenite during cooling, without the simultaneous formation of cementite. Also proeutectoid ferrite.
- **freezing range**
  - That temperature range between liquidus and solidus temperatures in which molten and solid constituents coexist.
- **full annealing**
  - An imprecise term that denotes an annealing cycle to produce minimum strength and hardness. For the term to be meaningful, the composition and starting condition of the material and the time-temperature cycle used must be stated.
- **full hard**
  - A temper of nonferrous alloys and some ferrous alloys corresponding approximately to a cold-worked state beyond which the material can no longer be formed by bending. In specifications, a full hard temper is commonly defined in terms of minimum hardness or minimum tensile strength (or, alternatively, a range of hardness or strength) corresponding to a specific percentage of cold reduction following a full anneal. For aluminum, a full hard temper is equivalent to a reduction of 75% from dead soft ; for austenitic stainless steels, a reduction of about 50 to 55%.
- **G**
- **gamma iron**
  - The face-centered cubic form of pure iron, stable from 910 to 1400 °C (1670 to 2550 °F).
- **gas cyaniding**
  - A misnomer for carbonitriding .
- **grain-boundary liquation**

- An advanced stage of overheating in which material in the region of austenitic grain boundaries melts. Also termed burning .
- **grain coarsening**
  - A heat treatment that produces excessively large austenitic grains.
- **grain growth**
  - An increase in the average size of the grains in polycrystalline metal, usually as a result of heating at elevated temperature.
- **grain refiner**
  - A material added to a molten metal to induce a finer-than-normal grain size in the final structure.
- **grain size**
  - For metals, a measure of the areas or volumes of grains in a polycrystalline material, usually expressed as an average when the individual sizes are fairly uniform. In metals containing two or more phases, the grain size refers to that of the matrix unless otherwise specified. Grain sizes are reported in terms of number of grains per unit area or volume, average diameter, or as a grain-size number derived from area measurements.
- **graphitic carbon**
  - Free carbon in steel or cast iron. See graphitization .
- **graphitization**
  - Formation of graphite in iron or steel. Where graphite is formed during solidification, the phenomenon is called primary graphitization; where formed later by heat treatment, secondary graphitization.
- **graphitizing**
  - Annealing a ferrous alloy in such a way that some or all of the carbon is precipitated as graphite.
- **Grossmann chart**
  - A chart describing the ability of a quenching medium to extract heat from a hot steel work-piece in comparison to still water.
- **Guinier-Preston (G-P) zone**
  - A small precipitation domain in a supersaturated metallic solid solution. A G-P zone has no well-defined crystalline structure of its own and contains an abnormally high concentration of solute atoms. The formation of G-P zones constitutes the first stage of precipitation and is usually accompanied by a change in properties of the solid solution in which they occur.
- **H**
- **half hard**
  - A temper of nonferrous alloys and some ferrous alloys characterized by tensile strength about mid-way between that of dead soft and full hard tempers.
- **hardenability**
  - The relative ability of a ferrous alloy to form martensite when quenched from a temperature above the upper critical temperature. Hardenability is commonly measured as the distance below a quenched surface where the metal exhibits a specific hardness (50 HRC, for example) or a specific percentage of martensite in the microstructure.
- **hardening**
  - Increasing hardness by suitable treatment, usually involving heating and cooling. When applicable, the following more specific terms should be used: age hardening , flame hardening , induction hardening , laser hardening , precipitation hardening , and quench hardening .
- **hardness profile**
  - Hardness as a function of distance from a fixed reference point (usually from the surface).
- **hard temper**
  - Same as full hard temper.
- **heat tinting**
  - Coloration of a metal surface through oxidation by heating to reveal details of the microstructure.
- **heat-treatable alloy**
  - An alloy that can be hardened by heat treatment.
- **heat-treating film**
  - A thin coating or film, usually an oxide, formed on the surface of metals during heat treatment.
- **heat treatment**
  - Heating and cooling a solid metal or alloy in such a way as to obtain desired conditions or properties. Heating for the sole purpose of hot working is excluded from the meaning of this definition.

- **holding**
  - The portion of the thermal cycle during which the temperature of the object is maintained constant.
- **holding temperature**
  - The constant temperature at which the object is maintained.
- **holding time**
  - Time for which the temperature of the object is maintained constant.
- **homogeneous carburizing**
  - Use of a carburizing process to convert a low-carbon ferrous alloy to one of uniform and higher carbon content throughout the section.
- **homogenizing**
  - Holding at high temperature to eliminate or decrease chemical segregation by diffusion.
- **horizontal batch furnace**
  - A versatile batch-type furnace that can give light or deep case depths, and because the parts are not exposed to air, horizontal batch furnaces can give surfaces almost entirely free of oxides.
- **hot quenching**
  - An imprecise term used to cover a variety of quenching procedures in which a quenching medium is maintained at a prescribed temperature above 70 °C (160 °F).
- **hot-wire analyzer**
  - An electrical atmosphere analysis device that is based on the fact that the electrical resistivity of steel is a linear function of carbon content over a range from 0.05% C to saturation. The device measures the carbon potential of furnace atmospheres (typically). This term is not to be confused with the hot-wire test which measures heat extraction rates.
- **hot-wire test**
  - Method used to test heat extraction rates of various quenchants. Faster heat-extracting quenchants will permit more electric current to pass through a standard wire because it is cooled more quickly. Compare with hot-wire analyzer .
- **hypereutectic alloy**
  - In an alloy system exhibiting a eutectic, any alloy whose composition has an excess of alloying element compared with the eutectic composition, and whose equilibrium microstructure contains some eutectic structure.
- **hypereutectoid alloy**
  - In an alloy system exhibiting a eutectoid, any alloy whose composition has an excess of alloying element compared with the eutectoid composition, and whose equilibrium microstructure contains some eutectoid structure.
- **hypoeutectic alloy**
  - In an alloy system exhibiting a eutectic, any alloy whose composition has an excess of base metal compared with the eutectic composition, and whose equilibrium microstructure contains some eutectic structure.
- **hypoeutectoid alloy**
  - In an alloy system exhibiting a eutectoid, any alloy whose composition has an excess of base metal compared with the eutectoid composition, and whose equilibrium microstructure contains some eutectoid structure.
- **I**
- **ideal critical diameter**
  - (D_I). Under an ideal quench condition, the bar diameter that has 50% martensite at the center of the bar when the surface is cooled at an infinitely rapid rate (that is, when $H = \infty$, where H is the quench severity factor).
- **immersed-electrode furnaces**
  - A furnace used for liquid carburizing of parts by heating molten salt baths with the use of electrodes immersed in the liquid. See submerged-electrode furnace .
- **impact tube**
  - Same as Pitot tube .
- **induction hardening**
  - A surface-hardening process in which only the surface layer of a suitable ferrous workpiece is heated by electromagnetic induction to above the upper critical temperature and immediately quenched.
- **induction heating**

    - Heating by combined electrical resistance and hysteresis losses induced by subjecting a metal to the varying magnetic field surrounding a coil carrying alternating current.
- **induction tempering**
    - Tempering of steel using low-frequency electrical induction heating .
- **infrared analyzer**
    - An atmosphere-monitoring device that measures a gas (usually carbon monoxide, carbon dioxide, and methane) presence based on specific wavelength absorption of infrared energy.
- **intense quenching**
    - Quenching in which the quenching medium is cooling the part at a rate at least two and a half times faster than still water. See Grossmann chart .
- **intercritical annealing**
    - Any annealing treatment that involves heating to, and holding at, a temperature between the upper and lower critical temperatures to obtain partial austenitization, followed by either slow cooling or holding at a temperature below the lower critical temperature.
- **intergranular**
    - Between crystals or grains. Also called intercrystalline. Contrast with transgranular .
- **intergranular cracking**
    - Cracking or fracturing that occurs between the grains or crystals in a polycrystalline aggregate. Also called intercrystalline cracking. Contrast with transgranular cracking .
- **intergranular fracture**
    - Brittle fracture of a metal in which the fracture is between the grains, or crystals, that form the metal. Also called intercrystalline fracture. Contrast with transgranular fracture .
- **intermediate annealing**
    - Annealing wrought metals at one or more stages during manufacture and before final treatment.
- **interrupted aging**
    - Aging at two or more temperatures, by steps, and cooling to room temperature after each step. See aging , and compare with progressive aging and step aging .
- **interrupted quenching**
    - A quenching procedure in which the workpiece is removed from the first quench at a temperature substantially higher than that of the quenchant and is then subjected to a second quenching system having a different cooling rate than the first.
- **interval test**
    - Method used to test heat extraction rates of various quenchants. This test measures the increase in temperature of a quenchant when a standard bar of metal is quenched for five seconds. Faster quenchants will exhibit greater temperature increases.
- **ion carburizing**
    - A method of surface hardening in which carbon ions are diffused into a workpiece in a vacuum through the use of high-voltage electrical energy. Synonymous with plasma carburizing or glow-discharge carburizing.
- **ion nitriding**
    - A method of surface hardening in which nitrogen ions are diffused into a workpiece in a vacuum through the use of high-voltage electrical energy. Synonymous with plasma nitriding or glow-discharge nitriding.
- **isothermal annealing**
    - Austenitizing a ferrous alloy and then cooling to and holding at a temperature at which austenite transforms to a relatively soft ferrite carbide aggregate.
- **isothermal transformation**
    - A change in phase that takes place at a constant temperature. The time required for transformation to be completed, and in some instances the time delay before transformation begins, depends on the amount of supercooling below (or superheating above) the equilibrium temperature for the same transformation.
- **isothermal transformation (IT) diagram**
    - Set of curves drawn using logarithmic time and linear temperature as coordinates, which define for each level of temperature the beginning and end of the transformation of the initial phase under isothermal conditions.
- **J**
- **Jominy test**
    - See end-quench hardenability test .

- K
- **kish**
  - Free graphite that forms in molten hypereutectic cast iron as it cools. In castings, the kish may segregate toward the cope surface, where it lodges at or immediately beneath the casting surface.
- L
- **laser hardening**
  - A surface-hardening process which uses a laser to quickly heat a surface. Heat conduction into the interior of the part will quickly cool the surface, leaving a shallow martensitic layer.
- **latent heat**
  - Thermal energy absorbed or released when a substance undergoes a phase change.
- **ledeburite**
  - The eutectic of the iron-carbon system, the constituents being austenite and cementite. The austenite decomposes into ferrite and cementite on cooling below the Ar_1.
- **Leidenfrost phenomenon**
  - Slow cooling rates associated with a hot vapor blanket that surrounds a part being quenched in a liquid medium such as water. The gaseous vapor envelope acts as an insulator, thus slowing the cooling rate.
- **liquation temperature**
  - The lowest temperature at which partial melting can occur in an alloy that exhibits the greatest possible degree of segregation.
- **liquid carburizing**
  - Surface hardening of steel by immersion into a molten bath consisting of cyanides and other salts.
- **liquid nitriding**
  - A method of surface hardening in which molten nitrogen-bearing, fused-salt baths containing both cyanides and cyanates are exposed to parts at subcritical temperatures.
- **liquid nitrocarburizing**
  - A nitrocarburizing process (where both carbon and nitrogen are absorbed into the surface) utilizing molten liquid salt baths below the lower critical temperature.
- **liquid spray quench**
  - Same as spray quenching .
- **localized precipitation**
  - Precipitation from a supersaturated solid solution similar to continuous precipitation , except that the precipitate particles form at preferred locations, such as along slip planes, grain boundaries, or incoherent twin boundaries.
- M
- **magnetic test**
  - Method used to test heat extraction rates of various quenchants. The test works by utilizing the change in magnetic properties of metals at their Curie point--the temperature above which metals lose their magnetism.
- **malleable cast iron**
  - A cast iron made by prolonged annealing of white cast iron in which decarburization or graphitization, or both, take place to eliminate some or all of the cementite. The graphite is in the form of temper carbon. If decarburization is the predominant reaction, the product will exhibit a light fracture surface, hence, "whiteheart malleable;" otherwise, the fracture surface will be dark, hence, "blackheart malleable." Ferritic malleable has a predominantly ferritic matrix; pearlitic malleable may contain pearlitic, spheroidite or tempered martensite depending on heat treatment and desired hardness.
- **malleablizing**
  - Annealing white cast iron in such a way that some or all of the combined carbon is transformed to graphite or, in some instances, part of the carbon is removed completely.
- **maraging**
  - A precipitation-hardening treatment applied to a special group of iron-base alloys to precipitate one or more intermetallic compounds in a matrix of essentially carbon-free martensite.
- **marquenching**
  - See martempering .
- **martempering**
  - (1) A hardening procedure in which an austenitized ferrous workpiece is quenched into an appropriate medium whose temperature is maintained substantially at the M_s of the workpiece,

held in the medium until its temperature is uniform throughout--but not long enough to permit bainite to form--and then cooled in air. The treatment is frequently followed by tempering. (2) When the process is applied to carburized material, the controlling M_s temperature is that of the case. This variation of the process is frequently called marquenching.

- **martensite**
  - A generic term for microstructures formed by diffusionless phase transformation in which the parent and product phases have a specific crystallographic relationship. Martensite is characterized by an acicular pattern in the microstructure in both ferrous and nonferrous alloys. In alloys where the solute atoms occupy interstitial positions in the martensitic lattice (such as carbon in iron), the structure is hard and highly strained; but where the solute atoms occupy substitutional positions (such as nickel in iron), the martensite is soft and ductile. The amount of high-temperature phase that transforms to martensite on cooling depends to a large extent on the lowest temperature attained, there being a rather distinct beginning temperature (M_s) and a temperature at which the transformation is essentially complete (M_f).
- **martensite range**
  - The temperature interval between M_s and M_f.
- **martensitic transformation**
  - A reaction that takes place in some metals on cooling, with the formation of an acicular structure called martensite .
- **McQuaid-Ehn test**
  - A test to reveal grain size after heating into the austenitic temperature range. Eight standard McQuaid-Ehn grain sizes rate the structure, No. 8 being finest, No. 1 coarsest.
- **M_f temperature**
  - For any alloy system, the temperature at which martensite formation on cooling is essentially finished. See transformation temperature for the definition applicable to ferrous alloys.
- **microhardness**
  - The hardness of a material as determined by forcing an indenter such as a Vickers or Knoop indenter into the surface of a material under very light load; usually, the indentations are so small that they must be measured with a microscope. Capable of determining hardnesses of different microconstituents within a structure, or of measuring steep hardness gradients such as those encountered in case hardening.
- **microscopic stresses**
  - Residual stresses that vary from tension to compression in a distance (presumably approximating the grain size) that is small compared with the gage length in ordinary strain measurements. They are not detectable by dissection methods, but can sometimes be measured from line shift or line broadening in an x-ray diffraction pattern.
- **microsegregation**
  - Segregation within a grain, crystal, or small particle.
- **mill scale**
  - The heavy oxide layer formed during hot fabrication or heat treatment of metals.
- **monotropism**
  - The ability of a solid to exist in two or more forms (crystal structures), but in which one form is the stable modification at all temperatures and pressures. Ferrite and martensite are a monotropic pair below Ac_1 in steels, for example. May also be spelled monotrophism.
- **M_s temperature**
  - For any alloy system, the temperature at which martensite starts to form on cooling. See transformation temperature for the definition applicable to ferrous alloys.
- **N**
- **natural aging**
  - Spontaneous aging of a supersaturated solid solution at room temperature. See aging , and compare with artificial aging .
- **neutral flame**
  - A gas flame in which there is no excess of either fuel or oxygen in the inner flame. Oxygen from ambient air is used to complete the combustion of CO_2 and H_2 produced in the inner flame.
- **neutralization number**
  - An ASTM number given to quenching oils that reflects the oil's tendency towards oxidation and sludging. See saponification number .
- **nitriding**

- Introducing nitrogen into the surface layer of a solid ferrous alloy by holding at a suitable temperature (below Ac_1 for ferritic steels) in contact with a nitrogenous material, usually ammonia or molten cyanide of appropriate composition. Quenching is not required to produce a hard case. See aerated bath nitriding , bright nitriding , and liquid nitriding .

- **nitrocarburizing**
  - Any of several processes in which both nitrogen and carbon are absorbed into the surface layers of a ferrous material at temperatures below the lower critical temperature and, by diffusion, create a concentration gradient. Nitrocarburizing is done mainly to provide an antiscuffing surface layer and to improve fatigue resistance. Compare with carbonitriding .
- **normalizing**
  - Heating a ferrous alloy to a suitable temperature above the transformation range and then cooling in air to a temperature substantially below the transformation range.
- **nucleation**
  - The initiation of a phase transformation at discrete sites, the new phase growing on nuclei. See nucleus .
- **nucleus**
  - The first structurally stable particle capable of initiating recrystallization of a phase or the growth of a new phase, and possessing an interface with the parent matrix. The term is also applied to a foreign particle that initiates such action.
- **O**
- **oil hardening**
  - Quench-hardening treatment involving cooling in oil.
- **oil quenching**
  - Hardening of carbon steel in an oil bath. Oils are categorized as conventional, fast, martempering , or hot quenching .
- **optical pyrometer**
  - An instrument for measuring the temperature of heated material by comparing the intensity of light emitted with a known intensity of an incandescent lamp filament.
- **order-disorder transformation**
  - A phase change among two solid solutions having the same crystal structure, but in which the atoms of one phase (disordered) are randomly distributed; in the other, the different kinds of atoms occur in a regular sequence upon the crystal lattice, that is, in an ordered arrangement. Compare with dissociation .
- **order hardening**
  - A low-temperature annealing treatment that permits short-range ordering of solute atoms within a matrix, which greatly impedes dislocation motion.
- **Orsat analyzer**
  - An atmosphere analysis device in which gases are absorbed selectively (volumetric basis) by passing them through a series of preselected solvents.
- **overaging**
  - Aging under conditions of time and temperature greater than those required to obtain maximum change in a certain property, so that the property is altered in the direction of the initial value. See aging .
- **overheating**
  - Heating a metal or alloy to such a high temperature that its properties are impaired. When the original properties cannot be restored by further heat treating, by mechanical working, or by a combination of working and heat treating, the overheating is known as burning .
- **oxidation**
  - (1) A reaction in which there is an increase in valence resulting from a loss of electrons. (2) A corrosion reaction in which the corroded metal forms an oxide; usually applied to reaction with a gas containing elemental oxygen, such as air.
- **oxidized surface (on steel)**
  - Surface having a thin, tightly adhering, oxidized skin (from straw to blue in color), extending in from the edge of a coil or sheet. Sometimes called annealing border.
- **oxidizing agent**
  - A compound that causes oxidation, thereby itself becoming reduced.
- **oxidizing flame**
  - A gas flame produced with excess oxygen in the inner flame.

- **oxygen probe**
  - An atmosphere-monitoring device that electronically measures the difference between the partial pressure of oxygen in a furnace or furnace supply atmosphere and the external air.
- **P**
- **pack carburizing**
  - A method of surface hardening of steel in which parts are packed in a steel box with the carburizing compound and heated to elevated temperatures.
- **pack nitriding**
  - A method of surface hardening of steel in which parts are packed in a steel box with the nitriding compound and heated to elevated temperatures.
- **partial annealing**
  - An imprecise term used to denote a treatment given cold-worked material to reduce the strength to a controlled level or to effect stress relief. To be meaningful, the type of material, the degree of cold work, and the time-temperature schedule must be stated.
- **patenting**
  - In wiremaking, a heat treatment applied to medium-carbon or high-carbon steel before the drawing of wire or between drafts. This process consists of heating to a temperature above the transformation range and then cooling to a temperature below Ae_1 in air or in a bath of molten lead or salt.
- **pearlite**
  - A metastable lamellar aggregate of ferrite and cementite resulting from the transformation of austenite at temperatures above the bainite range.
- **phase diagram**
  - A graphical representation of the temperature and composition limits of phase fields in an alloy system as they actually exist under the specific conditions of heating or cooling (synonymous with constitution diagram). A phase diagram may be an equilibrium diagram, an approximation to an equilibrium diagram, or a representation of metastable conditions or phases. Compare with equilibrium diagram .
- **Pirani gage**
  - An instrument used to measure the pressure inside a vacuum chamber. The gage measures electrical resistance in a wire filament which will change in temperature depending on atmospheric pressure.
- **Pitot tube**
  - An instrument that measures the stagnation pressure of a flowing fluid, consisting of an open tube pointing into the fluid and connected to a pressure-indicating device. Also known as impact tube .
- **plasma carburizing**
  - Same as ion carburizing .
- **plasma nitriding**
  - Same as ion nitriding .
- **plastic deformation**
  - The permanent (inelastic) distortion of metals under applied stresses that strain the material beyond its elastic limit .
- **polymorphism**
  - The property of a chemical substance crystallizing into two or more forms having different structures, such as diamond and graphite.
- **postheating**
  - Heating weldments immediately after welding, for tempering, for stress relieving, or for providing a controlled rate of cooling to prevent formation of a hard or brittle structure.
- **pot annealing**
  - Same as box annealing .
- **precipitation hardening**
  - Hardening caused by the precipitation of a constituent from a supersaturated solid solution. See also age hardening and aging .
- **precipitation heat treatment**
  - Artificial aging in which a constituent precipitates from a supersaturated solid solution.
- **preheating**
  - Heating before some further thermal or mechanical treatment. For tool steel, heating to an intermediate temperature immediately before final austenitizing. For some nonferrous alloys,

heating to a high temperature for a long time, to homogenize the structure before working. In welding and related processes, heating to an intermediate temperature for a short time immediately before welding, brazing, soldering, cutting, or thermal spraying.

- **press quenching**
  - A quench in which hot dies are pressed and aligned with a part before the quenching process begins. Then the part is placed in contact with a quenching medium in a controlled manner. This process avoids part distortion.
- **process annealing**
  - An imprecise term denoting various treatments used to improve workability. For the term to be meaningful, the condition of the material and the time-temperature cycle used must be stated.
- **progressive aging**
  - Aging by increasing the temperature in steps or continuously during the aging cycle. See aging and compare with interrupted aging and step aging.
- **pseudocarburizing**
  - See blank carburizing .
- **pseudonitriding**
  - See blank nitriding .
- **pusher furnace**
  - A type of continuous furnace in which parts to be heated are periodically charged into the furnace in containers, which are pushed along the hearth against a line of previously charged containers thus advancing the containers toward the discharge end of the furnace, where they are removed.
- **pyrometer**
  - A device for measuring temperatures above the range of liquid thermometers.
- **Q**
- **quarter hard**
  - A temper of nonferrous alloys and some ferrous alloys characterized by tensile strength about midway between that of dead soft and half hard tempers.
- **quench-age embrittlement**
  - Embrittlement of low-carbon steels resulting from precipitation of solute carbon at existing dislocations and from precipitation hardening of the steel caused by differences in ferrite at different temperatures. Quenchage embrittlement usually is caused by rapid cooling of the steel from temperatures slightly below Ac_1 (the temperature at which austenite begins to form), and can be minimized by quenching from lower temperatures.
- **quench aging**
  - Aging induced by rapid cooling after solution heat treatment .
- **quench annealing**
  - Annealing an austenitic ferrous alloy by solution heat treatment followed by rapid quenching.
- **quench cracking**
  - Fracture of a metal during quenching from elevated temperature. Most frequently observed in hardened carbon steel, alloy steel, or tool steel parts of high hardness and low toughness. Cracks often emanate from fillets, holes, corners, or other stress raisers and result from high stresses due to the volume changes accompanying transformation to martensite.
- **quench hardening**
  - (1) Hardening suitable alpha-beta alloys (most often certain copper to titanium alloys) by solution treating and quenching to develop a martensitic-like structure. (2) In ferrous alloys, hardening by austenitizing and then cooling at a rate such that a substantial amount of austenite transforms to martensite.
- **quenching**
  - Rapid cooling. When applicable, the following more specific terms should be used: brine quenching , caustic quenching , cold die quenching , forced-air quenching , intense quenching , oil quenching , press quenching , spray quenching , direct quenching , fog quenching , hot quenching , interrupted quenching , selective quenching , time quenching , and water quenching .
- **R**
- **racking**
  - A term used to describe the placing of parts to be heat treated on a rack or tray. This is done to keep pans in a proper position to avoid heat-related distortions and to keep the parts separated. See fixturing .
- **recalescence**

- A phenomenon, associated with the transformation of gamma iron to alpha iron on the cooling (supercooling) of iron or steel, revealed by the brightening (reglowing) of the metal surface owing to the sudden increase in temperature caused by the fast liberation of the latent heat of transformation. Contrast with decalescence .

- **recarburize**
    - (1) To increase the carbon content of molten cast iron or steel by adding carbonaceous material, high-carbon pig iron, or a high-carbon alloy. (2) To carburize a metal part to return surface carbon lost in processing; also known as carbon restoration.
- **recovery**
    - Reduction or removal of work-hardening effects, without motion of large-angle grain boundaries.
- **recrystallization**
    - (1) The formation of a new, strain-free grain structure from that existing in cold-worked metal, usually accomplished by heating. (2) The change from one crystal structure to another, as occurs on heating or cooling through a critical temperature.
- **recrystallization annealing**
    - Annealing cold-worked metal to produce a new grain structure without phase change.
- **recrystallization temperature**
    - The approximate minimum temperature at which complete recrystallization of a cold-worked metal occurs within a specified time.
- **recuperator**
    - Equipment for transferring heat from gaseous products of combustion to incoming air or fuel. The incoming material passes through pipes surrounded by a chamber through which the outgoing gases pass.
- **reducing flame**
    - A gas flame produced with excess fuel in the inner flame.
- **refractory**
    - (1) A material of very high melting point with properties that make it suitable for such uses as furnace linings and kiln construction. (2) The quality of resisting heat.
- **regenerator**
    - Same as recuperator except the gaseous products of combustion heat brick checkerwork in a chamber connected to the exhaust side of the furnace while the incoming air and fuel are being heated by the brick checkerwork in a second chamber, connected to the entrance side. At intervals, the gas flow is reversed so that incoming air and fuel contact hot checker-work while that in the second chamber is being reheated by exhaust gases.
- **residual stress**
    - An internal stress not depending on external forces resulting from such factors as cold working, phase changes, or temperature gradients.
- **retort**
    - A vessel used for distillation of volatile materials, as in separation of some metals and in destructive distillation of coal.
- **reverberatory furnace**
    - A furnace with a shallow hearth, usually nonregenerative, having a roof that deflects the flame and radiates heat toward the hearth or the surface of the charge.
- **Rockwell hardness test**
    - An indentation hardness test based on the depth of penetration of a specified penetrator into the specimen under certain arbitrarily fixed conditions.
- **rotary retort furnace**
    - A continuous-type furnace in which the work advances by means of an internal spiral, which gives good control of the retention time within the heated chamber.
- **S**
- **salt bath heat treatment**
    - Heat treatment carried out in a bath of molten salt.
- **saponification number**
    - A number given to quenching oils that reflects the oils amount of compounding with fatty materials, which thereby helps evaluate the condition of these oils in service. See neutralization number .
- **selective heating**
    - Intentionally heating only certain portions of a workpiece.

- **selective quenching**
  - Quenching only certain portions of an object.
- **self-hardening steel**
  - See preferred term, air-hardening steel .
- **sensitization**
  - In austenitic stainless steels, the precipitation of chromium carbides, usually at grain boundaries, on exposure to temperatures of about 540 °C to 845 °C (about 1000 to 1550 °F), leaving the grain boundaries depleted of chromium and therefore susceptible to preferential attack by a corroding (oxidizing) medium.
- **severity of quench**
  - Ability of quenching medium to extract heat from a hot steel workpiece; expressed in terms of the *H* value.
- **shaker-hearth furnace**
  - A continuous type furnace that uses a reciprocating shaker motion to move the parts along the hearth.
- **shell hardening**
  - A surface-hardening process in which a suitable steel workpiece, when heated through and quench hardened, develops a martensitic layer or shell that closely follows the contour of the piece and surrounds a core of essentially pearlitic transformation product. This result is accomplished by a proper balance among section size, steel hardenability, and severity of quench.
- **shim**
  - A thin piece of material placed between two surfaces to obtain a proper fit, adjustment, or alignment. The piece can also be analyzed to measure furnace carbon potential (that is, because while in the furnace it will quickly carburize to a level equal to the furnace carbon potential).
- **sigma phase**
  - A hard, brittle, nonmagnetic intermediate phase with a tetragonal crystal structure, containing 30 atoms per unit cell, space group $P4_2/mnm$, occurring in many binary and ternary alloys of the transition elements. The composition of this phase in the various systems is not the same, and the phase usually exhibits a wide range in homogeneity. Alloying with a third transition element usually enlarges the field of homogeneity and extends it deep into the ternary section.
- **sigma-phase embrittlement**
  - Embrittlement of iron-chromium alloys (most notably austenitic stainless steels) caused by precipitation at grain boundaries of the hard, brittle intermetallic sigma phase during long periods of exposure to temperatures between approximately 565 and 980 °C (1050 and 1800 °F). Sigma-phase embrittlement results in severe loss in toughness and ductility and can make the embrittled material structure susceptible to intergranular corrosion. See also sensitization .
- **signal-to-noise ratio**
  - Ratio of the average response to the root-mean-square variation about the average response. Ratio of variances associated with the two parts of the performance measurement.
- **siliconizing**
  - Diffusing silicon into solid metal, usually steel, at an elevated temperature.
- **sintering**
  - The bonding of adjacent surfaces in a mass of particles by molecular or atomic attraction on heating at high temperatures below the melting temperature of any constituent in the material. Sintering strengthens a powder mass and normally produces densification and, in powdered metals, recrystallization.
- **slack quenching**
  - The incomplete hardening of steel due to quenching from the austenitizing temperature at a rate slower than the critical cooling rate for the particular steel, resulting in the formation of one or more transformation products in addition to martensite.
- **slot furnace**
  - A common batch furnace where stock is charged and removed through a slot or opening.
- **snap temper**
  - A precautionary interim stress-relieving treatment applied to high-hardenability steels immediately after quenching to prevent cracking because of delay in tempering them at the prescribed higher temperature.
- **soaking**

- Prolonged holding at a selected temperature to effect homogenization of structure or composition.
- **soft temper**
  - Same as dead soft temper.
- **solution heat treatment**
  - Heating an alloy to a suitable temperature, holding at that temperature long enough to cause one or more constituents to enter into solid solution, and then cooling rapidly enough to hold these constituents in solution.
- **sorbite**
  - (obsolete) A fine mixture of ferrite and cementite produced either by regulating the rate of cooling of steel or by tempering steel after hardening. The first type is very fine pearlite difficult to resolve under the microscope; the second type is tempered martensite.
- **spalling**
  - A chipping or flaking of a surface due to any kind of improper heat treatment or material dissociation.
- **spinodal hardening**
  - See aging .
- **spheroidite**
  - An aggregate of iron or alloy carbides of essentially spherical shape dispersed throughout a matrix of ferrite.
- **spheroidizing**
  - Heating and cooling to produce a spheroidal or globular form of carbide in steel. Spheroidizing methods frequently used are:

1. Prolonged holding at a temperature just below Ae_1
2. Heating and cooling alternately between temperatures that are just above and just below Ae_1
3. Heating to a temperature above Ae_1 or Ae_3 and then cooling very slowly in the furnace or holding at a temperature just below Ae_1
4. Cooling at a suitable rate from the minimum temperature at which all carbide is dissolved, to prevent the reformation of a carbide network, and then reheating in accordance with method 1 or 2 above. (Applicable to hypereutectoid steel containing a carbide network.)

- **spinodal structure**
  - A fine homogeneous mixture of two phases that form by the growth of composition waves in a solid solution during suitable heat treatment. The phases of a spinodal structure differ in composition from each other and from the parent phase but have the same crystal structure as the parent phase.
- **spray quenching**
  - A quenching process using spray nozzles to spray water or other liquids on a part. The quench rate is controlled by the velocity and volume of liquid per unit area per unit of time of impingement.
- **spring temper**
  - A temper of nonferrous alloys and some ferrous alloys characterized by tensile strength and hardness about two-thirds of the way from full hard to extra spring temper.
- **stabilizing treatment**
  - (1) Before finishing to final dimensions, repeatedly heating a ferrous or nonferrous part to or slightly above its normal operating temperature and then cooling to room temperature to ensure dimensional stability in service. (2) Transforming retained austenite in quenched hardenable steels, usually by cold treatment . (3) Heating a solution-treated stabilized grade of austenitic stainless steel to 870 to 900 °C (1600 to 1650 °F) to precipitate all carbon as TiC, NbC, or TaC so that sensitization is avoided on subsequent exposure to elevated temperature.
- **statistical process control**
  - The application of statistical techniques for measuring and analyzing the variation in processes.
- **statistical quality control**
  - The application of statistical techniques for measuring and improving the quality of processes and products (includes statistical process control, diagnostic tools, sampling plans, and other statistical techniques).

- **Stead's brittleness**
  - A condition of brittleness that causes transcrystalline fracture in the coarse grain structure that results from prolonged annealing of thin sheets of low-carbon steel previously rolled at a temperature below about 705 °C (1300 °F). The fracture usually occurs at about 45° to the direction of rolling.
- **step aging**
  - Aging at two or more temperatures, by steps, without cooling to room temperature after each step. See aging , and compare with interrupted aging and progressive aging .
- **strain-age embrittlement**
  - A loss in ductility accompanied by an increase in hardness and strength that occurs when low-carbon steel (especially rimmed or capped steel) is aged following plastic deformation. The degree of embrittlement is a function of aging time and temperature, occurring in a matter of minutes at about 200 °C (400 °F) but requiring a few hours to a year at room temperature.
- **strain aging**
  - Aging following plastic deformation.
- **stress equalizing**
  - A low-temperature heat treatment used to balance stresses in cold-worked material without an appreciable decrease in the mechanical strength produced by cold working.
- **stress relieving**
  - Heating to a suitable temperature, holding long enough to reduce residual stresses, and then cooling slowly enough to minimize the development of new residual stresses.
- **subcritical annealing**
  - A process anneal performed on ferrous alloys at a temperature below Ac_1.
- **submerged-electrode furnace**
  - A furnace used for liquid carburizing of parts by heating molten salt baths with the use of electrodes submerged in the ceramic lining. See immersed-electrode furnace.
- **supercooling**
  - Cooling below the temperature at which an equilibrium phase transformation can take place, without actually obtaining the transformation.
- **superheating**
  - Heating above the temperature at which an equilibrium phase transformation should occur without actually obtaining the transformation.
- **surface hardening**
  - A generic term covering several processes applicable to a suitable ferrous alloy that produces, by quench hardening only, a surface layer that is harder or more wear resistant than the core. There is no significant alteration of the chemical composition of the surface layer. The processes commonly used are carbonitriding , carburizing , induction hardening , flame hardening , nitriding , and nitrocarburizing . Use of the applicable specific process name is preferred.
- **T**
- **temper**
  - (1) In heat treatment, reheating hardened steel or hardened cast iron to some temperature below the eutectoid temperature for the purpose of decreasing hardness and increasing toughness. The process also is sometimes applied to normalized steel. (2) In tool steels, temper is sometimes used, but inadvisedly, to denote the carbon content. (3) In nonferrous alloys and in some ferrous alloys (steels that cannot be hardened by heat treatment), the hardness and strength produced by mechanical or thermal treatment, or both, and characterized by a certain structure, mechanical properties, or reduction in area during cold working.
- **temper carbon**
  - Same as annealing carbon .
- **temper color**
  - A thin, tightly adhering oxide skin that forms when steel is tempered at a low temperature, or for a short time, in air or a mildly oxidizing atmosphere. The color, which ranges from straw to blue depending on the thickness of the oxide skin, varies with both tempering time and temperature.
- **tempered martensite embrittlement**
  - Embrittlement of ultrahigh-strength steels caused by tempering in the temperature range of 205 to 400 °C (400 to 750 °F); also called 350 °C or 500 °F embrittlement. Tempered martensite embrittlement is thought to result from the combined effects of cementite precipitation on prior-

austenite grain boundaries or interlath boundaries and the segregation of impurities at prior-austenite grain boundaries.

- **temper embrittlement**
  - Embrittlement of alloy steels caused by holding within or cooling slowly through a temperature range just below the transformation range. Embrittlement is the result of the segregation at grain boundaries of impurities such as arsenic, antimony, phosphorus, and tin; it is usually manifested as an upward shift in ductile-to-brittle transition temperature. Temper embrittlement can be reversed by retempering above the critical temperature range, then cooling rapidly.
- **thermal analysis**
  - A method for determining transformations in a metal by noting the temperatures at which thermal arrests occur. These arrests are manifested by changes in slope of the plotted or mechanically traced heating and cooling curves. When such data are secured under nearly equilibrium conditions of heating and cooling, the method is commonly used for determining certain critical temperatures required for the construction of equilibrium diagrams.
- **thermal electromotive force**
  - The electromotive force generated in a circuit containing two dissimilar metals when one junction is at a temperature different from that of the other. See also thermocouple .
- **thermal fatigue**
  - Fracture resulting from the presence of temperature gradients that vary with time in such a manner as to produce cyclic stresses in a structure.
- **thermal shock**
  - The development of a steep temperature gradient and accompanying high stresses within a structure.
- **thermal stresses**
  - Stresses in metal resulting from nonuniform temperature distribution.
- **thermochemical treatment**
  - Heat treatment carried out in a medium suitably chosen to produce a change in the chemical composition of the object by exchange with the medium.
- **thermocouple**
  - A device for measuring temperatures, consisting of lengths of two dissimilar metals or alloys that are electrically joined at one end and connected to a voltage-measuring instrument at the other end. When one junction is hotter than the other, a thermal electromotive force is produced that is roughly proportional to the difference in temperature between the hot and cold junctions.
- **thermomechanical working**
  - A general term covering a variety of processes combining controlled thermal and deformation treatments to obtain specific properties. Same as thermal-mechanical treatment.
- **three-quarters hard**
  - A temper of nonferrous alloys and some ferrous alloys characterized by tensile strength and hardness about midway between those of half hard and full hard tempers.
- **time quenching**
  - A term used to describe a quench in which the cooling rate of the part being quenched must be changed abruptly at some time during the cooling cycle.
- **time-temperature-transformation (TTT) diagram**
  - See isothermal transformation (IT) diagram.
- **total carbon**
  - The sum of the free and combined carbon (including carbon in solution) in a ferrous alloy.
- **total indicator reading**
  - See preferred term total indicator variation .
- **total indicator variation**
  - The difference between the maximum and minimum indicator readings during a checking cycle.
- **toughness**
  - The ability of a metal to absorb energy and deform plastically before fracturing.
- **transcrystalline**
  - See transgranular .
- **transformation hardening**
  - Heat treatment comprising austenitization followed by cooling under conditions such that the austenite transforms more or less completely into martensite and possibly into bainite.
- **transformation-induced plasticity**

- A phenomenon, occurring chiefly in certain highly alloyed steels that have been heat treated to produce metastable austenite or metastable austenite plus martensite, whereby, on subsequent deformation, part of the austenite undergoes strain-induced transformation to martensite. Steels capable of transforming in this manner, commonly referred to as TRIP steels, are highly plastic after heat treatment, but exhibit a very high rate of strain hardening and thus have high tensile and yield strengths after plastic deformation at temperatures between about 20 and 500 °C (70 and 930 °F). Cooling to -195 °C (-320 °F) may or may not be required to complete the transformation to martensite. Tempering usually is done following transformation.

- **transformation ranges**
  - Those ranges of temperature within which a phase forms during heating and transforms during cooling. The two ranges are distinct, sometimes overlapping but never coinciding. The limiting temperatures of the ranges depend on the composition of the alloy and on the rate of change of temperature, particularly during cooling. See transformation temperature .
- **transformation temperature**
  - The temperature at which a change in phase occurs. The term is sometimes used to denote the limiting temperature of a transformation range. The following symbols are used for iron and steels.
- **Ac_{cm}**
  - In hypereutectoid steel, the temperature at which the solution of cementite in austenite is completed during heating.
- **Ac_1**
  - The temperature at which austenite begins to form during heating.
- **Ac_3**
  - The temperature at which transformation of ferrite to austenite is completed during heating.
- **Ac_4**
  - The temperature at which austenite transforms to delta ferrite during heating.
- **Ae_{cm}, Ae_1, Ae_3, Ae_4**
  - The temperatures of phase changes at equilibrium.
- **Ar_{cm}**
  - In hypereutectoid steel, the temperature at which precipitation of cementite starts during cooling.
- **Ar_1**
  - The temperature at which transformation of austenite to ferrite or to ferrite plus cementite is completed during cooling.
- **Ar_3**
  - The temperature at which austenite begins to transform to ferrite during cooling.
- **Ar_4**
  - The temperature at which delta ferrite transforms to austenite during cooling.
- **Ar'**
  - The temperature at which transformation of austenite to pearlite starts during cooling.
- **M_f**
  - The temperature at which transformation of austenite to martensite finishes during cooling.
- **M_s, (or Ar'')**
  - The temperature at which transformation of austenite to martensite starts during cooling.

    Note: All these changes except the formation of martensite occur at lower temperatures during cooling than during heating, and depend on the rate of change of temperature.

- **transgranular**
  - Through or across crystals or grains. Also called intracrystalline or transcrystalline.
- **transgranular cracking**
  - Cracking or fracturing that occurs through or across a crystal or grain. Also called transcrystalline cracking. Contrast with intergranular cracking .
- **transgranular fracture**
  - Fracture through or across the crystals or grains of a metal. Also called transcrystalline fracture or intracrystalline fracture. Contrast with intergranular fracture .
- **transition temperature**

- (1) An arbitrarily defined temperature that lies within the temperature range in which metal fracture characteristics (as usually determined by tests of notched specimens) change rapidly, such as from primarily fibrous (shear) to primarily crystalline (cleavage) fracture. Commonly used definitions are "transition temperature for 50% cleavage fracture," "10 ft · lbf transition temperature," and "transition temperature for half maximum energy." (2) Sometimes used to denote an arbitrarily defined temperature within a range in which the ductility changes rapidly with temperature.
- **TRIP steel**
  - A commercial steel product exhibiting transformation-induced plasticity .
- **troostite**
  - (obsolete) A previously unresolvable rapidly etching fine aggregate of carbide and ferrite produced either by tempering martensite at low temperature or by quenching a steel at a rate slower than the critical cooling rate. Preferred terminology for the first product is tempered martensite; for the latter, fine pearlite.
- **U**
- **undercooling**
  - Same as supercooling .
- **V**
- **vacuum annealing**
  - Annealing carried out at subatmospheric pressure.
- **vacuum carburizing**
  - A high-temperature gas carburizing process using furnace pressures between 7 and 55 kPa during the carburizing portion of the cycle.
- **vacuum furnace**
  - A furnace using low atmospheric pressures instead of a protective gas atmosphere like most heat-treating furnaces. Vacuum furnaces are categorized as hot wall or cold wall, depending on the location of the heating and insulating components.
- **vacuum nitrocarburizing**
  - A subatmospheric nitrocarburizing process using a basic atmosphere of 50% ammonia/50% methane, containing controlled oxygen additions of up to 2%.
- **W**
- **walking-beam furnace**
  - A continuous-type furnace consisting of two sets of rails, one stationary and the other movable. Only the work being processed has to be heated because trays or fixtures are not needed.
- **water quenching**
  - A quench in which water is the quenching medium. The major disadvantage of water quenching is its poor efficiency at the beginning or hot stage of the quenching process.
- **white layer**
  - Compound layer that forms as a result of the nitriding process.

Abbreviations, Symbols, and Tradenames

- **Abbreviations and Symbols**
- **a**
  - crack length; edge length in crystal structure
- **a_C**
  - activity of carbon
- **a_N**
  - activity of nitrogen
- **a_O**
  - activity of oxygen
- **A**
  - austenite; ampere; air
- ***A***
  - area

- Å
  - angstrom
- **AA**
  - Aluminum Association
- **ac**
  - alternating current
- **AC**
  - air cool
- **Ac_{cm}**
  - in hypereutectoid steel, temperature at which cementite completes solution in austenite
- **Ac_1**
  - The temperature at which austenite begins to form during heating
- **Ac_3**
  - The temperature at which transformation of ferrite to austenite is completed during heating
- **Ae_{cm}, Ae_1, Ae_3**
  - equilibrium transformation temperatures in steel
- **ADI**
  - austempered ductile iron
- **AES**
  - Auger electron spectroscopy
- **AFS**
  - American Foundrymen's Society
- **AGA**
  - American Gas Association
- **AISI**
  - American Iron and Steel Institute
- **AMS**
  - Aerospace Material Specification
- **ANSI**
  - American National Standards Institute
- **AOD**
  - argon oxygen decarburization
- **A/D**
  - analog-to-digital
- **Ar_{cm}**
  - temperature at which cementite begins to precipitate from austenite on cooling
- **Ar_1**
  - temperature at which transformation to ferrite or to ferrite plus cementite is completed on cooling
- **Ar_3**
  - temperature at which transformation of austenite to ferrite begins on cooling
- **ASME**
  - American Society of Mechanical Engineers
- **ASTM**
  - American Society for Testing and Materials
- **at.%**
  - atomic percent
- **atm**
  - atmospheres (pressure)
- **AWG**
  - American Wire Gage
- **AWS**
  - American Welding Society
- **b**
  - Burgers vector; barn
- **B**
  - bainite

- **bal**
    - balance
- **bcc**
    - body-centered cubic
- **bct**
    - body-centered tetragonal
- **BDT**
    - brittle-ductile transition
- **BHP**
    - Broken Hill Proprietary
- ***c***
    - edge length in crystal structure; speed of light; specific heat
- **C**
    - cementite; coulomb; heat capacity
- **CAD/CAM**
    - computer-aided design/computer-aided manufacturing
- **CCR**
    - conventional controlled rolling
- **CCT**
    - continuous-cooling-transformation
- **CE**
    - carbon equivalent
- **CHR**
    - conventional hot rolling
- **cm**
    - centimeter
- **CNC**
    - computer numerical control
- ***CR***
    - cooling rate
- **CT**
    - continuous transformation
- **CVD**
    - chemical vapor deposition
- **CVM**
    - consumable-electrode vacuum remelted
- **CVN**
    - Charpy V-notch (impact test or specimen)
- **d**
    - day
- ***d***
    - used in mathematical expressions involving a derivative (denotes rate of change); depth; diameter
- ***D***
    - diameter; diffusion coefficient
- ***da/dN***
    - fatigue crack growth rate
- **dB**
    - decibel
- **DBTT**
    - ductile-to-brittle transition temperature
- **dc**
    - direct current
- **dhcp**
    - double hexagonal close-packed
- **diam**
    - diameter
- **DIN**

  - Deutsche Industrie-Normen (German Industrial Standards)
- **DoD**
  - Department of Defense
- **DOT**
  - Department of Transportation
- **DPH**
  - diamond pyramid hardness
- **DRX**
  - dynamic recrystallization
- **DS**
  - directionally solidified
- **DB**
  - deformation bands
- **DU**
  - depleted uranium
- ***e***
  - natural log base, 2.71828; charge of an electron
- ***E***
  - Young's modulus; applied voltage; activation energy
- **EAF**
  - electric arc furnace
- **EB**
  - electron beam
- **EBHT**
  - electron beam hardening treatment
- **EDM**
  - electrical discharge machining
- **ELI**
  - extra-low interstitial
- **emf**
  - electromotive force
- **EPA**
  - Environmental Protection Agency
- **Eq**
  - equation
- **ESCA**
  - x-ray photoelectron spectroscopy
- **ESR**
  - electroslag remelting
- ***et al.***
  - and others
- **eV**
  - electron volt
- **exp**
  - base of the natural logarithm
- ***f***
  - frequency; transfer function; precipitate volume fraction
- **F**
  - ferrite
- ***F***
  - force
- **FAC**
  - forced-air cool
- **FATT**
  - fracture-appearance transition temperature
- **FC**
  - furnace cool

- **fcc**
    - face-centered cubic
- **FCC**
    - Federal Communications Commission
- **fct**
    - face-centered tetragonal
- **FDM**
    - finite-difference method
- **FEM**
    - finite-element method
- **FIFO**
    - first in, first out
- **Fig**
    - figure
- **FMS**
    - flexible manufacturing system
- **ft**
    - foot
- **g**
    - gram
- ***g***
    - acceleration due to gravity
- **G**
    - graphite; gauss
- **gal**
    - gallon
- **GB**
    - grain boundary
- **GP**
    - Guinier-Preston (zone)
- **GPa**
    - gigapascal
- **h**
    - hour
- ***h***
    - hardness penetration; hardening depth; heat-transfer coefficient; Planck's constant, 6.626×10^{-27} erg · s
- **H**
    - Henry
- ***H***
    - Grossmann number; enthalpy; magnetic field; height
- **H_a**
    - applied magnetic field; activation enthalpy
- **H_c**
    - coercive force; thermodynamic critical field
- **H_P**
    - hardness predicted
- **HAZ**
    - heat-affected zone
- **HB**
    - Brinell hardness
- **hcp**
    - hexagonal close-packed
- **HIP**
    - hot isostatic pressing
- **HK**
    - Knoop hardness

- **hp**
  - horsepower
- **HR**
  - Rockwell hardness (requires scale designation, such as HRC for Rockwell C hardness)
- **HRMF**
  - Rockwell microficial (microhardness)
- **HV**
  - Vickers hardness
- **Hz**
  - hertz
- ***I***
  - intensity; electrical current; bias current
- **IACS**
  - International Annealed Copper Standard
- **ICR**
  - intensified controlled rolling
- **ID**
  - inside diameter
- **IF**
  - interstitial free
- **I/M**
  - ingot metallurgy
- **in.**
  - inch
- **IPTS**
  - International Practical Temperature Scale
- **IR**
  - infrared
- **ISA**
  - Instrument Society of America
- **ISCC**
  - intergranular stress-corrosion cracking
- **ISO**
  - International Standards Organization
- **IT**
  - isothermal transformation
- **ITT**
  - impact transition temperature
- **J**
  - joule
- J_{eq}
  - Jominy equivalent
- **JIT**
  - just in time (manufacturing)
- **k**
  - karat
- ***k***
  - thermal conductivity; wave number; Boltzmann constant
- **K**
  - Kelvin
- ***K***
  - stress intensity factor; thermal conductivity
- K_f
  - fatigue notch factor
- K_{Ic}
  - plane-strain fracture toughness
- K_{ISCC}

- threshold stress intensity to produce stress-corrosion cracking
- **kg**
  - kilogram
- **km**
  - kilometer
- **kN**
  - kilonewton
- **kPa**
  - kilopascal
- **ksi**
  - kips (1000 lbf) per square inch
- **kV**
  - kilovolt
- **kW**
  - kilowatt
- ***l***
  - length
- **l**
  - length
- **L**
  - longitudinal; liter
- **lb**
  - pound
- **lbf**
  - pound force
- **LMP**
  - Larson-Miller parameter
- **ln**
  - natural logarithm (base *e*)
- **LNG**
  - liquefied natural gas
- **log**
  - common logarithm (base 10)
- **LPCVD**
  - low pressure chemical vapor deposition
- **LT**
  - long transverse (direction)
- **m**
  - meter
- **M_f**
  - temperature at which martensite formation finishes during cooling
- **M_s**
  - temperature at which martensite starts to form from austenite on cooling
- **mA**
  - milliampere
- **MA**
  - microalloyed
- **MAE**
  - microalloying elements
- **MDRX**
  - metadynamic recrystallization
- **MEA**
  - monoethanolamine
- **MEK**
  - methyl ethyl ketone
- **MeV**
  - megaelectronvolt

- **mg**
  - milligram
- **Mg**
  - megagram (metric tonne, or kg × 10^3)
- **MIBK**
  - methyl isobutyl ketone
- **MIG**
  - metal inert gas
- **min**
  - minute; minimum
- **mL**
  - milliliter
- **mm**
  - millimeter
- **MMC**
  - metal-matrix composite
- **mPa**
  - millipascal
- **MPa**
  - megapascal
- **mpg**
  - miles per gallon
- **mph**
  - miles per hour
- **ms**
  - millisecond
- **MS**
  - megasiemens
- **mT**
  - millitesla
- **mV**
  - millivolt
- **MV**
  - megavolt
- **N**
  - newton
- ***N***
  - number of cycles; normal solution
- **N_f**
  - number of cycles to failure
- **NASA**
  - National Aeronautics and Space Administration
- **NBS**
  - National Bureau of Standards
- **NDT**
  - nil ductility temperature
- **NFPA**
  - National Fire Prevention Association
- **nm**
  - nanometer
- **NMR**
  - nuclear magnetic resonance
- **No.**
  - number
- **ns**
  - nanoseconds
- **O**

    - oil
- **OD**
    - outside diameter
- **Oe**
    - oersted
- **OM**
    - optical micrograph
- **OQ**
    - oil quenched
- **ORNL**
    - Oak Ridge National Laboratory
- **OSHA**
    - Occupational Safety and Health Administration
- **oz**
    - ounce
- **p**
    - page
- **P**
    - pearlite
- ***P***
    - number of passes; applied load; pressure
- **Pa**
    - pascal
- **PA**
    - polyacrylates
- **PAG**
    - polyalkylene glycol
- **pH**
    - negative logarithm of hydrogen-ion activity
- **PH**
    - precipitation hardenable
- **PLCs**
    - programmable logic controllers
- **P/M**
    - powder metallurgy
- **PMS**
    - Process Management System
- **ppb**
    - parts per billion
- **ppba**
    - parts per billion atomic
- **ppm**
    - parts per million
- **PPS**
    - property prediction system
- **ppt**
    - parts per trillion
- **psi**
    - pounds per square inch
- **psig**
    - gage pressure (pressure relative to ambient pressure) in pounds per square inch
- **PVA**
    - polyvinyl alcohol
- **PVP**
    - polyvinyl pyrrolidone
- ***q***
    - incremental quench factor

- ***Q***
  - quench factor; heat removal rate
- ***r***
  - radius
- **R**
  - roentgen
- ***R***
  - stress (load) ratio; radius; gas constant; bulk resistance; reluctance (reciprocal of permeance); rolling reduction ratio
- ***RA***
  - reduction in area; recrystallization annealed
- **rad**
  - absorbed radiation dose
- **RB**
  - rigid boundary (model)
- **RCR**
  - recrystallization controlled rolling
- **RE**
  - rare earth
- **Ref**
  - reference
- **rf, RF**
  - radio frequency
- **RGA**
  - residual gas analyzer
- **RH**
  - refrigeration hardened
- **rms**
  - root mean square
- **RSW**
  - resistance spot welding
- **RT**
  - room temperature
- **s**
  - second
- **S**
  - siemens
- **SAE**
  - Society of Automotive Engineers
- **SB**
  - subgrain boundary (model)
- **SCC**
  - stress-corrosion cracking
- **SCR**
  - silicon controlled rectifier
- **SDI**
  - strategic defense initiative
- **SEM**
  - scanning electron microscope
- **sfm**
  - surface feet per minute
- **SHE**
  - standard hydrogen electrode
- **SHT**
  - Sumitomo high toughness
- **SI**
  - Système International d'Unités

- **SMAW**
  - shielded metal-arc welding
- **SPC**
  - statistical process control
- **spf**
  - seconds per foot
- **SRX**
  - static recrystallization
- **ST**
  - short transverse (direction)
- **STA**
  - solution-treated and aged
- **std**
  - standard
- **SUS**
  - Saybolt Universal Seconds (viscosity)
- **Sv**
  - sievert
- t
  - thickness; time
- **T**
  - tesla
- T
  - temperature
- T_b
  - boiling temperature
- T_c
  - critical ordering temperature; Curie temperature; critical transition temperature
- T_{GC}
  - grain coarsening temperature
- T_m
  - melting temperature
- T_{RXN}
  - recrystallization stop temperature
- **TC**
  - total carbon
- **TEM**
  - transmission electron microscopy
- **TH**
  - transformation hardened
- **TIG**
  - tungsten inert gas (welding)
- **TIR**
  - total indicator reading
- **TMP**
  - thermomechanical processing
- **tsi**
  - tons per square inch
- **TTT**
  - time-temperature transformation
- **ULCB**
  - ultralow-carbon bainitic
- **UNS**
  - Unified Numbering System
- **UTS**
  - ultimate tensile strength
- v

    - velocity
- **V**
    - volt
- ***V***
    - volume; velocity
- **VAR**
    - vacuum arc remelting
- **V-D**
    - vacuum degassing
- **VIM**
    - vacuum induction melting
- **vol**
    - volume
- **vol%**
    - volume percent
- **W**
    - watt
- ***W***
    - width; weight
- **WC**
    - water cooled
- **wt%**
    - weight percent
- **yr**
    - year
- °
    - angular measure; degree
- **°C**
    - degree Celsius (centigrade)
- **°F**
    - degree Fahrenheit
- **€**
    - direction of reaction
- ÷
    - divided by
- =
    - equals
- ;
    - approximately equals
- ≠
    - not equal to
- ≡
    - identical with
- >
    - greater than
- **?**
    - much greater than
- ≥
    - greater than or equal to
- ∞
    - infinity
- ∝
    - is proportional to; varies as
- ∫
    - integral of
- <
    - less than

- =
  - much less than
- ≤
  - less than or equal to
- ±
  - maximum deviation
- **-**
  - minus; negative ion charge
- ×
  - diameters (magnification); multiplied by
- ·
  - multiplied by
- /
  - per
- **%**
  - percent
- \+
  - plus; positive ion charge
- √
  - square root of
- ~
  - approximately; similar to
- ∂
  - partial derivative
- **α**
  - thermal diffusivity
- **Δ**
  - change in quantity; an increment; a range
- **ε**
  - strain
- $\dot{\epsilon}$
  - strain rate
- **θ**
  - angle
- **λ**
  - wavelength
- **μ**
  - friction coefficient; magnetic permeability
- **μF**
  - microfarads
- **μin.**
  - microinch
- **μm**
  - micrometer (micron)
- **μs**
  - microsecond
- **ν**
  - Poisson's ratio
- **π**
  - pi (3.141592)
- **ρ**
  - density
- **σ**
  - stress
- **Σ**
  - summation of
- **τ**

        - applied stress (shear)
    - **ω**
        - frequency
    - **Ω**
        - ohm

- **Greek Alphabet**
    - **Α, α**
        - alpha
    - **Β, β**
        - beta
    - Γ, **γ**
        - gamma
    - Δ, **δ**
        - delta
    - **Ε, ε**
        - epsilon
    - **Ζ,** *z*
        - zeta
    - **Η, η**
        - eta
    - Θ, **θ**
        - theta
    - **Ι,** *ι*
        - iota
    - **Κ, κ**
        - kappa
    - Λ, **λ**
        - lambda
    - **Μ, μ**
        - mu
    - **Ν, ν**
        - nu
    - Ξ, *x*
        - xi
    - **Ο, ο**
        - omicron
    - Π, **π**
        - pi
    - **Ρ, ρ**
        - rho
    - Σ **σ**
        - sigma
    - **Τ,** *t*
        - tau
    - ϒ, *u*
        - upsilon
    - Φ, *f*
        - phi
    - **Χ, χ**
        - chi
    - Ψ, *y*
        - psi
    - **Ω, ω**
        - omega

- **Tradenames**
- **AF-56**
  - is a registered tradename of Allison Gas Turbine, Division of General Motors Corporation.
- **AL-6X, AL-6XN, AL 29-4C, AL 29-4-2, AL 904L, AL-36, AL-42, AL-52, AL 2205, AL-4750, ALFA IV, E-Brite 26-1, Sealmet, and 203 EZ**
  - are registered tradenames of Allegheny Ludlum Steel, Division of Allegheny Ludlum Corporation.
- **Allcor**
  - is a registered tradename of Teledyne Industries, Inc.
- **AM1**
  - is a registered tradename of SNECMA/ONERA.
- **CBS-600 and CBS-1000M**
  - are registered tradenames of the Timken Company.
- **CM 247 LC and CMSX**
  - are registered tradenames of Cannon-Muskegon Corporation.
- **Cronifer**
  - is a registered tradename of Vereingte Deutsche Metallwerks.
- **Cryogenic Tenelon and Tenelon**
  - are registered tradenames of USS, Division of USX Corporation.
- **Custom 450, Custom 455, Gall-Tough, Glass Sealing "49", Invar "36", Kovar, Low Expansion "42", Pyromet, TrimRite, 7-Mo PLUS, 18-8 PLUS, 20Cb-3, 20Mo-4, and 20Mo-6**
  - are registered tradenames of Carpenter Technology Corporation.
- **CU78, CW67, and CZ42**
  - are registered tradenames of Aluminum Company of America.
- **Discaloy**
  - is a registered tradename of Westinghouse Electric Corporation.
- **DISPAL**
  - is a registered tradename of Sinter-metallwerk Krebsöge GmbH.
- **DP3**
  - is a registered tradename of Sumitomo Metal America, Inc.
- **Elinvar and Invar**
  - are registered tradenames of Imphy, S.A.
- **Esshete**
  - is a registered tradename of British Steel Corporation.
- **Ferralium**
  - is a registered tradename of Bonar Langley Alloy Ltd.
- **FVS-0611, FVS-0812, FVS-1212, and Metglas**
  - are registered tradenames of Allied-Signal Inc.
- **GlidCop**
  - is a registered tradename of SCM Metal Products, Inc.
- **Hastelloy and Haynes**
  - are registered tradenames of Haynes International, Inc.
- **Incoloy, Inconel, IncoMAP AL-905XL, IncoMAP AL-9052, Monel, Nimocast, Nimonic, NI-Rod, and NI-Span-Cl**
  - are registered tradenames of Inco Alloys International, Inc.
- **JS700**
  - is a registered tradename of Jessop Steel Company.
- **Kapton, Teflon, and Tefzell**
  - are registered tradenames of E.I. Du Pont de Nemours & Company, Inc.
- **MAR-M**
  - is a registered tradename of Martin Marietta Corporation.
- **Monit**
  - is a registered tradename of Uddeholms Aktiebolag.
- **MP (Multiphase)**
  - is a registered tradename of Standard Pressed Steel Company.
- **Nextel**

    - is a registered tradename of 3M Company.
- **Nitronic and PH 13-8 Mo**
    - are registered tradenames of Baltimore Specialty Steels Corporation.
- **PH 15-7 MO, 12SR, 15-5 PH, 17-4 PH, 18 SR, and 21-6-9**
    - are registered tradenames of Armco Advanced Materials Corporation.
- **PWA 1484**
    - is a registered tradename of Pratt & Whitney Aircraft.
- **RA85H**
    - is a registered tradename of Rolled Alloys, Inc.
- **Refrasil**
    - is a registered tradename of Thompson Company.
- **René**
    - is a registered tradename of General Electric Company.
- **René 41**
    - is a registered tradename of Allvac Metals Company, a Teledyne Company.
- **RR 2000 and SRR 99**
    - are registered tradenames of Rolls Royce, Inc.
- **Sanicro and 3RE60**
    - are registered tradenames of Sandvik, Inc.
- **Sea-Cure**
    - is a registered tradename of Crucible, Inc.
- **Stellite**
    - is a registered tradename of Deloro Stellite, Inc.
- **Tantaloy and Tribocor**
    - are registered tradenames of Fansteel Inc.
- **Transage 134 and Transage 175**
    - are registered tradenames of Lockheed Missile and Space Company.
- **Tufftride**
    - is a registered tradename of Kolene Corporation.
- **UCON**
    - is a registered tradename of Union Carbide Chemicals and Plastics Company, Inc.
- **Udimet**
    - is a registered tradename of Special Metals Corporation.
- **Unitemp**
    - is a registered tradename of Universal Cyclops Steel Corporation.
- **Uranus**
    - is a registered tradename of Compagnie des Ateliers et Forges de la Loire.
- **Vitallium**
    - is a registered tradename of Pfizer Hospital Products Group, Inc.
- **Waspaloy**
    - is a registered tradename of United Technologies, Inc.
- **Weldalite**
    - is a registered tradename of Martin Marietta Corporation.
- **253MA and 254SMO**
    - are registered tradenames of Avesta Stainless, Inc.

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